Synthesis and Properties of Ligands Based on Benzo[g]quinoline

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Received October 15, 1993[⊗]

The preparation of 3-amino-2-naphthaldehyde is described. Ammonolysis of 3-hydroxy-2-naphthoic acid affords the corresponding amino acid which can be esterified and then reduced with LAH. Protection of the amino group, MnO_2 oxidation of the primary alcohol to an aldehyde, and deprotection gave the amino aldehyde which is an excellent Friedländer synthon for benzo[g]quinolines. Dimethylene-bridged analogues of 2,2′-bipyridine and 2,2′;6,2″-terpyridine were prepared as well as orthocyclophanes derived from tetracyclo[6.3.0.$0^{4,11}$.$0^{5,9}$]undecane-2,7-dione (TCU-2,7-dione). The absorption and emission spectra of these species are consistent with the parent benzo[g]quinoline where bathochromic shifts result from increased delocalization. The TCU derivative evidences exciplex formation so that its benzo[g]quinoline emission is almost completely quenched and an exciplex emission appears at 525 nm. Electrochemical analysis indicates that both reduction and UV absorption involve the same π^* orbital.

Introduction

One of the most useful ligands available to coordination chemists is 2,2′-bipyridine (bpy). Over the past two decades there has been a significant effort to develop analogues to bpy wherein differences in electronic and steric properties would lead to modification of the metal complex chemistry.[1] From a spectroscopic perspective, it is the nature of the metal-to-ligand charge-transfer (MLCT) state which dictates the important properties of many bpy complexes, especially those of Ru(II). If this MLCT state is long-lived and of appropriate energy, it might be able to participate in energy or electron transfer with an appropriate substrate leading to useful chemistry which ideally would be catalytic in nature.

The MLCT state is derived from excitation of an electron from a high-energy metal orbital to a low-lying unoccupied ligand orbital. For Ru(II) complexes this process typically involves the promotion of a metal t_{2g} electron to a bpy π^* orbital. Therefore, one approach to ligand design has centered on modification of bpy so as to raise or lower the π^* level and thereby modify the energy of the MLCT transition. To this end one can design more electronegative analogues of bpy with better electron-accepting capabilities. The effect of annulating benzo and pyrido rings to both halves of bpy has been examined and a correlation has been established between ligand electronegativity and the properties of the MLCT state of the corresponding Ru(II) complexes.[2] This paper will extend that concept by examining the effect of fusing a 2,3-naphtho ring to bpy and the closely related 2,2′:6,2″-terpyridine (tpy).

Synthesis

We have found that the most-convenient synthetic approach to modified bpy derivatives is the Friedländer condensation wherein an α,β-unsaturated β-amino aldehyde or ketone condenses with an enolizable ketone to lose two molecules of water directly generating the pyridine nucleus.[3] The use of β-aminoacrolein in this process is somewhat limited by the high reactivity of this species. Annulated derivatives behave much better so that quinolines can readily be prepared from 2-aminobenzaldehyde, and 1,8-naphthyridines result from 2-aminonicotinaldehyde. To incorporate a benzo[g]quinoline moiety using this methodology would require 3-amino-2-naphthaldehyde (1) as the appropriate synthon. Inspection of the literature indicated that an acetal analog had been prepared and used as a protected aldehyde.[4] A substituted ketone derivative had also been employed to provide a 5-substituted benzo[g]quinoline derivative.[5]

We prepared the free amino aldehyde 1 in six steps from commercially available 3-hydroxy-2-naphthoic acid as shown in Scheme 1. Zinc chloride catalyzes *ipso*-substitution of the hydroxyl group to provide the amino acid 3. Esterification followed by LAH reduction gives the amino alcohol 5. The amino group is sensitive toward oxidation and therefore must be protected as the trimethylacetamide prior to treatment with activated MnO_2, giving the protected aldehyde 7. Ultimately, deprotection with 2 N HCl gives 3-amino-2-naphthaldehyde (1). It has been known for some time that 2-aminobenzaldehyde is somewhat unstable, undergoing self-condensation to form a cyclic trimer as well as higher oligomers. It appears that 1 is more stable, and samples stored in the freezer for one month showed no appreciable decomposition.

