Acid-Catalyzed Cyclization of 1,19-Unsubstituted a,c-Biladienes

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A new route for the synthesis of corroles through cyclization of a,c-biladienes in acidic media is reported. Spectroscopic analysis of the reaction mixture shows that it proceeds with an intramolecular pathway through the formation of a totally conjugated open-chain tetrapyrrole. The presence of substituents at the 10-position of the tetrapyrrole strongly influences the fate of the reaction: phenyl groups accelerate the cyclization to corrole, whereas in the presence of alkyl substituents this reaction does not occur. This effect has been examined by means of computational methods, and it has been demonstrated that conformational factors are dominant in driving the reaction toward the formation of the macrocycle.

Introduction

Over 2500 papers are published every year on tetrapyrrolic macrocycles testifying the great interest in their properties and applications.[1−4] Although the porphyrin is certainly the most studied, a large number of related macrocycles have been synthesized recently in order to study the structure and property relationships.[5−7] Among cyclic tetrapyrrole corroles, aromatic macrocycles with a direct link between two pyrrole rings have exhibited some very interesting properties such as the capability of maintaining a planar conformation even when completely substituted at the peripheral positions and the stabilization of high oxidation states for coordinated metal ions.[8−11]

The synthesis of tetrapyrrolic macrocycles can be easily achieved by cyclization of a proper linear precursor: since a variety of substitution patterns can be introduced in linear tetrapyrroles, a wide range of symmetrically and asymmetrically substituted macrorings is now accessible. The nature of the product of the cyclization reaction depends on the substitution pattern at the 1,19-positions; thus, corroles can be obtained via cyclization of 1,19-dibromo, 1,19-diiodo, and 1,19-diunsubstituted a,c-biladienes.[8−13] In the latter case the reaction proceeds through the base-catalyzed formation of an aromatic intermediate, bilatriene, which then generates the direct pyrrole−pyrrole link.

The formation of the bilatriene free base has been considered an essential step in the synthetic pathway to corroles until the formation of these macrocycles was noted as byproducts in the recently developed 4 + 1 synthesis of sapphyrins which occurs in acidic ethanol.[14] This surprising result lead us to investigate the possibility that the cyclization reaction of 1,19-diunsubstituted a,c-biladienes can occur also under acidic conditions and that this new simple procedure could be utilized for the synthesis of corroles.

The reaction has been investigated spectroscopically and by means of computational methods in order to ascertain its applicability and to study the influence of substituents at the 10-position of the linear tetrapyrrole.

Results and Discussion

The classical route to corroles is the base-catalyzed cyclization of 1,19-dideoxy-a,c-biladienes that proceeds through the formation of the green bilatriene free-base in the basic reaction conditions. Such synthetic procedure has been extensively applied for over 30 years, and the methodology has been only recently improved by using chloranil as oxidizing agent.[9] Different synthetic schemes such as a 2 + 2 McDonald type condensation of a dipyrromethane dialdehyde unit with a 2,2′-bipyrrole[15] or the self-condensation of a monopyrrolic precursor[16] have been reported, but these reactions proceed only in the presence of cobalt ions and lead to the formation of corrole cobalt complexes. Our serendipitous discovery that corroles could be formed also in acidic solutions[14] prompted us to investigate this reaction to optimize the preparative conditions and verify if it could be generally applied to the synthesis of corroles.

