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Preparation of Some Polycyclic Diamine Derivatives

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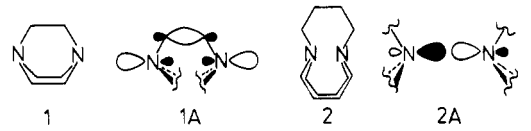
The preparation of 3,11-disubstituted-3,11-diazahexacyclo[11.2.1.$0^{2,12}$.$0^{4,15}$.$0^{5,9}$.$0^{10,14}$]hexadecanes (**3**(X)) and the related pentacyclic compounds lacking the 2,12 C–C bond (**4**(X)) is reported. Included are **3**(X) with X = H, Cl, CH_3, NO, NH_2, $N(CH_3)_2$, and $N(CH_2CH_3)_2$ and **4**(X) with X = H, CH_3, NO, NH_2, and $N(CH_3)_2$. Molecular mechanics calculations on **3**(Me) and **4**(Me) are discussed.

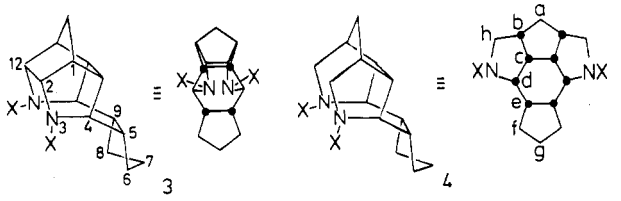
Alder and Sessions emphasize in their excellent review[1] that the special properties of diamines arise from interactions between the lone-pair electrons. For saturated diamines, these interactions have limiting cases of σ through-bond and σ through-space types. An excellent case of the σ through-bond interaction occurs in 1,4-diazabicyclo[2.2.2]octane (**1**) and of the σ through-space type, in 1,6-diazabicyclo[4.4.4]tetradecane (**2**). The HOMO of



1 1A 2 2A

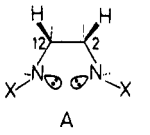
1 is dominated by the symmetric combination of the lone-pair and CC σ bond orbitals symbolized in **1A**, while the HOMO of **2** is dominated by the antisymmetric lone-pair combination symbolized in **2A**.[1] In contrast to almost all other trialkylamines, both 1^+ and 2^+ are long lived in the presence of their neutral forms in solution, so that the thermodynamics of electron removal can be studied.

In this work we describe the preparation of two related series of bis(dialkylamino) compounds, in which special effects of through-bond and through-space N,N interaction on electron removal can be probed. The two systems described are derivatives of 3,11-diazahexacyclo-[11.2.1.$0^{2,12}$.$0^{4,15}$.$0^{5,9}$.$0^{10,14}$]hexadecane **3**, hereafter called the hexacyclic series, and derivatives of 3,11-diazapentacyclo[11.2.1.$0^{4,15}$.$0^{5,9}$.$0^{10,14}$]hexadecane **4**, the pentacyclic series.



3 4

In the hexacyclic series **3** the nitrogens are held close in space because they are connected by a two-carbon bridge with the NC,CN dihedral angle fixed at 0° (see A). Be-



A

cause there is reasonably good overlap between the nitrogen lone pairs and the C_2C_{12} σ bond, there is a possibility for significant through-bond, as well as through-space, lone-pair,lone-pair interaction. The pentacyclic series lacks the C_2C_{12} bond, and the shortest path between the nitrogens is through four saturated carbon atoms (connectivity pattern $N_3C_4C_{15}C_{14}C_{10}N_{11}$). Only through-space interactions might reasonably be expected to be important in the pentacyclic series. Models show that **4** is quite flexible. Although the nitrogens can be rather close, as indicated in the perspective view of **4**, torsions in the central six-membered ring can force the nitrogens apart, as emphasized in the flat projection structure of **4**. Greatly increasing the distance between the nitrogens, however, forces the five-membered rings into each other, and it certainly is not obvious from models how close the nitrogens will actually be.

This work describes the preparation of several derivatives of **3** and **4**, including the X = NMe_2 compounds, which we expected to show reversible oxidation behavior in solution, so that the thermodynamics effects of N,N interaction in these componds could be studied. The electrochemical work will be discussed elsewhere.

Compound Preparation

We chose **3** and **4** for study in order to exploit the ready availability of the precursor to both systems, **8**, through the remarkable reactions shown in Scheme I, which were discovered by Hünig and Bernig.[2] They showed that

(1) Alder, R. W.; Sessions, R. B. "The Chemistry of Amino, Nitroso, and Nitro Compounds and Their Derivatives"; Patai, S., Ed.; Wiley: New York, 1982; Part 2 Chapter 18.

(2) Hünig, S.; Bernig, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 777.

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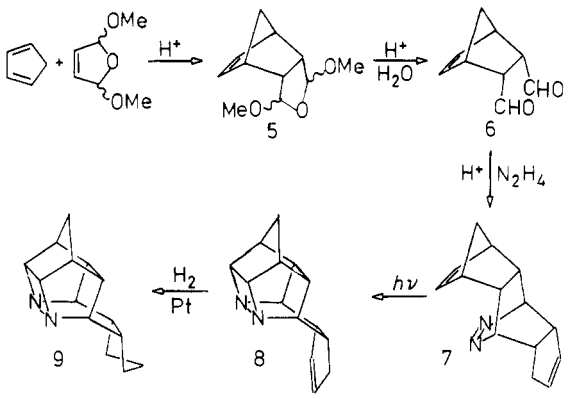
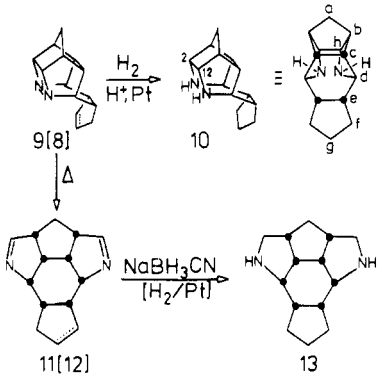
Scheme I



Scheme II

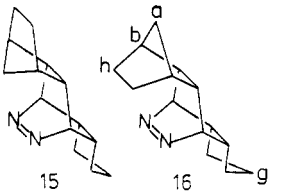


condensation of dialdehyde **6** (first prepared by Alder and co-workers[3]) with hydrazine hydrochloride gives azo compound **7** and pyrazine in good yield. Furthermore, photolysis of this "reluctant" (to give nitrogen upon photolysis[4]) azo compound produces the heptacyclic diazetidine **8**. Hünig and Bernig's route produces **8**, a compound with all syn relative stereochemistry at 10 contiguous tertiary carbons, in four steps from commercially available starting materials, emphasizing the power of cycloaddition reactions in synthesis. A trival hydrogenation gives **9**, a more symmetrical hydrazine that has the lone-pair,lone-pair dihedral angle forced to be 0° and that cannot flatten much upon electron removal, properties we have previously exploited.[5]

The reactions used to make the secondary diamines in the hexacyclic and pentacyclic series (**10** and **13**, respectively) are shown in Scheme II. Catalytic hydrogenation of either **8** or **9** in the presence of acetic acid causes the expected NN bond cleavage without cleaving the CC bond of the diazetidine ring (C_2C_{12}). Entry to the pentacyclic series is easily achieved by pyrolysis of either **8** or **9**, which causes cleavage of the diazetidine ring in the sense opposite to that in which it is formed, as precedented in the work of Landis and co-workers on other diazetidines.[6] Although 1-pyrroline itself trimerizes readily,[7] **11** and **12** are easily characterized as their monomers, presumably because of their large substituents. **11** shows a C=N stretch in its IR spectrum at 1624 cm^{-1}, close to the band at 1620 observed for the small concentration of 1-pyrroline in equilibrium with its trimer.[7] We usually reduced **11** to **13** immediately after its preparation.