The Friedländer reaction of 1 with a variety of ketones and diketones occurs readily under basic conditions leading to the polyaza cavities shown in Scheme 2. Condensation with 5,6,7,8-tetrahydro-8-quinolone (8)[6] provides the dimethylene bridged 2-(2′-pyridyl)benzo[g]quinoline 11 while a 2:1 reaction with 1,2-cyclohexanedione gives the symmetrical 3,3′-dimethylene-2,2′-bibenzo[g]quinoline (12). An analogous 2:1 reaction with 1,2,3,4,5,6,7,8-octahydroacridine-2,8-dione (10)[7] provides the tpy derivative 13.

While compounds 12 and 13 allow for the orientation of two benzo[g]quinoline subunits in a cavity-shaped planar array, the incorporation of two of these moieties in

⊗ Abstract published in *Advance ACS Abstracts*, January 15, 1994.

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(2) (a) Thummel, R. P.; Decloitre, Y. *Inorg. Chem. Acta* **1987**, *128*, 245. (b) Thummel, R. P.; Lefoulon, F. *Inorg. Chem.* **1987**, *26*, 675.

(3) (a) Caluwe, P. *Tetrahedron* **1980**, *36*, 2359. (b) Cheng, C.-C.; Yan, S.-J. *Org. React.* **1982**, *28*, 37. (c) Thummel, R. P. *Synlett* **1992**, 1.

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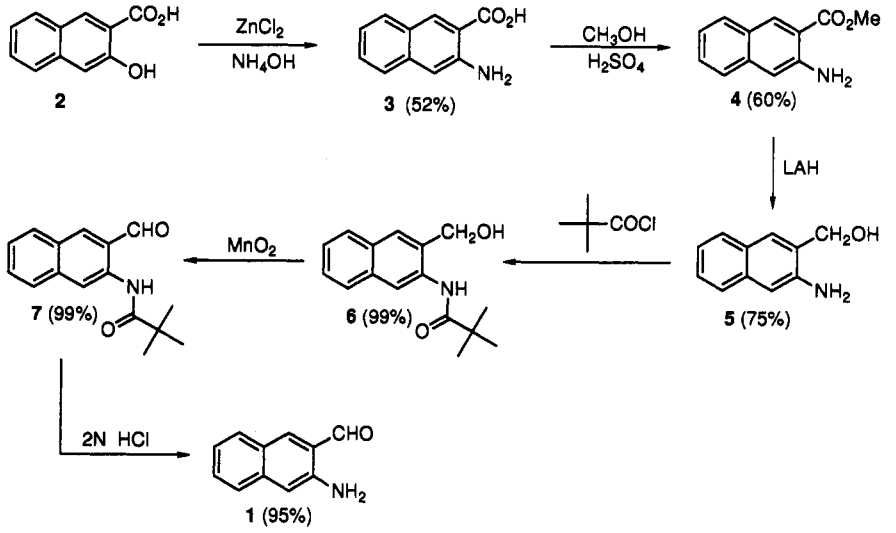
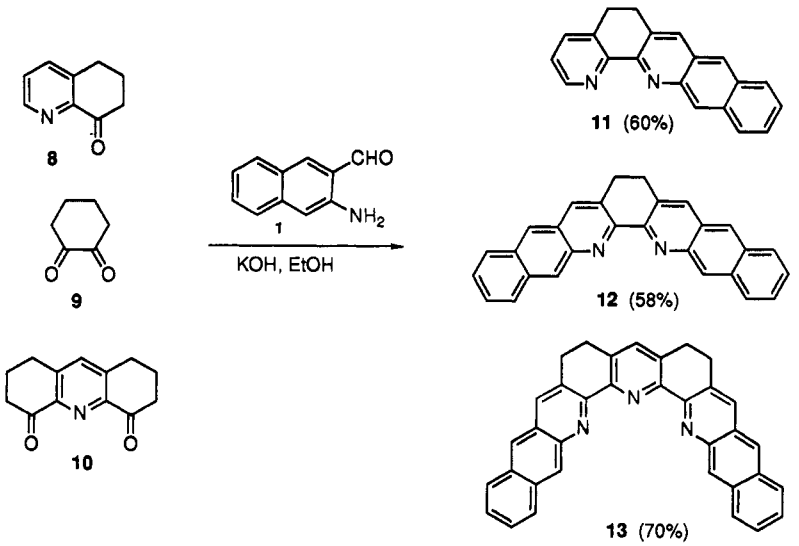
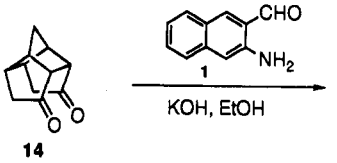
Scheme 1