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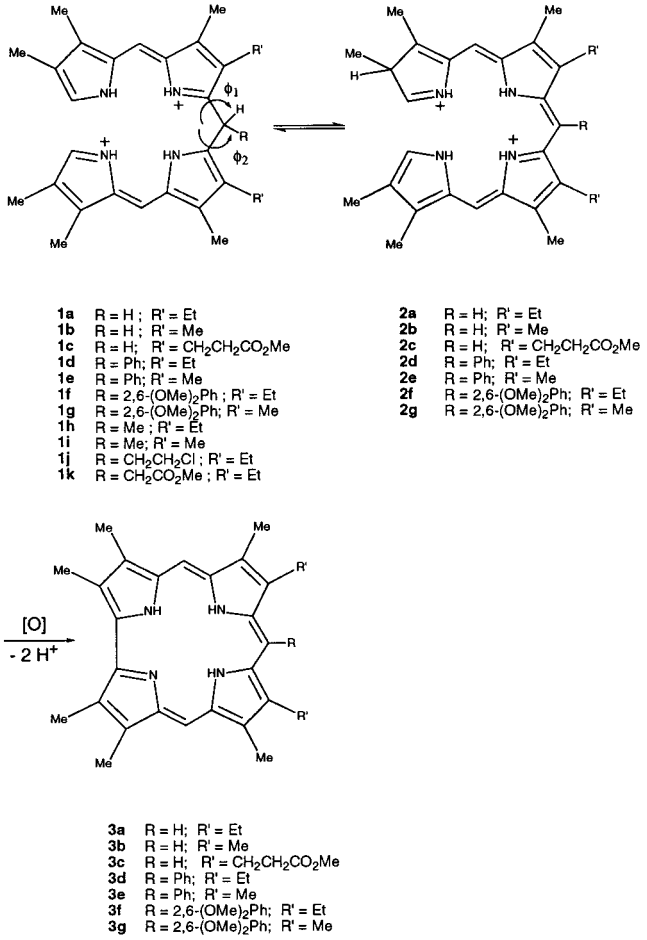
Scheme 1



It is well-known that the nature of substituents influences the acid−base equilibria of a,c-biladienes and that when a methyl substituent is present at the 10-position no bilatriene is formed even in the presence of piperidine.[17]

We have then examined a series of 10-substituted 1,19-dideoxy-10-R-8,12-R′-2,3,7,13,17,18-hexamethyl-a,c-biladienes (Scheme 1).

The cyclization reactions were carried out in refluxing ethanol in the presence of excess PTSA; a,c-biladienes **1d**,**1f,g**, however, failed to precipitate as pure materials, and all the attempts to purify these compounds led to their extensive decomposition. In this case we synthesized these linear tetrapyrroles in acidic absolute ethanol and carried out the subsequent cyclization reaction in situ. The progress of the reaction was monitored by observing the disappearance of the two absorptions characteristic of a,c-biladienes[18] and the concomitant increase, when observed, of the absorption typical of corrole in its protonated form.[8]

Table 1 summarizes the reaction conditions for the a,c-biladienes investigated. No cyclization at all was observed for **1h**−**k** and prolonging the reaction time to 48 h led only to decomposition. Neutralization of the reaction mixture and chromatographic separation afforded corroles **3a**−**g** in good yields: all products have been characterized by ^{1}H NMR spectroscopy and FAB−MS analysis, and also by comparison with authentic specimens. As previously observed in the case of *meso*-phenyl-substituted corroles and their cobalt complexes,[8,16] the corrole skeleton easily accommodates very hindered substituents, maintaining aromaticity and without substantial deviation from planarity. In the case of **3g**, where a 2,6(OMe)$_2$Ph substituent is present at C−10, this is demonstrated by the appearance in its electronic spectrum of an intense Soret band at 401 nm, a value almost identical to that of the *meso*-unsubstituted macrocycle.[8] Also in the NMR spectrum of **3g** the existence of an aromatic ring current is demonstrated by the chemical shift values of the resonances due to the 5,15-protons (δ = 9.35 ppm) and to the inner NH (δ = −2.5 ppm).

Table 1. Experimental Conditions for Cyclization Reactions. Initial Concentration of 1a−k was 8.5 × 10^{-3} M in EtOH/PTSA ([PTSA] = 2.6 × 10^{-3} M)

reagent	reaction time	*T*, °C	yield (%)
1a	4 h	reflux	28 (40)[a]
1b	4 h	reflux	42
1c	4 h	reflux	45
1d	5 min	25	35
1e	5 min	25	65
1f	20 min	reflux	24
1g	20 min	reflux	29
1h−k	48 h	reflux	0

[a] Yield obtained for an initial concentration 5 × 10^{-4} M.

No differences were observed if the reactions were carried out in the dark or by substituting PTSA with TFA. Also acetic acid can be used as solvent instead of acidic ethanol with no substantial differences in reaction time or yield. Best conditions were obtained when the reactions were carried out in dilute solution (initial concentration of a,c-biladienes being ca. 5 × 10^{-4} M) as expected for an intramolecular reaction pathway.