The same reactions were used to functionalize the nitrogen atoms in both series and are summarized in Scheme III. Bis(chloroamine) formation was only carried out in the hexacyclic series, because **14** has kinetic protection of its α-hydrogens and might be expected to give a long-lived radical cation. Interestingly, attempted chlorination of **10** with *N*-chlorosuccinimide[8] failed to give a significant amount of **14**, but a 63% yield of diazetidine **9** was isolated. *tert*-Butyl hypochlorite successfully converted **10** to **14** without giving a significant amount of **9**. **14** is rather unstable and was not completely characterized. Addition of a 2:1 molar ratio of *tert*-butyllithium/bis(chloroamine) **13** (THF, −78 °C) resulted in an approximately 80:20 ratio of closure (to diazetidine **9**)/cleavage product (bisimine **12**), determined by NMR integration.

In the course of functionalizing **10** we isolated the same compound, **15**, in low yield from several different reactions.



It shows weak UV absorption peaks in the 350–390-nm region, has empirical formula $C_{14}H_{20}N_2$ (that of **7** + 4 H), and exhibits a ^{13}C NMR spectrum consisting of 4 CH and 4 CH_2 peaks. **15** is clearly an isomer of **16**, which is obtained upon catalytic hydrogenation of **7**[2] (2,3-diazabicyclooctanes rapidly air oxidize to the azo compounds). The CH chemical shifts of the two compounds are similar (**15**, δ 71.1, 46.5, 44.3, 40.3; **16** δ 69.2, 47.9, 44.6, 40.1), as are the upfield single-intensity CH_2 shifts (**15**, δ 25.3; **16**, δ 26.2), which we assign to C_g. The other single-intensity CH_2 peaks, assigned to C_a, appear at δ 34.5 in **15** and 42.6 in **16**, while the double-intensity CH_2 peaks come at δ 30.6 and 30.1 in **15** and 30.5 and 26.9 in **16**. The principal differences in shifts between **15** and **16** are, then, that **15** shows C_a δ 7.1 upfield of **16** and C_h δ 3.2 or 3.7 downfield of **16**. These differences are reasonable if **15** has the opposite relative configuration at C_b, as indicated in the drawings. We presume that the exo Diels–Alder adduct was formed in making **5** (the exo adducts are formed in higher yields at higher temperatures[3]) and was carried through the sequence as an impurity. We now purify **7** by liquid chromatography in 10-g batches, separating out small amounts of three compounds believed to be isomers of **7** (weights relative to **7** = 1.0 are 0.13, 0.04, and 0.006; the relative weight 0.13 material is the precursor of **15**, see Experimental Section), and have not seen **15** since.

Condensation of **10** and **13** with formaldehyde gave compounds of the empirical formula of **17** and **18**, which clearly have the nitrogens bridged by a CH_2 group (**17** ^1H NMR shows doublets, J = 12 Hz, at δ 4.23 and 3.25, and **18** ^1H NMR shows doublets, J = 15 Hz, at δ 4.14 and 3.30). This provides welcome verification that the relative stereochemistry indicated was still intact and also that in the pentacyclic series the nitrogens can indeed approach each other without difficulty.

The stability of **17** and **18** toward reductive methylation conditions caused us to prepare the bis(methylamines) **21**

(3) Alder, K.; Betzing, H.; Heimbach, K. *Liebigs Ann. Chem.* **1960**, *638*, 187.
(4) Adam, W.; DeLucchi, O. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762.
(5) Nelsen, S. F.; Kessel, C. R.; Brace, H. N. *J. Am. Chem. Soc.* **1979**, *101*, 1874.
(6) Landis, M. E.; Bell, L. M.; Madoux, D. C.; Mitchell, J. C.; Schmidt, J. M.; Spencer, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 837.
(7) Fuhlhage, D. W.; VanderWerf, C. A. *J. Am. Chem. Soc.* **1958**, *80*, 6429.
(8) (a) Grundon, M. T.; Reynolds, B. E. *J. Chem. Soc.* **1963**, 3898. (b) Ruenilz, P. C.; Smissman, E. E. *J. Org. Chem.* **1977**, *42*, 937.

Scheme III

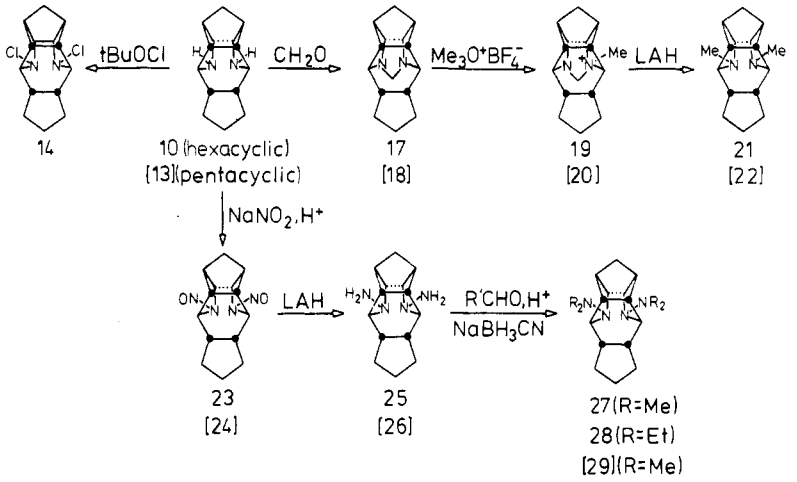


Table I. Local Minimum Energy Conformations of Bis(methylamine) 22, Calculated by MM2

conformation	rel steric energy	d(NN), Å	dihedral angle, deg		
			C_6C_5,C_9C_8	$N_3C_4,C_{14}C_{15}$	$N_{11}C_{10},C_{15}C_{14}$
22A (eclipsed)	3.1	2.8_4	0	82.0	−82.0
22B (closed)	0.5	2.9_7	23.8	79.7	−86.9
22C (open)	0	4.2_0	48.1	113.7	−102.4

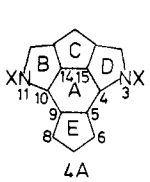
and **22** by lithium aluminum hydride reduction of the methylated formaldehyde adducts **19** and **20**, which were not highly purified and only characterized by NMR spectroscopy. Routine nitrosation, reduction reactions gave the bishydrazines **25** and **26**. These bishydrazines were smoothly reductively alkylated to **27–29**.