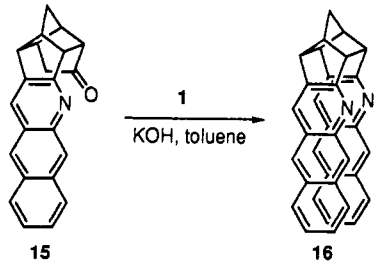


Scheme 2



a more-parallel orientation was also of interest. To this end we condensed **1** with an equimolar amount of tetracyclo[6.3.0.0^{4,11}.0^{5,9}]undecane-2,7-dione (TCU-2,7-dione, **14**)[8] to obtain monoketone **15**. The further condensation of **15** with a second equivalent of **1** provided the layered TCU derivative **16**.





Characterization and Properties

The benzo[*g*]quinolines **11**–**13**, **15**, and **16** were all readily characterized by their ^{1}H NMR spectra. The protons at positions 4, 5, and 10 all appear as sharp singlets with H_{10} being the lowest field signal in the spectrum, occurring between 8.6–9.2 ppm. The next lowest field signal is normally H_4, which is deshielded by the *para*-nitrogen. By analogy to quinoline and anthracene, H_7 and H_8 are assigned as the highest field peaks at about 7.5 ppm and they are almost always unresolved. Very similar, closely spaced multiplets are evidenced by H_6 and H_9 with the latter assigned at lower field, being closer to the electronegative nitrogen.

Comparison of the aromatic chemical shifts of **16** with the model compound **17** in $CDCl_3$ evidences shielding of the former signals by 0.19–0.44 ppm. This upfield shift is typical for cyclophanes of this type and is most pronounced for H_4 and H_5 where the two benzo[*g*]quinoline moieties are more proximate.[9] In C_6D_6 the chemical shifts

(8) (a) Mehta, G.; Srikrishna, A.; Veera Reddy, A.; Nair, M. S. *Tetrahedron* **1981**, *37*, 4543. (b) Cookson, R. C.; Crundwell, E.; Hudec, J. *Chem. Ind. (London)* **1958**, 1003. (c) Wenkert, E.; Yoder, J. E. *J. Org. Chem.* **1970**, *35*, 2986.

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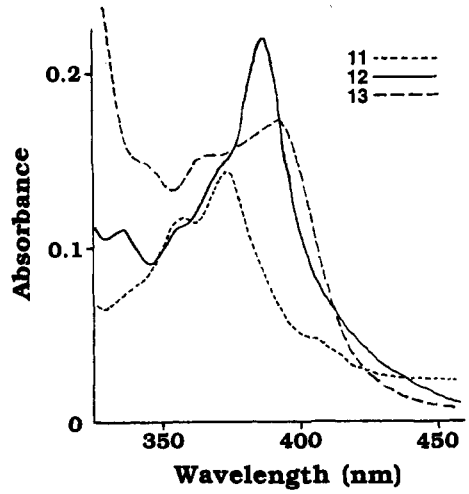
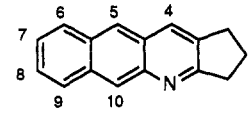


Figure 1. Long wavelength region of the UV absorption spectra of 11–13 (10^{-5} M CH_3CN).

all move to higher field but the overall shielding of **16** *versus* **17** is comparable to what is observed in chloroform with the exception of H_6, H_9, and H_{10}, where more organized solvent intercalation may be occurring.