To gain a better understanding of the reaction pathway, the cyclization of **1c** was monitored by means of ^{1}H NMR spectroscopy. The poor solubility of a,c-biladiene salts prevented a detailed analysis of the spectra; however, the spectrum of an acidic (TFA) ethanolic solution of **1c** showed a major variation in the low-field region where the original single resonance due to the 1,19-protons (7.65 ppm) (Figure 1a) appeared shifted at lower field and split into two peaks of equal intensity: a split one centered at 8.00 ppm and a singlet at 7.8 ppm (Figure 1b). This observation indicates a differentiation of the two terminal positions of the tetrapyrrole and is consistent with the formation of the tautomeric form **2c**. There is no experimental evidence for the exclusive formation of this intermediate: different sites of protonation are possible, generating different tautomeric forms of the same molecule. The α positions of pyrroles are generally preferred for protonation,[19] but we choose to indicate the site of protonation at C-2 since it can represent the active species for the cyclization to corrole by an intramolecular electrophilic attack of C-1 on C-19; a similar pathway has been reported for the acid-catalyzed polymerization of pyrrole.[20]

Variable temperature experiments, performed by heating the sample to 340 K (near to the solution boiling

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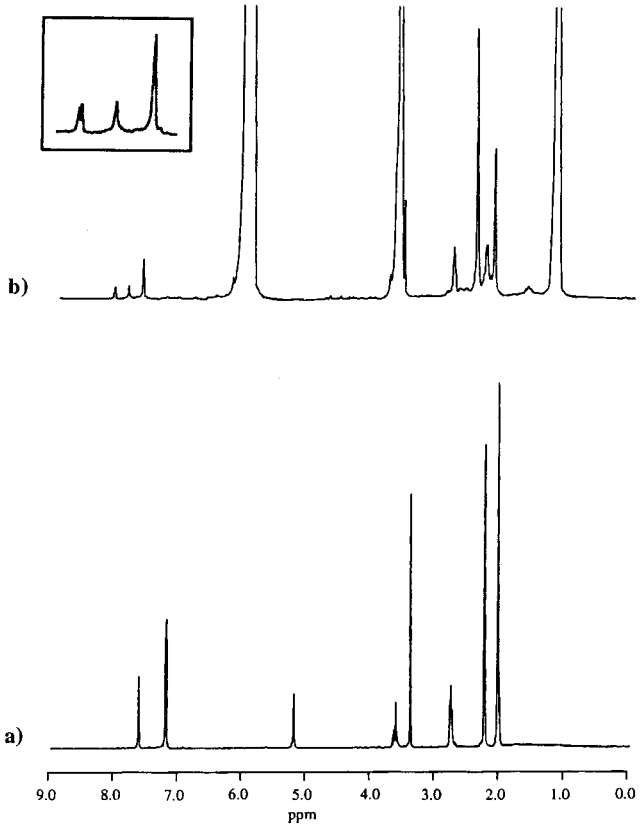

Figure 1. ^{1}H NMR spectrum of **1c** in $CDCl_3$ (a) and in EtOH/TFA (b). Inset shows an enlargement of the low-field region of the spectrum.

point) did not show the presence of any other intermediate but only the formation of the macrocycle **3c** in its protonated form. The lack of a resonance due to the residual 10-H in compound **2c** could be ascribed with exchange with the deuterated solvent.[17]

The same experiment was performed using biladiene **1j**: no spectral variations were observed by adding TFA to an ethanolic solution of **1j**. The resonances due to the 1,19- and 5,15-protons appeared as two equally intense singlets at 7.90 and 7.60 ppm and that due to the 10-H as a triplet at 5.25 ppm even when the temperature was raised 340 K, indicating the lack of protonation on pyrrole A or D. Exchange with deuterium of the 10-H has been observed, as a decrease in intensity of its resonance, only by heating the sample to 340 K for over 2 h. The presence of *meso*-alkyl substituents greatly influences the acid−base equilibria of biladienes **1h**−**k** that do not undergo cyclization even in basic media.