The verification of structures for these compounds is based principally upon the products expected, empirical formulae, and spectral properties. The ^{13}C NMR spectra show the expected number of signals for the plane of symmetry present in most compounds, but we cannot unambigously assign the CH carbons, except to NCH and CCH sets, due to the rather large differences in shift caused by fairly remote structural changes, as will be seen by examining the Experimental Section. The arbitrary letters a–h (see **4**) are used for identifying carbons in the ^{13}C data.

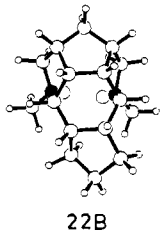
(**Note added in proof**: Professor Hünig has kindly sent preprints of five papers on Scheme I chemistry which will appear in *Chemische Berichte*. Compounds **7**, **8**, **9**, and **16** from our paper appear in these papers. Our ^{13}C NMR δ values are 1.0–1.2 smaller for **8**, 0.4–0.8 smaller for **7**, and agree well for **9** and **16** except for the upfield CH_2 carbons of **16**, for which we observe δ 26.2 and 26.9, while they observed 26.6 and 27.9.)

Results and Discussion: Molecular Shape

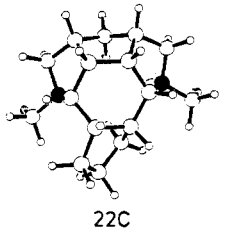
The hexacyclic system **3** has little conformational freedom because of the C_2C_{12} bond. Allinger's MM2 program gives the minimum energy for the bis(dimethylamine) **21** as that with a mirror plane of symmetry and an NN distance of 2.71 Å. In contrast, the pentacyclic system **4** is quite flexible. When the two C_4N rings (B and D in **4a**)



4A



22B



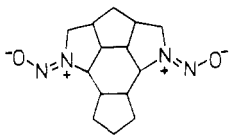
22C

are close to each other (which we will call a "closed" conformation), the C_5 rings C and E are far apart, but if rings B and D are pulled apart, rings C and E approach each other. Allinger[9] MM2 calculations on the dimethylamine **22** give two quite shallow minima that are close to each other in steric energy but have very different molecular shapes, as indicated in the drawings **22B** and **22C** (nitrogen atoms are filled in). In a compound with so many cooperative motions required to change conformations, one cannot be sure a global minimum has really been found, but we explored for local minima by starting with several different conformations and using the "dihedral driver" option of the MM2 program to change one dihedral angle while minimizing the energy of the rest of the structure. Some MM2 results are summarized in Table I. A "closed" conformation with an enforced symmetry plane bisecting the C, A, and E rings of **4A** gives a structure (**22A**) lying 2.6 kcal/mol higher in steric energy than that of a closed conformation that has been allowed to relax, **22B**. The largest twist is about the AE ring fusion. If the $N_3C_4,C_{14}C_{15}$ and/or $N_{11}C_{10},C_{14}C_{15}$ dihedral angles are enlarged or twist in the E ring is increased, the conformation of **22** becomes more open and a slightly lower energy structure, **22C**, is obtained. The energy barrier required to interconvert **22B** to **22C** is low and certainly under the barrier required to interconvert the mirror image forms of **22b** conformations, which presumably passes through **22A**. These calculations establish that **22** can open and close the NN distance very easily. The nitrogens can approach nearly as close as those of **21** (the NN distance of **22B** is only 0.13 Å greater than that of **21**). The barrier to open the structure to that of **22C**, which has the nitrogens quite far apart (**22C** has a NN distance 1.49 Å greater than that of **21**), is under 2.5 kcal/mol.

We suggest that the substantial twist of ring E given by the MM2 calculations influences the conformations of pentacyclic dinitroso compound **24**, which exhibits a 30-line ^{13}C NMR spectrum. All three combinations of *Z* and *E* nitroso groups are present. The most intense set of lines

(9) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127; Quantum Chemistry Program Exchange 395.

(eight) was assigned to **24EE**, which has the oxygens syn



24EE

to the C_hH_2 carbons, while the least intense set (also eight lines) is assigned to **24ZZ**. The remaining 14 lines are assigned to **24ZE** and **24EZ** (which have the same NMR spectrum and energy and only differ if the numbering of the system is included; we retain them as separate conformations to facilitate discussion of energy differences in this system). From the relative heights of the various sets of carbons, the relative amounts of these conformations are about 0.58 (±0.02) (*EE*), 0.19 (each of *EZ* and *ZE*), and 0.04 (*ZZ*). Thus *ZE* and *EZ* lie about 0.6_7 kcal/mol higher in free energy than does *EE* and *ZZ* about 1.5_4 kcal/mol higher. This means that turning the second nitroso group to a *Z* conformation costs about 0.2 kcal/mol (30%) more energy than does turning the first. We believe this is a result of the twist in ring E (see **4A**), which makes steric hindrance to a second *Z* nitroso group larger than that of the first, which can be tucked toward the side of the *E* ring, which produces the smaller strain.

The electrochemistry of these molecules will be presented elsewhere.

Experimental Section

Adduct of 2,5-Dimethoxy-2,5-dihdyrofuran and Cyclopentadiene (5). A mixture of 150 g (1.15 mol) of 2,5-dimethoxy-2,5-dihydrofuran, 150 g (2.27 mol) of cyclopentadiene, 300 mL of water, and 6 mL of concentrated hydrochloric acid was stirred under nitrogen in an ice bath for 12 h for 12 h and, with tap water cooling, for an additional 24 h. The mixture was neutralized (saturated sodium carbonate) and extracted three times with 100 mL of ether. After drying with calcium chloride, the ether was distilled, and the product distilling at 45–90 °C (0.7 torr) was collected. The condenser was cooled with 30 °C water to prevent clogging. The yield was 145.55 g (64%, lit.[3] yield 66%); mp 40–45 °C; ^{1}H NMR ($CDCl_3$) δ 6.31 (t, J = 1.8 Hz, 2 H), 4.52 (s, 2 H), 3.35 (s, 6 H), 3.01 (m, 2 H), 2.94 (m, 2 H), 1.44 (dt, J = 8.3, 1.7 Hz, 1 H), 1.33 (d, J = 8.3 Hz, 1 H).