17

For the TCU derivative **16**, the eight protons on the cage portion of the molecule give rise to four two-proton signals. The methylene group appears as an apparent AB quartet at 2.31 ppm and the remaining cage protons appear as broad singlets at 3.82, 3.69, and 3.56 ppm. The lack of splitting in these systems makes definite assignment difficult. A broad water peak appears at 1.75 ppm and scrupulous drying by heating under high vacuum will not completely remove this peak. We have noted similar hydration behavior for the analogous layered quinoline.[9] The addition of D_2O to the NMR sample causes the disappearance of this water peak and the appearance of a new HOD peak at 4.77 ppm.

It is noteworthy that the exchange of the hydrogen-bound water by D_2O causes a pronounced sharpening of the singlets at 8.30 and 3.82 ppm. These changes are consistent with these protons being H_{10} and the cage proton proximate to the nitrogen. These two signals therefore serve as sensitive probes toward changes in hydrogen bonding to the nitrogens.

The long wavelength region of the UV absorption spectra of **11–13** is shown in Figure 1 and of **16** and **17** is shown in Figure 2. Absorptions below 350 nm may be attributed to the pyridine moiety and are conspicuously absent from **12**. The existence of two benzo[*g*]quinoline subunits causes a bathochromic shift and an increase in intensity for **12** which may be viewed as a dimer of this subunit. In Figure 2 we observe that the absorption of the layered molecule **16** very closely resembles the model compound **17**, being more intense and exhibiting a bathochromic shift of about 2 nm.

Where the absorption spectrum gives us information about the excited-state population of a molecule, the emission spectrum addresses the depopulation of this state. Strong emission indicates a relatively long-lived excited

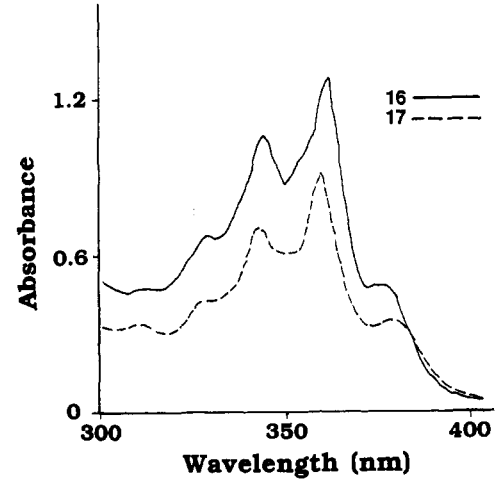


Figure 2. Long wavelength region of the absorption spectra of **16** and **17** (10^{-4} M CH_3CN).

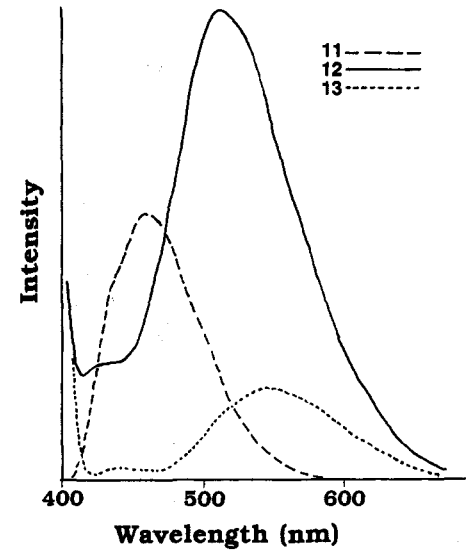


Figure 3. Room temperature fluorescence spectra of 11–13 (10^{-6} M CH_3CN) with excitation at the long wavelength absorption maximum.

state and the absence of nonradiative pathways for its depopulation. Figure 3 shows the emission spectra for **11–13**. The emission maximum of benzo[*g*]quinoline has been reported at 422 nm.[10] This emission shifts to 461 nm for **11**, 514 nm for **12**, and 544 nm for **13**, reflecting a steady progression to lower energy with increasing delocalization of the system. The greater emission intensity of **12** relative to **11** reflects the presence of two benzo[*g*]quinolines in the former which also correlates with the more efficient absorption of **12**.