The observed reactivity cannot be simply explained on the basis of the electronic effect of the 10-R substituents. The most efficient reactions are in fact those involving **1d**−**g** where R is an electron-withdrawing group, but cyclization does not occur either with an electron-donating substituent such as Me (**1h**−**i**) or when R is a group with a weak electron-withdrawing effect (**1j**−**k**).

NMR spectroscopy showed that cyclization occurs through the formation of the protonated, totally conjugated species. We then considered the possibility that the acidity of the 10-H and hence the stabilizing effect of the 10-R substituent could lead to the difference in reactivity observed. The atomic charges of the centers involved in the reactions have been calculated by using

Table 2. Atomic Charges Derived *via* Mulliken Population Analysis (MPA) and CHELPG Analysis

			MPA		CHELPG	
label	R	R′	C_{10}	H_{10}	C_{10}	H_{10}
1a	H	Et	−0.281	0.218	0.429	0.030
1d	Ph	Et	−0.257	0.226	0.440	−0.005
1f	2,6-$(OMe)_2$Ph	Et	−0.250	0.261	0.532	−0.037
1h	Me	Et	−0.233	0.217	0.502	−0.027
1j	CH_2CH_2Cl	Et	−0.196	0.218	0.338	0.015
1k	CH_2CO_2Me	Et	−0.207	0.259	0.539	−0.021

both the Mulliken population analysis (MPA) and the CHELPG analysis[21] by means of RHF/6-31G** single point calculations. The geometries used were calculated at a semiempirical level (AM1) considering the comparison of biladienes **1a**−**k** starting from the 5,15-*Z*, syn conformation. Tetrapyrroles can exist in a variety of interconvertible conformational forms: hydrogen bonding favors the *Z*, syn conformation and the *Z* stereochemistry is that associated with the most stable and naturally occurring diastereoisomer of bilirubin.[22,23] In our analysis the torsion angles ϕ_1 [$N_{22}-C_9-C_{10}-C_{11}$] and ϕ_2 [$C_9-C_{10}-C_{11}-N_{23}$] are defined as $\approx 0°$ for corrole-like conformation. Since atomic charges are not quantum mechanical observable methods for their calculation are necessarily arbitrary and this explains the very different numerical values obtained with the two analyses. It is clear, however, from data reported in Table 2 that no trend exists correlating atomic charges and observed reactivity. ΔH_f have been calculated for **1a**−**k** and **2a**−**k** by means of semiempirical AM1 and PM3 methods (see Experimental Section). The difference in the heats of formation [ΔH_f(**2**) − ΔH_f(**1**)] resulted to be comparable and again in disagreement with the observed reactivity. Thus, for instance, [ΔH_f(**2d**) − ΔH_f(**1d**)] = 16.6 kcal/mol and [ΔH_f(**2h**) − ΔH_f(**1h**)] = 17.1 kcal/mol.

To ascertain if the lack of cyclization observed for 10-alkyl-substituted biladienes could be due to steric factors, a conformational study of compounds **1a**, **1h**, **2a**, and **2h**, chosen as examples of a reactive and an unreactive species, has been carried out at a semiempirical level (AM1). Semiempirical methods are certainly less reliable and more restrictive than ab initio but do not require considerable computer capacity and computational time. In the case of dipyrroles, for which both types of calculations have been reported, the AM1 method yielded structures and their relative energetic ordering in agreement with ab initio results (MP2) although with underestimated values for rotational barriers.[23] The AM1 results reported conform better to MP2 data than those obtained with other semiempirical methods (PM3). Its reliability in comparing similar structures and its being relatively inexpensive as far as computer capability is concerned can be considered to counterbalance the limits inherent to the AM1 method.