15,16-Diazapentacyclo[9.2.1.2^{3,9}.0^{2,10}.0^{4,8}]hexadeca-5,12,15-triene (7). A mixture of 20.86 g of **2**, 20 mL of acetone, 6 mL of concentrated hydrochloric acid, and 54 mL of water was stirred for 18 h and decanted from a small residue of insoluble brown oil. After dilution to 800 mL with water, a mixture of 10 mL of hydrazine hydrate, 25 mL of concentrated hydrochloric acid, and 200 mL of water was added, and the solution was allowed to stand in the dark for 2 h. The flocculant white precipitate that formed was collected by vacuum filtration, washed with water, and dried in a vacuum oven to give 8.3 g (73.6%, lit. yield[2] 91%) of crude **7**. This material was dissolved in ethyl acetate and filtered through a pad of silica gel; 10.0 g of this material dissolved in 25 mL of methylene chloride was injected onto a 2 × 12 in. silica gel column (Waters LC-500 apparatus) and eluted with 10% ethyl acetate in hexane, at 0.25 L/min. After three small peaks that we believe are isomers of **7** (weights 0.04, 0.24, 0.86 g), 6.70 g of pure **7** was collected. The peak for **7** tailed badly, and 2.15 g of material containing significant amounts of **7** was washed off the column with pure ethyl acetate and recycled (total recovery 9.90 g). Empirical formula[10] of **7**, $C_{14}H_{16}N_2$; mp 188–189 °C (lit.[2] mp 193–194 °C); ^{1}H NMR ($CDCl_3$) δ 5.27 (m, H(12,13)), 5.24 (br s, H(6)), 5.20 (s, H(5)), 3.01 (m, H(3,9)), 2.80 (br, s, H(1,11)), 2.59 (m, 2 H(7)), 2.24 (t, J = 4 Hz, H(4)), 2.17 (t, J = 4 Hz, H(8)), 1.35 (d, J = 8 Hz, H(14a)), 1.23 (d, J = 8 Hz, H(14)); ^{13}C NMR ($CDCl_3$) δ 131.8 (CH), 131.54 (CH), 131.4_6 (CH), 129.1 (CH), 69.1 (CH), 67.1 (CH), 51.9 (CH), 50.8 (CH_2), 45.2 (CH, double intensity), 39.9 (CH), 39.0 (CH), 38.8 (CH), 36.4 (CH_2).

The major isomer of **7**, separated by LC (0.86 g from 10 g of crude material), is identified as **(1*S**,2*R**,3*S**,4*S**)-15,16-diazapentacyclo[9.2.1.2^{3,9}.0^{2,10}.0^{4,8}]hexadeca-5,12,15-triene** (didehydro **15**): empirical formula,[10] $C_{14}H_{16}N_2$ (m/e 212 is 2.8% of base peak at 118); mp 190–192 °C; ^{1}H NMR ($CDCl_3$) δ 6.10 (br s, 2 H), 5.55–5.49 (m, 2 H), 5.51 (s, 2 H), 3.10–2.96 (m, 1 H), 2.80 (br s, 2 H), 2.65–2.15 (m, 3 H), 1.82 (br s, 2 H), 1.38 (d, J = 9.6 Hz, 1 H), 0.94 (d, J = 9.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 138.7 (CH), 138.5 (CH), 132.2 (CH), 129.7 (CH), 71.0 (CH), 68.9 (CH), 51.3 (CH), 45.6 (double intensity CH), 43.4 (CH), 43.3 (CH), 42.8 (CH_2), 39.3 (CH), 36.9 (CH_2); UV (hexane) λ_{max} (ε) 355 (20), 379 (44), 385 (43), 395 (30).

3,11-Diazaheptacyclo[11.2.1.0^{2,12}.0^{3,11}.0^{4,15}.0^{5,9}.0^{10,14}]hexadecane (9). A solution of 0.80 g of **8** in 200 mL of hexane was stirred with 200 mg of PtO_2 under about 1 atm of hydrogen until H_2 uptake was complete (about 5 h). Filtration through a Filter-cel pad and evaporation gave 0.79 g of crude **9**, which was recrystallized from hexane to give **9** as a white powder: mp 126–128 °C; empirical formula,[10] $C_{14}H_{18}N_2$; ^{1}H NMR δ 4.17 (dd, J = 3.4, 2.1 Hz, 2 H), 2.70 (m, 2 H_d), 2.65 (m, 2 H_b), 2.40 (m, 2 H_c), 2.26 (m, 2 H_e), 1.86 (d, J = 11.0 Hz, 1 $H_{a'}$), 1.77 (m, 4 H_f), 1.45 (m, 2 H_g), 1.31 (d, J = 11.0 Hz, 1 H_a); ^{13}C NMR δ 70.0 (C_hH), 61.6 (C_dH), 45.8 and 45.3 (C_cH and C_bH), 33.8 (C_eH), 31.1 (C_fH_2), 31.5 and 26.3 (C_aH_2 and C_gH_2).

The photochemical closure of **7** to **8** was carried out by the method of Hünig and Bernig.[2]

3,11-Diazahexacyclo[11.2.1.0^{2,12}.0^{4,15}.0^{5,9}.0^{10,14}]hexadecane (10). A solution of 1.0 g of **9** (or **8**) in 20 mL of acetic acid and 80 mL of ethanol was stirred under a hydrogen atmosphere with 200 mg of PtO_2 (or 10% Pd/C) until hydrogen uptake ceases (about 6 h for **9**, 8 h for **8**). The mixture was filtered through a Filter-cel pad, the solvent removed by rotary evaporation, the residue dissolved in water and made basic with KOH, and the product extracted into 5 × 25 mL fractions of methylene chloride. Concentration gave a brown solid, which was sublimed (100 °C (0.1 mmHg)) to give 0.61 g of **10** as a white solid: empirical formula,[10] $C_{14}H_{20}N_2$; mp 261–264 °C; IR 3380, 3300 cm^{-1} (NH stretch); ^{1}H NMR δ 3.39 (br s, 2 H_h), 3.02 (br s, 2 H_d), 2.59 (s, 2 NH), 2.48 (br s, 2 H_b), 2.03 (br s, 2 H_c), 1.81 (m, 4 H_f), 1.69 (m, 2 H_e), 1.58 (d, J = 10.5 Hz, 1 $H_{a'}$), 1.48 (d, J = 10.7 Hz, 1 H_a), 1.41 (m, 2 H_g); ^{13}C NMR δ 60.9 (C_hH), 58.1 (C_dH), 46.3 and 42.4 (C_cH and C_bH), 40.1 (C_cH), 31.4 (C_fH_2), 28.4 and 26.6 (C_aH_2 and C_gH_2).