The much-reduced intensity of **13** is interesting and possibly reflects the existence of a competing pathway for depopulation of the n,π^* state. It is possible that intersystem crossing from the n,π^* singlet to a lower energy π,π^* triplet may account for the decreased fluorescence. An unsuccessful attempt was made to detect the possible phosphorescence of this triplet in a methanol–ethanol glass at 77 K.

The emission spectra of **15–17** are shown in Figure 4. The model compound **17** shows a strong emission at 420

(10) Vo-Dinh, T.; Miller, G. H.; Abbott, D. W.; Moody, R. L.; Ma, C. Y.; Ho, C.-H. *Anal. Chem. Acta* **1985**, *175*, 181.

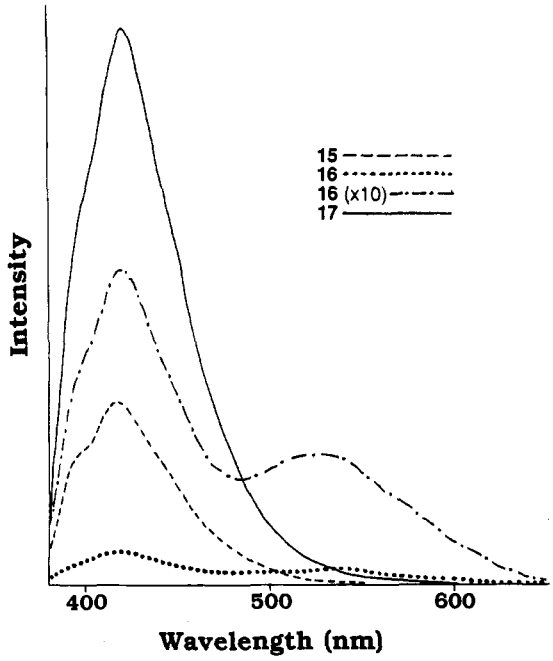


Figure 4. Room temperature fluorescence spectra of **15–17** (10^{-6} M CH_3CN) with excitation at 362 nm.

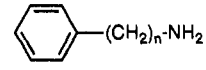
nm comparable to the parent benzo[*g*]quinoline. The monoketone exhibits considerably diminished emission which is explained by intramolecular quenching involving the carbonyl group. The layered compound **16** shows two emission bands at 421 and 525 nm. The shorter wavelength band corresponds to a weak benzo[*g*]quinoline emission. One possible explanation for the strong quenching of this signal might be the influence of the hydrogen-bound water, particularly through the formation of a cyclic complex.[11] To test this theory, we added small increments of methanol to the sample which should exchange with water but not allow formation of a cyclic H-bonded complex. No change in the emission spectrum was observed.

An alternative explanation was self-quenching *via* exciplex formation which might also explain the band at 525 nm. Excitation spectra were recorded monitoring both emission bands and very good agreement with the absorption spectrum was observed, confirming that both bands are attributable to **16**. To probe this exciplex theory we examined the emission of **17** at concentrations from 10^{-6} to 10^{-2} M. At 10^{-4} M the emission was too intense to measure while at 10^{-2} M it essentially disappears and a weak excimer band appears at 520 nm. The spectrum of **17** at 10^{-2} M correlates well with that of **16** at 10^{-6} M.

To quantitatively probe the electron affinity of **11–13** we measured their reduction potentials by cyclic voltammetry in benzonitrile at 25 °C. The reduction of benzo[*g*]quinoline involves electron addition to a π^* orbital so that the potential required for this reduction is a good measure of the relative energy of the orbital. For **11** we observe a clear, reversible reduction with a half-wave potential of −1.59 V (vs SCE). This can be compared to potentials of −1.75 V for 2,2′-biquinoline and −2.20 V for 3,3′-biisoquinoline.[12] Clearly the energy of the π^* level of **11** is lowered significantly.