Given the high number of degrees of freedom present in the tetrapyrroles under investigation we did not carry out a systematic study of the potential energy surfaces but only varied (in 45° steps) the torsional angles ϕ_1 and ϕ_2 maintaining the 5,15−*Z*, syn conformation. The most stable conformers resulted in (90°,90°) for **1a** and

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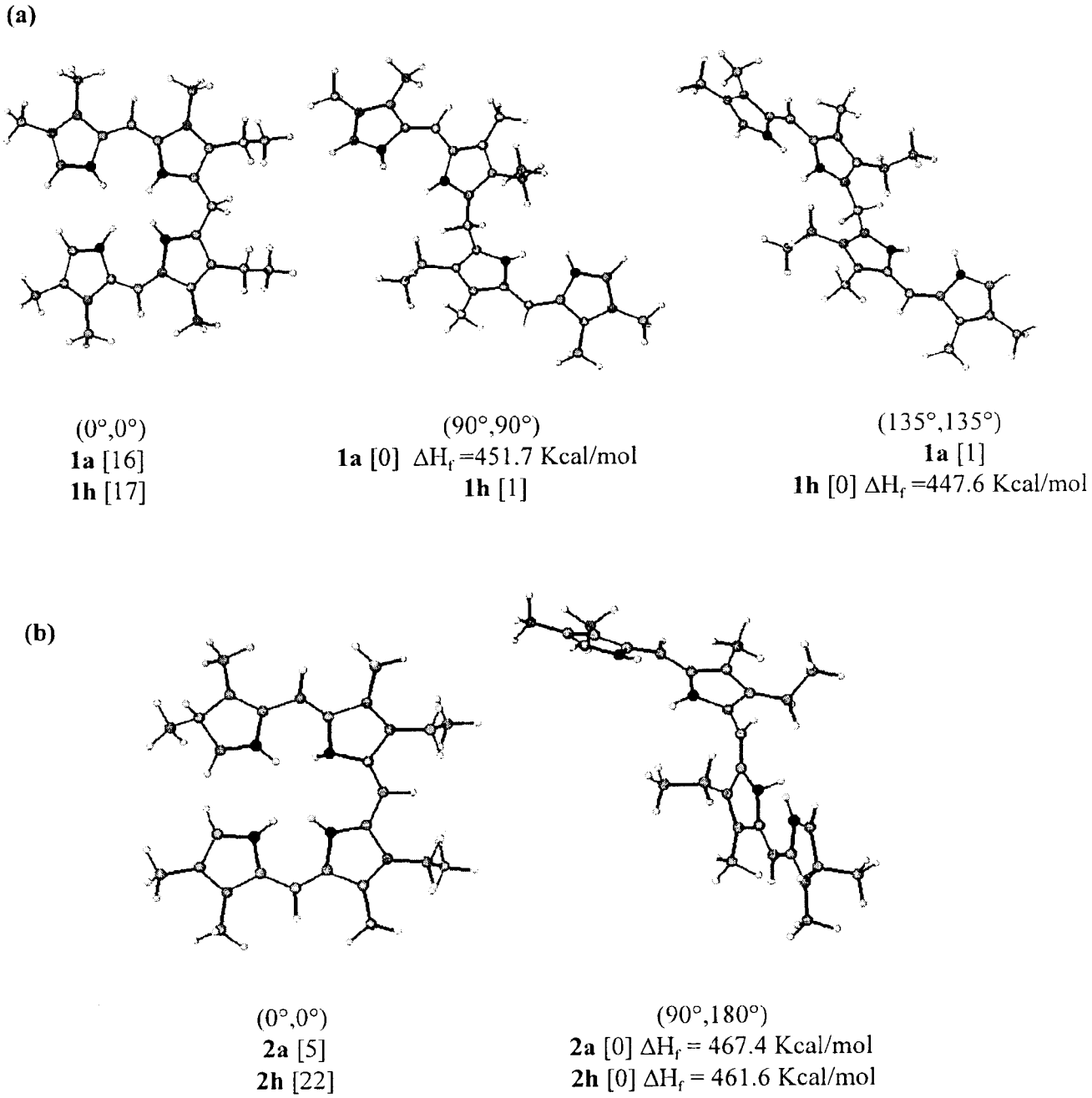

Figure 2. Representations, defined by torsion angles (ϕ_1 and ϕ_2) and energies [kcal/mol], for (a) **1a** and **1h**; (b) **2a** and **2h** (**1a** and **2a** are shown).

(135°,135°) for **1h** (Figure 2a). For both species the energy difference between the most stable form and that of the (0°,0°) conformation is almost identical. For **2a** and **2h**, global minima are located at (90°,180°). The difference between the energy values of such minima and those relative to the other conformations for which the molecule's skeleton is planar (0°,0°) is 5 kcal/mol for **2a** and 22 kcal/mol for **2h**, indicating that a planar conformation, necessary to achieve cyclization, cannot be easily achieved for the latter species (Figure 2b).