3,11-Diazapentacyclo[11.2.1.0^{4,15}.0^{5,9}.0^{10,14}]hexadeca-2,11-diene (11). A solution of 4.0 g (18.7 mmol) of diazetidine **9** in 17 mL of ethanol was injected dropwise (via syringe pump) onto an 8 × $^1/_2$ in. column packed with glass beads and heated to 350 °C. The pyrolysis products were collected in a trap cooled to −78 °C. Removal of ethanol gives crude **11** as a reddish solid, which was purified by crystallization from hexane: mp 69–70 °C; empirical formula,[10] $C_{14}H_{18}N_2$ (m/e 214 is 26% of base peak at 170); IR, C=N stretch at 1624 cm^{-1}, ^{1}H NMR δ 7.23 (d, J = 3.1 Hz, 2H), 4.06 (m, 2 H), 3.34–3.27 (m, 2 H), 2.63 (m, 2 H) 2.53–2.30 (m, 2 H), 2.33 (d, J = 14.0 Hz, 1 H_a), 2.1–1.7 (m, 5 H), 1.6–1.3 (m, 2 H); ^{13}C NMR 168.8 (C_hH), 73.4 (C_dH), 57.9 (CH), 41.8 (CH), 39.0 (CH), 30.6 (C_fH_2), 28.9 (C_aH_2), 25.3 (C_gH_2).

3,11-Diazapentacyclo[11.2.1.0^{4,14}.0^{5,9}.0^{10,14}]hexadeca-2,6,11-triene (12) was prepared from **8**, using the same method as for **11**. Removal of ethanol gave crude **12**: empirical formula,[10] $C_{14}H_{16}N_2$; IR, C=N stretch at 1626 cm^{-1}; ^{1}H NMR δ 7.26 (br s, 2 H_h), 5.98 (m, 1 H), 5.93 (m, 1 H), 4.14 (m, 2 H), 3.5–3.2 (m, 2 H), 3.0–2.5 (m, 6 H), 2.33 (d, J = 13.5, 1 H_a), 1.97 (d of t, J = 13.7, 8.4 Hz, 1 H_a); ^{13}C NMR δ 170.2, 168.9, 131.8, 129.9, 72.7, 72.2, 58.2, 57.9, 46.0, 41.9, 40.8, 36.19, 36.6, 28.4.

3,11-Diazapentacyclo[11.2.1.0^{4,15}.0^{5,9}.0^{10,14}]hexadecane (13). The crude pyrolysis product from 4.0 g (18.7 mmol) of **9** was diluted to 125 mL with ethanol and stirred with 2.37 g (37.7 mmol) of sodium cyanoborohydride. Acetic acid was added to keep the pH (solution spotted on moist pH paper) between 5 and 6. After 15 h, 25 mL of concentrated hydrochloric acid was added, the solvents were removed by rotary evaporation, and the residue was dissolved in 100 mL of 15% sodium hydroxide solution. After five extractions with 25 mL of ether and drying with sodium

(10) Determined by high-resolution mass spectroscopy peak match on an AEI MS 9 spectrometer.

sulfate, concentration gave 5.0 g of a brown oil, which gave 3.87 g of **13**: empirical formula,[10] $C_{14}H_{22}N_2$ (*m/e* 218, 2.2% of base peak at 69); a light yellow oil upon Kugelrohr distillation; IR 3200 cm^{-1} (NH stretch); ^1H NMR δ 3.20 (br s, 2 H), 2.95 (m, 4 H), 2.40 (br t, J = 4 Hz, 2 H), 2.22 (m, 2 H), 1.8 (m, 4 H), 1.62 (d, J = 13.5 Hz, 1 H), 1.55 (m, 2 H), 1.4 (m, 1 H); ^{13}C NMR δ 60.8 (C_dH), 54.6 (C_hH_2), 47.0 (CH), 46.4 (CH), 41.5 (CH_2), 37.4 (CH), 30.8 (CH_2), 26.2 (CH_2). **13** was also prepared from crude **12** by cyanoborohydride reduction followed by catalytic hydrogenation in 25% acetic acid in ethanol, using PtO_2 as catalyst.

3,11-Dichloro-3,11-diazahexacyclo[11.2.1.0^{2,12}.0^{4,15}.0^{5,9}.0^{10,14}]hexadecane (14). A solution of 1.41 g (13 mmol) of *tert*-butyl hypochlorite in 25 mL of THF was added in one portion to 1.41 g (6.5 mmol) of **10** in 50 mL of dry THF, which had been cooled in an ice bath. A white precipitate formed immediately. After stirring in the dark (vessel wraped in aluminum foil) for 24 h, the mixture was cooled to −78 °C and filtered rapidly. The filtrate was washed cautiously with cold ether, giving 0.66 g (51%) of crude **14**, which decompooses to a black tar very suddenly between 68 and 72 °C upon rapid heating. This material discolors in air and decomposes in 24 h in $CDCl_3$ solution. We were unable to obtain a mass spectrum showing a parent ion. ^1H NMR δ 4.76 (br s, 2 H), 3.32 (br s, 2 H), 2.99 (br s, 2 H), 2.81 (br s, 2 H), 2.47 (br s, 2 H), 2.09 (d, J = 11.6 Hz, 1 $H_{a'}$), 1.88 (br s, 4 H), 1.61 (d, J = 12.1 Hz, 1 H_a), 1.51 (m, 2 H); ^{13}C NMR δ 69.8 (C_hH), 60.6 (C_dH), 44.0 and 43.8 (C_cH and C_bH), 31.7 (C_eH), 30.1 (C_fH), 31.3 and 25.6 (C_aH_2 and C_gH_2).

(1*S,2*R**,3*S**,4*S**)-15,16-Diazapentacyclo[9.2.1.2^{3,9}.0^{2,10}.0^{4,8}]hexadec-15-ene (15)** was isolated in several reactions after it had been carried as a contaminant for several steps. Sublimation (80 °C (0.5 mm Hg)) and recrystallization from hexane provides **15** as a white solid; empirical formula,[10] $C_{14}H_{20}N_2$; mp 199–200 °C; ^1H NMR δ 5.52 (s, 2 H), 2.25–2.10 (m, 4 H), 2.0–1.9 (m, 2 H), 1.8–1.7 (m, 4 H), 1.4–1.0 (m, 7 H), 0.64 (d, J = 10.3 Hz, 1 H); ^{13}C NMR δ 71.1 (C_dH), 46.5 (CH), 44.3 (CH), 40.3 (CH), 34.5 (C_aH_2), 30.6 and 30.1 (C_hH_2 and C_fH_2), 25.3 (C_gH_2); UV (hexane) λ_{max} (ϵ) 392 (95), 382 (68), 354 (39).