For **12** we see the reduction split into two quasireversible waves with $E_{1/2}$ = −1.38 and −1.70 V. These two waves correspond to stepwise reduction of each of the two benzo[*g*]quinoline moieties. For **13**, which contains a tetrahydroacridine spacer between the two benzo[*g*]quinolines, these moieties become less interacting and two quasireversible waves are observed at −1.32 and −1.44 V. A third irreversible cathodic wave is observed at −1.86 V. If the first reduction potentials for these three ligands are plotted *versus* the lowest energy transition of the absorption spectrum, a linear relation is observed with a correlation coefficient of 1.00 and a slope of −0.44, indicating that these two processes are related and involve the same π^* orbital.

We expected that the TCU derivative **16** might act as a unique type of host system, being able to hydrogen bond a primary amine between its two nitrogens and possibly intercalate an aromatic ring into the cleft between its benzo[*g*]quinolines. To this end, we examined the effect of added phenylalkyl amines **18a,b** on the NMR spectrum of **16**. Although we saw clear evidence for the amine group binding by replacement of water, we saw no evidence for intercalation of the phenyl group, in that the aromatic resonances of both the host and guest were unperturbed. It appears that the entropic demands of restricting **18** to a favorable binding conformation were not compensated by the stabilization of complex formation.



18 a n = 3
b n = 4

We expect that molecules such as **11–13** should behave as good bidentate and tridentate chelators and their transition metal chemistry, particularly with Ru(II), will be investigated.

Experimental Section

Nuclear magnetic resonance spectra were recorded at 300 MHz for ^1H and 75 MHz for ^{13}C. Cyclic voltammograms were recorded in benzonitrile according to a procedure which has been previously described.[13] Melting points are uncorrected. All solvents were reagent grade. THF was dried over sodium and benzophenone and freshly distilled. Elemental analysis were performed by Canadian Microanalytical Service, Ltd, Delta, B. C., and HRMS were obtained by Dr. Terry Marriott at Rice University.

3-Amino-2-naphthoic Acid (3). In an autoclave were combined 30% aqueous ammonia (100 mL), zinc chloride (20 g, 0.2 mol), and 3-hydroxy-2-naphthoic acid (42.0 g, 0.22 mol). The autoclave was gradually heated to 195 °C over 3 h and was shaken at this temp for an additional 36 h. After cooling, the mixture was transferred to a 1-L round-bottom flask, and the autoclave was rinsed with water (3 × 100 mL). Concentrated HCl (150 mL) was carefully added to the mixture which was refluxed for 30 min and then filtered while hot. The residue was suspended in 100 mL of water and refluxed with concd HCl (30 mL) for an additional 30 min and again filtered while hot. The combined filtrates were cooled at 0 °C overnight and the precipitated aminonaphthoic acid hydrochloride was collected by filtration and dried.

The filter cake was placed in a 1-L flask with water (300 mL) and treated with 40% NaOH until no further solid dissolved. The mixture was heated to 85 °C and filtered to remove the insoluble matter. The filtrate was made acidic to Congo red by the addition of concentrated HCl, stirred for 15 min, and then neutralized to pH 7 with 10% NaOAc. The mixture was filtered and the precipitated product was washed with hot water and

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(12) Reference 1a, p 91.
(13) Thummel, R. P.; Goulle, V.; Chen, B. *J. Org. Chem.* **1989**, *54*, 3057.

dried at 50 °C to provide 21.5 g (52%) of 3-amino-2-naphthoic acid, mp 210–216 °C (lit.[14] mp 215–220 °C).

Methyl 3-Amino-2-naphthoate (4). Concentrated H_2SO_4 (60 mL) was added to methanol (120 mL), followed by 3-amino-2-naphthoic acid (11.7 g, 62 mmol). The solution was heated to reflux and a mixture of concd H_2SO_4 (12 mL) in methanol (120 mL) was added over a period of 3 h and the reflux was maintained overnight. The mixture was cooled, concentrated under vacuum, poured onto ice, and neutralized with saturated Na_2CO_3. The resulting precipitate was filtered, washed with water, and dissolved in CH_2Cl_2. The filtrate was extracted with CH_2Cl_2. The combined organic layers were washed with water and dried over $MgSO_4$. The solvent was evaporated to dryness to give 7.6 g (60%) of a deep yellow solid, mp 103–105 °C (lit.[15] mp 104–105 °C).