The TS search has been carried out for the reactions that, starting from the biladienes most stable conformers, led to the formation of the protonated species in their planar corrole-like conformation (0°,0°). The value of the heat of formation found for the structure calculated as representative of the TS of the reaction **1a** (90°,90°) → **2a** (0°,0°), resulted in $\Delta H_f^{\ddagger}$ = 473.5 kcal/mol and its difference from the heat of formation of **1a** is $\Delta H_f^{\ddagger} - \Delta H_f$ = 21.8 kcal/mol. For the reaction **1h** (135°,135°) → **2h** (0°,0°), $\Delta H_f^{\ddagger}$ = 591.3 kcal/mol and the difference $\Delta H_f^{\ddagger} - \Delta H_f$ = 143.7 kcal/mol. The barrier that cannot be overcome by the 10-alkyl substituted biladiene is then a conformational one. The conclusion is supported by data resulting from the TSs performed for the tautomerism **1a** (0°,0°) → **2a** (0°,0°) and **1h** (0°,0°) → **2h** (0°,0°) that do not involve conformational variations. For such reactions the values of $\Delta H_f^{\ddagger} - \Delta H_f$ are very close, 17.0 and 23.5 kcal/mol, respectively.

Dolphin[17] attributed to steric hindrance the lack of formation of bilatriene in basic conditions for 1,19-dideoxy-a,c-biladienes containing a 10-methyl substituent. Furthermore, a comparison of the conformations of decasubstituted porphyrin showed that large distortion from planarity is observed for 5,15-dialkyl substituted

species while almost no out-of-plane distortion is present when the 5,15 substituents are aryl groups.[24]

A nearly planar conformation is necessary to achieve cyclization of a,c-biladienes to corroles and only when such requirement is met the reaction can be successful.

Experimental Section

General conditions are as previously reported.[14] All chemicals (Aldrich) were reagent grade and were used without further purification.

a,c-Biladienes **1a**−**c**,**e**,**h**−**k** have been prepared following the published procedure.[17,25]

Cyclization Reactions. a,c-Biladiene dihydrobromide **1a** (0.5 g, 0.85 mmol) and *p*-toluenesulfonic acid hydrate (0.5 g) were dissolved in 100 mL of absolute ethanol and refluxed. Progress of the reaction was monitored spectrophotometrically; when absorbances attributable to starting material disappeared, the solution was cooled at room temperature, neutralized with NaOH 2 N and evaporated under vacuum. The resulting solid was redissolved in CH_2Cl_2 and then washed with water (three times) and dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum, and the crude mixture was chromatographed on neutral alumina (Brockmann Grade III); the column was eluted with CH_2Cl_2 to yield a red-violet fraction which was crystallized from CH_2Cl_2/*n*-hexane. This compounds were identified on the basis of comparison of their spectral properties with those reported in the literature,[25] and by comparison with an authentic sample.

a,c-Biladiene dihydrobromides **1b**, **1c**, and **1e** were reacted as described for **1a**, yielding the corresponding corroles **3b**, **3c**, and **3e**.

a,c-Biladienes **1h**−**k** were reacted as described for **1a**. No evidence for cyclization was obtained.

Dibenzyl 5-Phenyl-3,7-diethyl-2,8-dimethyldipyrromethane-1,9-dicarboxylate. To a 500 mL flask were added benzaldehyde (0.73 g, 6.9 mmol), benzyl 3-methyl-4-ethylpyrrole-2-carboxylate[26] (3.38 g, 13.9 mmol), and 200 mL of absolute EtOH. The flask was purged with N_2, and PTSA (0.1 g) was added. The mixture was then heated at reflux for 3 h under N_2 with magnetic stirring. Triethylamine (2.0 mL) was added and the ethanol was removed in vacuo. The light-yellow solid was recrystallized from MeOH to yield the title dipyrromethane (3.10 g, 5.4 mmol; 78% yield). ^{1}H NMR: ($CDCl_3$) δ 0.81 (t, *J* 7 Hz, 6 H), 2.18 (s,6 H), 2.25 (q, *J* 7 Hz, 4 H), 5.24 (s, 4 H), 5.48 (s, 1 H), 7.34 (m, 15 H), 8.36 (br s, 2 H). LRMS (FAB): 573 (M^+). Anal. Calcd for $C_{37}H_{38}N_2O_4$: C, 77.33; H, 6.66; N, 4.87. Found: C, 77.51; H, 6.40; N, 4.62.