(1*R,2*R**,3*S**4*S**)-15,16-Diazapentacyclo[9.2.1.2^{3,9}.0^{2,10}.0^{4,8}]hexadec-15-ene (16)** was prepared by catalytic hydrogenation of **7**, using the method of Hünig and Bernig:[2] ^1H NMR δ 5.24 (br s, 2 H), 2.36 (br t, J = 5.3 Hz, 2 H), 2.12 (br s, 2 H), 2.09 (br s, 2 H), 1.8–1.7 (m, ca, 2 H), 1.4–1.1 (m, ca. 8 H), 0.79 (dd, J = 9.3, 2.5 Hz, 2 H); ^{13}C NMR δ 69.2 (C_dH), 47.9 (CH), 44.6 (CH), 42.6 (C_aH_2), 40.1 (CH), 30.5 and 26.9 (C_hH_2 and C_fH_2), 26.2 (C_gH_2).

3,11-Diazaheptacyclo[11.2.1.1^{3,11}.0^{2,12}.0^{4,15}.0^{5,9}.0^{10,14}]heptadecane (17). A mixture of 1.27 g (5.87 mmol) of **10**, 5 mL of 37% formalin (58.7 mmol CH_2), and 100 mL of toluene was refluxed over a Dean–Stark trap for 24 h. Concentration gave 1.27 g of a brownish solid, which was sublimed to give 0.67 g of **17** (empirical formula,[10] $C_{15}H_{20}N_2$) as a white powder still contaminated with **10**: mp 106–108 °C; ^1H NMR δ 4.23 (d, J = 12.1 Hz, 1 $H_{j'}$), 3.25 (d, J = 12.7 Hz, 1 H_j), 3.48 and 3.42 (2 br s, 2 H_h, 2 H_d), 2.50 and 2.38 (br s, m, 2 H_b and 2 H_d), 2.00 (br s, 2 H_e), 1.95–1.75 (m, 6 H), 1.54 (m, 4 H_g); ^{13}C NMR δ 75.1 (C_jH_2), 71.7 (C_hH), 62.8 (C_dHO), 45.2 and 42.3 (C_cH, C_bH), 40.0 (C_eH), 35.4 (C_fH_2), 28.5 (C_aH_2), 26.4 (C_gH_2).

3-Methyl-3-azonia-11-azaheptacyclo[11.2.1.1^{3,11}.0^{2,12}.0^{4,15}.0^{5,9}.0^{10,14}]heptadecane Tetrafluoroborate (19). A suspension of 1.25 g (0.84 mmol) of Me_3OBF_4 in 10 mL of CH_2Cl_2 was added to a solution of 0.194 (0.85 mmol) of formaldehyde adduct **17** in 7 mL of CH_2Cl_2, which had been cooled to −78 °C in a dry ice–ethanol bath. The mixture was stirred magnetically and allowed to warm to room temperature over 18 h. Removal of CH_2Cl_2 gave 0.29 g of solid **19**: mp 156–158 °C, which was used for preparation of **21** without purification: ^1H NMR δ 4.96 (d, J = 11 Hz, 1 $H_{4'}$), 4.25 (d, J = 11 Hz, 1 H_j), 4.15 (m, 1 H), 4.07 (m, 1 H), 3.65 (br t, J = 2.9 Hz, 1 H), 3.24 (s, NCH_3), 3.06 (br t, J = 3.7 Hz, 1 H), 2.72 (m, 1 H), 2.7–2.5 (m, 3 H), 2.3 (2 s, m, 1 H), 2.2–1.7 (m, 5 H), 2.0 (d, J = 12 Hz, 1 H), 1.9 (d, J = 12 Hz, 1 H), 1.7–1.45 (m, 2 H); ^{13}C NMR δ 84.1 (CH), 80.6 (CH_2), 76.9 (CH), 75.5 (CH), 61.8 (CH), 47.7 (CH_3), 45.3 (CH), 44.9 (CH), 42.9 (CH), 40.4 (CH), 38.5 (CH), 38.0 (CH), 34.5 (CH), 28.0 (CH_2), 27.9 (CH_2), 26.3 (CH_2).

3,11-Diazahexacyclo[11.2.1.1^{3,11}.0^{4,15}.0^{5,9}.0^{10,14}]heptadecane (18) was prepared from **13** by the same method as for the preparation of **17**, giving **18** as an oil, which freezes below room temperature: empirical formula,[10] $C_{15}H_{22}N_2$; ^1H NMR δ 4.14 (d, J = 15.1 Hz, $H_{j'}$), 3.30 (d, J = 15.1 Hz, 1 H_j), 3.35 (d, H = 11 Hz, 1 $H_{a'}$), 2.88 (dd, J = 13.3, Hz, 1 H_a), 2.7–2.5 (m, 2 H), 2.5–2.3 (m, 4 H), 2.1–1.8 (m, 6 H), 1.8–1.6 (m, 2 H), 1.6–1.4 (m, 2 H); ^{13}C NMR δ 68.6 (C_jH_2), 63.5 (C_dH), 62.1 (C_hH_2), 49.1 (CH), 46.1 (CH), 40.7 (C_aH_2), 37.2 (CH), 29.5 (C_fH_2), 26.4 (C_gH_2).

3-Methyl-3-azonia-11-azahexacyclo[11.2.1.1^{3,11}.0^{4,15}.0^{5,9}.0^{10,14}]heptadecane tetrafluoroborate (20) was prepared from 0.38 g of **18** by the same method as for the preparation of **19**, giving 0.87 g of crude **20** as an oil, which was crystallized from ethyl acetate: mp 158–162 °C; ^{13}C NMR δ 79.6 (CH_2), 74.5 (CH), 71.4 (CH_2), 61.6 (CH), 59.0 (CH_2), 50.5 (CH_3), 49.3 (CH), 49.2 (CH), 44.5 (CH), 40.2 (CH), 38.0 (CH), 36.7 (CH), 36.6 (CH), 29.1 (CH_2), 28.8 (HC_2), 26.4 (CH_2); ^1H NMR, exceedingly complex, NCH_3 at δ 3.09.

3,11-Dimethyl-3,11-diazahexacyclo[11.2.1.0^{2,12}.0^{4,15}.0^{5,9}.0^{10,14}]hexadecane (21). A suspension of 0.25 g (0.76 mmol) of crude methyl salt **19** in 25 mL of dry THF was added to 60 mg of LAH in 25 mL of dry THF, and the mixture was refluxed and stirred for 18 h. After cooling, quenching with 0.06 mL of H_2O, 0.06 mL of 15% NaOH, and 0.18 mL of H_2O, stirring for 2 h, and filtration through a Celite pad to remove the salts, concentration gave 0.24 g of an off-white solid. Sublimation (80 °C, (0.5 mmHg)) gave 0.12 g of **21** as a white powder: empirical formula,[10] $C_{16}H_{24}N_2$; mp 56–58 °C; ^1H NMR δ 2.76 (br s, 2 H), 2.66 (br s, 2 H), 2.62 (br s, 2 H), 2.39 (s, 6 H), 2.09 (br s, 2 H), 1.89–1.75 (m, 6 H), 1.43–1.32 (m, 2 H), 1.62 (dt, J = 10.7, 1.8 Hz, 1 $H_{a'}$), 1.34 (d, J = 10.7 Hz, 1 H_a); ^{13}C NMR δ 71.0, 68.5 (C_hH, C_dH), 48.8 (CH_3), 43.9, 42.7 (C_cH, C_bH), 40.1 (C_eH), 30.7 (C_fH_2), 28.3 (Ca_{H2}), 26.6 (C_gH_2).