3-Amino-2-(hydroxymethyl)naphthalene (5). A solution of methyl 3-amino-2-naphthoate (7.5 g, 37 mmol) in dry THF (100 mL) was cooled to 5 °C. $LiAlH_4$ (2.25 g, 60 mmol) suspended in dry THF (60 mL) was added over a period of 15 min. The mixture was stirred at 5 °C for 2 h and then quenched with water (5 mL). The precipitate was filtered and washed with THF (4 × 30 mL). The solvent was removed and the crude product was digested with hot benzene (40 mL) for 5 min. After cooling, the benzene was removed by filtration to provide 4.7 g (75%) of a white powder, mp 181–183 °C : ^{1}H NMR (DMSO-d_6) δ 7.64 (d, 1H, J = 8.2 Hz), 7.61 (s, 1H), 7.51 (d, 1H, J = 8.2 Hz), 7.27 (t, 1H, J = 7.4 Hz), 7.11 (t, 1H), 6.90 (s, 1H), 5.26 (t, 1H, J = 5.3 Hz), 5.18 (s, 2H), 4.55 (d, 2H); ^{13}C NMR (DMSO-d_6) δ 144.9, 134.0, 129.5, 127.3, 126.4, 125.8, 125.4, 124.7, 121.1, 107.1, 61.1.

3-(Trimethylacetamido)-2-(hydroxymethyl)naphthalene (6). To an ice-cold solution of 3-amino-2-(hydroxymethyl)-naphthalene (2.61 g, 15 mmol) and triethylamine (2.25 g, 22.2 mmol) in $CHCl_3$ (90 mL) was added a solution of trimethylacetyl chloride (2.25 g, 18.8 mmol) in $CHCl_3$ (30 mL) dropwise over a period of 15 min. The reaction mixture was stirred at 0 °C for 1 h and at rt overnight. The product was concentrated and the crude solid was digested with 3% HCl (25 mL) for 1 h to give 3.65 g (95%) of a white powder, mp 168–171 °C: ^{1}H NMR ($CDCl_3$) δ 9.14 (broad, 1H), 8.70 (s, 1H), 7.82 (d, 1H, J = 8.0 Hz), 7.74 (d, 1H, J = 7.8 Hz), 7.63 (s, 1H), 7.45 (t, 1H, J = 7.3 Hz), 7.41 (t, 1H), 4.87 (s, 2H), 1.37 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 177.5 (CO), 135.2, 134.0, 129.9, 129.0, 127.8, 127.7, 127.4, 126.6, 125.2, 119.1, 65.1, 39.9, 27.6. Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.71; H, 7.39; N, 5.45. Found: C, 74.71; H, 7.28; N, 5.50.

3-(Trimethylacetamido)-2-naphthaldehyde (7). To a solution of 6 (1.00 g, 39 mmol) in $CHCl_3$ (100 mL) was added dry, freshly activated MnO_2 (4.0 g, 46 mmol). The reaction mixture was stirred at rt and monitored by TLC on silica gel eluting with hexane/EtOAc (3:1). An additional portion of MnO_2 (4.0 g) was added after 1 h and a third portion after 2 h and each 24 h until the completion of the reaction. The solution was filtered through Celite and the solvent was evaporated to obtain 0.95 g (95%) of a yellow solid, mp 112–115 °C : ^{1}H NMR ($CDCl_3$) δ 11.25 (s, 1H), 10.11 (s, 1H), 9.22 (s, 1H), 8.23 (s, 1H), 7.90 (d, 1H, J = 8.2 Hz), 7.84 (d, 1H, J = 8.3 Hz), 7.62 (t, 1H, J = 7.2 Hz), 7.47 (t, 1H), 1.40 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 195.6 (CHO), 178.5 (NHCO), 140.2, 137.3, 135.9, 130.3, 128.9, 128.6, 128.0, 125.7, 123.1, 117.1, 40.3, 27.6. Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.29; H, 6.66; N, 5.49. Found: C, 75.53; H, 6.50; N, 5.64.