Dibenzyl 5-(2,6-Dimethoxyphenyl)-2,3,7,8-tetramethyldipyrromethane-1,9-dicarboxylate. This compound was similarly prepared in 82% yield from benzyl 3,4-dimethylpyrrole 2-carboxylate[27] and 2,6-dimethoxybenzaldehyde. ^{1}H NMR: ($CDCl_3$) δ 0.81 (s, 6 H), 2.12 (s, 6 H), 3.61 (s, 6 H), 5.21 (s, 4 H), 6.02 (s, 1 H), 6.53 (d, *J* 7.5 Hz, 2 H), 7.13 (t, *J* 7.5 Hz, 1 H), 7.35 (m, 10 H), 8.32 (br s, 2 H). LRMS (FAB): 607 (M^+). Anal. Calcd for $C_{37}H_{38}N_2O_6$: C, 73.25; H, 6.31; N, 4.62. Found: C, 73.03; H, 6.16; N, 4.47.

Dibenzyl 5-(2,6-Dimethoxyphenyl)-3,7-diethyl-2,8-dimethyldipyrromethane-1,9-dicarboxylate. This compound was similarly prepared in 76% yield from benzyl 3-methyl-4-ethylpyrrole-2-carboxylate[26] and 2,6-dimethoxybenzaldehyde. ^{1}H NMR: ($CDCl_3$) δ 1.66 (t, *J* 7 Hz, 6 H), 2.06 (s, 6 H), 2.22 (q, *J* 7 Hz, 4 H), 3.66 (s, 6 H), 5.26 (s, 4 H), 6.08 (s, 1 H), 6.47(d, *J* 7.5 Hz, 2 H), 7.17 (t, *J* 7.5 Hz, 1 H), 7.38 (m, 10 H), 8.58 (br s, 2 H). LRMS (FAB): 635 (M^+). Anal. Calcd for $C_{39}H_{42}N_2O_6$: C, 73.79; H, 6.67; N, 4.41. Found: C, 73.54; H, 6.46; N, 4.23.

8,12-Diethyl-2,3,7,13,17,18-hexamethyl-10-phenylcorrole 3d. 5-Phenyl-3,7-diethyl-2,8-dimethyldipyrromethane-1,9-dicarboxylic acid was obtained in quantitative yield after catalytic hydrogenation of dipyrromethane dibenzylic ester in THF containing 10% palladized charcoal and triethylamine. The diacid (500 mg, 1.27 mmol) was dissolved in trifluoroacetic acid (10 mL) and stirred for 5 min. 2-Formyl-3,4-dimethylpyrrole[28] (310 mg, 2.54 mmol) in MeOH (20 mL) was added, and the red solution was stirred for 5 min, before addition of 30% HBr in acetic acid (5 mL). The solution was heated at reflux, and the progress of the reaction was monitored spectrophotometrically; when absorbances attributable to starting material disappeared, the solution was cooled at room temperature, neutralized with NaOH 2 N, and evaporated under vacuum. The resulting solid was redissolved in CH_2Cl_2 and then washed with water (three times) and dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum, and the crude mixture was chromatographed on basic alumina (Brockmann Grade III); the column was eluted with CH_2Cl_2 to yield a red-violet fraction which was crystallized from CH_2Cl_2/*n*-hexane to give 227 mg of the desired corrole as red crystals, mp > 250 °C. UV−vis: λ_{max} 401 nm (ϵ 112 000), 545 (14 300), 598 (16 000). ^{1}H NMR: ($CDCl_3$) δ −2.58 (br s, 3 H), 1.18 (t, *J* 7 Hz, 6 H), 2.63 (q, *J* 7 Hz, 4 H), 3.38 (s, 12 H), 3.51 (s, 6 H),7.75 (m, 5 H), 9.38 (s, 2 H). LRMS (FAB): 515 (M^+). Anal. Calcd for $C_{35}H_{38}N_4$: C, 81.67; H, 7.44; N, 10.88. Found: C, 81.33; H, 7.13; N, 10.82.