3,11-Dimethyl-3,11-diazapentacyclo[11.2.1.0^{4,15}.0^{5,9}.0^{10,14}]hexadecane (22) was prepared by LAH reduction of 0.55 g of methyl salt **20**, using the same conditions as for **21**, giving 0.27 g of **22** (empirical formula,[10] $C_{16}H_{26}N_2$) as a clear oil: IR 2750 cm^{-1} (NCH_3); ^1H NMR δ 2.83 (d, J = 8.6 Hz, 2 H), 2.7–2.5 (m, 2 H), 2.4–2.3 (m, 2 H), 2.25 (s, 6 H), 2.6–1.8 (m, 11 H), 1.65–1.45 (m, 2 H), 1.5 (d, J = 12 Hz, 2 H); ^{13}C NMR δ 66.0 (C_dH), 63.3 (C_hH_2), 43.5 (CH_3), 46.9, 44.5 and 40.4 (3 CH), 38.6 (C_aH_2), 27.7 (C_fH_2), 22.8 (C_gH_2).

3,11-Dinitroso-3,11-diazahexacyclo[11.2.1.0^{2,12}.0^{4,15}.0^{5,9}.0^{10,14}]hexadecane (23). A solution of 0.27 g (1.25 mmol) of diamine **10** in 5 mL of H_2O and 7 mL of acetic acid was cooled in an ice bath, and 10.6 g (154 mmol) of $NaNO_2$ in 7 mL of H_2O was added over 30 min. After standing under nitrogen without stirring for 2 days, the mixture was extracted five times with 10-mL fractions of Ch_2Cl_2, and the organic phases were washed twice with 20 mL of saturated aqueous Na_2CO_3. After washing with 10 mL of 10% HCl and drying over sodium sulfate, solvent removal gave 0.28 g (82%) of crude **23** as an off-white powder, mp 147–150 °C. The mass spectrum did not show a parent peak, but the 244 peak (P − 30) peak matched for $C_{14}H_{18}N_3O$, as expected if an NO group had been lost from **23**. This material showed the UV expected for an *N*-nitrosamine (λ_{max} 237 (ϵ 12400)). Its ^1H and ^{13}C spectra are very complex, as expected for a mixture of rotational isomers about the two N–NO bonds. A total of 30 ^{13}C peaks would be expected if all three conformations were occupied and 22 if only one oxygen could be syn to the interior of the molecule at a time. We observed 19 ^{13}C peaks: δ 66.2, 62.0, 61.0, 59.1, 58.2, 57.9, 44.6, 43.3, 42.9, 42.0, 40.4, 40.0, 39.5, 39.4, 32.8, 29.9, 29.4, 28.0, 25.7.

3,11-Diamino-3,11-diazahexacyclo[11.2.1.0^{2,12}.0^{4,15}.0^{5,9}.0^{10,14}]hexadecane (25). A solution of 2.17 g (7.9 mmol) of crude **23** in a 50 mL of dry THF was added to 1.7 g (42.5 mmol) of LAH in 50 mL of dry THF. A 10-mL portion was added and allowed to stir 1.5 h, and the remainder was added dropwise (too rapid addition can lead to excessive temperature rises, as the reduction has an induction period, but is very exothermic, once started). After 1:1:3 quench and stirring for 2 h, the aluminum salts were filtered off through a filter cell pad, and the salts were placed in a Soxhlet cup and extracted for 18 h with CH_2Cl_2. After drying with Na_2SO_4 and solvent removal, a yield of 1.26 g of brown material was obtained, from which 0.25 g of **25** was obtained as an off-white powder of crystallization from hexane: empirical formula,[10] $C_{14}H_{22}N_4$ (*m/e* 246, 13% of base peak); mp 79–82 °C; ^1H NMR δ 3.48 (br s, 4 NH), 3.16 (s, 2 H), 2.95 (s, 2 H), 2.75 (s, 2 H), 2.15–1.76 (m, 8 H), 1.73 (d, J = 11.2 Hz, 1 H), 1.50–1.25 (m, 2 H), 1.42 (d, J = 11.4 Hz, 1H); ^{13}C NMR δ 75.0, 74.6 (C_dH and

Table II. ^{13}C NMR Spectral Data of 24

mult (carbon no.)	ZZ (major)	ZE + EZ	EE (minor)
CH (4, 10)	59.5	60.2, 54.5	54.4
CH_2 (2, 12)	49.8	50.2, 54.5	55.2
CH (1, 13)	43.0	42.4, 43.2	43.3
CH (5, 9)	40.7	41.5, 40.5	41.2
CH (14, 15)	38.8	38.7, 37.7	38.4
CH_2 (16)	35.8	33.1	31.1 (est)
CH_2 (6, 8)	27.2	26.8, 26.6	26.5
CH_2 (7)	21.7	20.2	19.9 (est)

C_hH), 43.3, 43.0, 39.5 (3 × CH), 30.7 (C_fH_2), 28.6 (C_aH_2), 26.7 (C_gH_2); UV (EtOH) λ_{max} 275 (ϵ 290), and end absorption; IR (KBr disc) 3350 cm^{-1} (br).

3,11-Bis(dimethylamino)-3,11-diazahexacyclo-[11.2.1.$0^{2,12}$.$0^{4,15}$.$0^{5,9}$.$0^{10,14}$]hexadecane (27). A mixture of 0.88 g (3.57 mmol) of **25**, 30 mL of acetonitrile, 5.0 mL (61.6 mmol CH_2O) of 35% formalin, and 1.80 g (28.6 mmol) of $NaBH_3CN$ was stirred at room temperature while 30 drops of acetic acid was added over 2 h. After the mixture was stirred for 3 h more, 10 mL of concentrated hydrochloric acid was added, and the solvent was removed. The residue was dissolved in 15% sodium hydroxide and extracted five times with 25-mL portions of ether. Drying with sodium sulfate and concentration gave 1.4 g (130%) of crude **27**, which was recrystallized from hexane and sublimed: mp 98–103 °C; empirical formula,[10] $C_{18}H_{30}N_4$ (*m/e* 302, 6.7% of base peak at 43); ^1H NMR δ 3.21 (br s, 2 H), 3.13 (br s, 2 H), 2.35–2.20 (m, 2 H), 2.30 (s, 12 H), 2.06 (m, 2 H), 2.0–1.8 (m, 4 H), 1.8–1.7 (m, 2 H), 1.53 (d, J = 11 Hz, 1 H), 1.41 (d, J = 11 Hz, 1 H), 1.4–1.2 (m, 2 H); ^{13}C NMR δ 63.8, 57.2 (C_dH and C_hH), 45.8, 42.7, 40.6 (3 × CH), 41.4 (CH_3), 31.0 (C_fH_2), 29.2 (C_aH_2), 27.0 (C_gH_2).