8,12-Diethyl-2,3,7,13,17,18-hexamethyl-10-(2,6-dimethoxyphenyl)corrole 3f. This corrole was prepared as reported for corrole **3d** from 5-(2,6-dimethoxyphenyl)-3,7-diethyl-2,8-dimethyldipyrromethane-1,9-dicarboxylic acid and 2-formyl-3,4-dimethylpyrrole. UV−vis: λ_{max} 404 nm (ϵ 109 000), 543 (13 700), 599 (15 000). ^{1}H NMR: ($CDCl_3$) δ −2.59 (br s, 3 H), 1.24 (t, *J* 7 Hz, 6 H), 2.79 (q, *J* 7 Hz, 4 H), 3.25 (s, 6 H), 3.23 (s, 6 H), 3.49 (s, 12 H), 6.88 (d, *J* 7.5 Hz, 2H), 7.61 (t, *J* 7.5 Hz, 1 H), 9.32 (s, 2 H). LRMS (FAB): 575 (M^+). Anal. Calcd for $C_{35}H_{38}N_4O_2$: C, 77.32; H, 7.37; N, 9.75. Found: C, 77.14; H, 7.43; N, 9.58.

2,3,7,8,12,13,17,18-Octamethyl-10-(2,6-dimethoxyphenyl)corrole 3g. This corrole was prepared as reported for corrole **3d** from 5-(2,6-dimethoxyphenyl)-2,3,7,8-tetramethyldipyrromethane-1,9-dicarboxylic acid and 2-formyl-3,4-dimethylpyrrole. UV-Vis: λ_{max} 401 nm (ϵ 114 000), 541 (16 000), 598 (19 000). ^{1}H NMR: ($CDCl_3$) δ −2.50 (br s, 3 H), 2,45 (s, 6 H), 3.25 (s, 6 H), 3.28 (s, 6 H), 3.47 (s, 12H), 6.90 (d, *J* 7.5 Hz, 2 H), 7.65 (t, *J* 7.5 Hz, 1 H), 9.35 (s, 2 H). LRMS (FAB): 547 (M^+). Anal. Calcd for $C_{37}H_{42}N_4O_2$: C, 76.89; H, 7.01; N, 10.25. Found: C, 77.01; H, 6.93; N, 9.98.

Computations. Semiempirical calculations were carried out using the AM1[29] and PM3[30] methods using the Hyperchem program.[31] Geometric optimizations were terminated when the energy difference among successive iterations was lower than 10^{-3} kcal/mol. Starting from AM1 geometries, single point ab initio computation were performed using the Gaussian 94 system of programs.[32]

ΔH_f(0°,0°) (AM1, PM3, kcal/mol): **1a**: 462.4, 402.2; **1b**: 469.8; **1d**: 496.8, 462.0; **1e**: 508.1; **1f**: 414.6, 366.3; **1g**: 426.0; **1h**: 463.0, 405.4; **1i**: 474.2; **1j**: 452.6, 400.7; **1k**: 381.8, 333.8;

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2a: 472.5, 422.4; **2b**: 482.7; **2d**: 513.4, 442.1; **2e**: 520.2; **2f**: 435.9, 386.0; **2g**: 442.9; **2h**: 480.1, 426.0; **2i**: 487.4; **2j**: 474.6, 420.3; **2k**: 408.1, 347.2.

TSs (AM1) were performed using the synchronous transit linear algorithm ($A = 0.5$). Termination conditions: RMS gradient ≤ 0.1 kcal Å^{-1} mol^{-1}.

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Supporting Information Available: Heats of formation of corroles **3a**−**g** and of their protonated forms **4a**−**g** in the (0°,0°) conformation (Table SI). Conformational analyses (energy *vs* ϕ_1 and ϕ_2) of **1a**, **1h**, **2a**, **2h** (Table SII) (2 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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