3,11-Dinitroso-3,11-diazapentacyclo[11.2.1.$0^{4,15}$.$0^{5,9}$.$0^{10,14}$]-hexadecane (24). Treatment of 3.87 g (17.7 mmol) of diamine **13** with sodium nitrite under the same conditions as in the preparation of **23** gave 3.5 g of crude product, which was recrystallized from ethyl acetate to give **24** as brownish crystals, mp 126–126.5 °C. The mass spectrum showed no parent ion, but the 246 peak (p − 30) peak matched for $C_{14}H_{20}N_3O$,[10] as expected if one nitroso group had been lost. ^1H NMR, exceedingly complex; ^{13}C NMR is shown in Table II, with assignments to conformations.

3,11-Diamino-3,11-diazapentacyclo[11.2.1.$0^{4,15}$.$0^{5,9}$.$0^{10,14}$]-hexadecane (26). Reduction of 3.78 g of nitroso compound **24** with 3.0 g of lithium aluminum hydride under the same conditions and workup as for **25** gave 3.0 g of an oil, which gave 2.53 g of a light yellow oil upon Kugelrohr distillation: empirical formula,[10] $C_{14}H_{24}N_4$; ^1H NMR δ 3.06 (d, J = 9 Hz, 2 H), 3.05 (br s, 4 H), 2.7–2.6 (m, 2 H), 2.5–2.3 (m, 2 H), 2.20 (dd, J = 9.0, 6.1 Hz, 2 H), 2.2–2.0 (m, 2 H), 2.0–1.75 (m, 6 H), 1.66–1.50 (m, 2 H), 1.48 (dt, J = 12.5, 10.3 Hz, 2 H); ^{13}C NMR δ 68.7 (C_dH), 65.7 (C_hH_2), 44.8, 42.2, 39.5 (3 × CH), 39.0 (C_aH_2), 27.7 (C_fH_2), 22.4 (C_gH_2).

3,11-Bis(dimethylamino)-3,11-diazapentacyclo-[11.2.1.$0^{4,15}$.$0^{5,9}$.$0^{10,14}$]hexadecane (29) was made by reductive methylation of **26**, using the same conditions as in the preparation of **27**, in 87% crude yield. Sublimation and recrystallization from hexane gave **27**: empirical formula,[10] $C_{18}H_{32}N_4$ (*m/e* 304, 1.2% of base peak at 260); mp 96–101 °C; ^1H NMR δ 2.93 (br t, 2 H), 2.66 (d, J = 7.7 Hz, 2 H), 2.5–2.4 (m, 2 H), 2.37–2.30 (m, 2 H), 2.30 (s, 12 H), 2.2–2.0 (m, 2 H), 2.0–1.9 (m, 2 H), 1.85–1.65 (m, 5 H), 1.55–1.35 (m, 3 H); ^{13}C NMR δ 57.6 (C_dH), 43.7 (C_hH_2), 43.2, 42.6, 40.5 (3 × CH), 39.0 (CH_3), 38.0 (C_aH_2), 28.0 (C_fH_2), 22.7 (C_gH_2).

3,11-Bis(diethylamino)-3,11-diazahexacyclo-[11.2.1.$0^{2,12}$.$0^{4,15}$.$0^{5,9}$.$0^{10,14}$]hexadecane (28) was prepared by reductive ethylation of **25** with acetaldehyde, using the same method as for the methyl derivative **27**, giving a crude yield of 100%. Purer **20** was obtained by Kugelrohr distllation, as an oil; empirical formula,[10] $C_{22}H_{38}N_4$ (present at *m/e* 358, 25.3% of base peak at 286); ^1H NMR δ 3.25–3.14 (m, 4 H); ethyl group ABX_3 pattern, δ_A 2.50, δ_B 2.78, δ_X 1.03, J_{AB} = 12.5 Hz, J_{AX} = 6.9 Hz, J_{BX} = 7.2; 2.34 (br s, 2 H), 2.25–2.0 (m, 4 H), 1.97–1.87 (br m, 2 H), 1.86–1.75 (m, 2 H), 1.7–1.58 (br m, 2 H), 1.50 (dt, J = 10.5, 1.6 Hz, 1 H), 1.35 (dt, J = 10.5, 1.6 Hz, 1 H); ^{13}C NMR δ 63.9, 61.3 (C_dH and C_hH), 46.0, 43.0, 40.8 (3 × CH), 44.7 (CH_2CH_3), 30.1 (C_fH_2), 29.3 (C_aH_2), 26.7 (C_gH_2), 13.5 (CH_2CH_3).

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Coal Liquefaction Model Studies: Radical-Initiated and Phenol-Inhibited Decomposition of 1,3-Diphenylpropane, Dibenzyl Ether, and Phenethyl Phenyl Ether

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The thermal decompositions of 1,3-diphenylpropane (**1**), dibenzyl ether (**2**), and phenethyl phenyl ether (**3**) have been studied in the temperature range of 138–250 °C in the presence of various free-radical initiators. Thermodynamic calculations of the conversion of **1** to toluene and styrene indicate the reaction is unfavorable below 300 °C, and **1** was found to be unreactive with di-*tert*-butyl peroxide (TPO) at 138 °C, di-*tert*-butyldiazene (TBD) at 200 °C, and 1,1,2,2-tetraphenylethane (TPE) at 250 °C. Reactions of **2** to toluene and benzaldehyde and of **3** to phenol and styrene were calculated to be energetically favorable at these temperatures. **2** reacted in the presence of TPO, TBD, and TPE to give toluene, benzaldehyde, and 1,2-diphenylethane in a free-radical chain process. **3** reacted in the presence of TBD and TPE to give phenol and styrene but did not react with TPO. Reaction of **2** can be inhibited with 2,6-di-*tert*-butyl-4-methylphenol. With TPO as the initiator the reaction was −0.61 order in phenol, while with TBD as the initiator the reaction was −1.1 order in phenol. The change in reaction order is due to changes in the rates of the various hydrogen-tranfer reactions. The hindered phenol did not inhibit reaction of **2** at temperatures above 200 °C. The mechanisms of these reactions and the implications for coal liquefaction processes are discussed.

The thermal decompositions of 1,3-diphenylpropane (**1**), dibenzyl ether (**2**) and phenethyl phenyl ether (**3**) as neat liquids or as solutions in hydrogen-donating solvents have been found to proceed by free-radical chain reactions in

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