3-Amino-2-naphthaldehyde (1). A mixture of 7 (510 mg, 2 mmol) and 2 N HCl (75 mL) in EtOH (37 mL) was refluxed for 15 h. The reaction mixture was cooled and filtered, and the filtrate was neutralized to pH 8 with $NaHCO_3$. The precipitate was filtered, dissolved in CH_2Cl_2 (50 mL), and dried over Na_2SO_4, and the solvent was evaporated to afford 330 mg (95%) of a yellow solid, mp 139–142 °C: ^{1}H NMR ($CDCl_3$) δ 10.11 (s, 1H), 8.11 (s, 1H), 7.78 (d, 1H, J = 8.1 Hz), 7.57 (d, 1H, J = 8.3 Hz), 7.46 (t, 1H, J = 7.1 Hz), 7.23 (t, 1H), 6.95 (s, 1H), 5.79 (broad s, 2H), 1.8 (broad s, H_2O); ^{13}C NMR ($CDCl_3$) δ 194.5 (CO), 145.1, 139.6, 137.8, 129.8, 129.2, 126.1, 125.4, 122.7, 122.3, 109.5.

3,3′-Dimethylene-2-(2′-pyridyl)benzo[g]quinoline (11). A mixture of 3-amino-2-naphthaldehyde (130 mg, 0.76 mmol), 5,6,7,8-tetrahydro-8-quinolone[6] (103 mg, 0.70 mmol), and saturated ethanolic KOH (0.35 mL) in EtOH (15 mL) was refluxed under Ar for 15 h. After cooling, water (15 mL) was added and the mixture was extracted with CH_2Cl_2 (2 × 20 mL). The organic phase was dried over Na_2SO_4 and the solvent was evaporated to afford 180 mg of a brown solid which was chromatographed on alumina (12 g) eluting with EtOAc/hexane (1:1) followed by EtOAc to give 120 mg (60%) of a yellow brown solid, mp 207–209 °C: ^{1}H NMR ($CDCl_3$) δ 9.05 (s, 1H), 8.90 (d, 1H, J = 4.4 Hz), 8.35 (s, 1H), 8.18 (s, 1H), 8.12 (m, 1H), 8.03 (m, 1H), 7.70 (d, 1H, J = 7.8 Hz), 7.54 (m, 2H), 7.38 (dd, 1H), 3.26 (t, 2H, J = 6.5 Hz), 3.12 (t, 2H), 1.75 (broad s, H_2O); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8, 151.2, 149.1, 144.2, 136.0, 135.4, 133.5, 131.8, 130.6, 128.5 (2C), 127.5, 126.1, 125.8, 125.4, 124.9, 123.8, 28.0, 27.5. Anal. Calcd for $C_{20}H_{14}N_2 \cdot 0.5H_2O$: C, 82.47; H, 5.15; N, 9.62. Found: C, 82.21; H, 5.10; N, 9.37.

3,3′-Dimethylene-2,2′-bibenzo[g]quinoline (12). A mixture of 3-amino-2-naphthaldehyde (171 mg, 1 mmol), 1,2-cyclohexanedione[16] (50 mg, 0.45 mmol), and saturated ethanolic KOH (0.8 mL) in EtOH (20 mL) was refluxed under Ar for 15 h. The mixture was then cooled and quenched with water (15 mL). The yellow precipitate (145 mg) was filtered and then chromatographed on alumina (7 g), eluting with EtOAc followed by $CHCl_3$ to afford 100 mg (58%) of a deep yellow solid, mp >300 °C: ^{1}H NMR ($CDCl_3$) δ 9.12 (s, 2H), 8.38 (s, 2H), 8.26 (s, 2H), 8.17 (dd, 2H), 8.05 (dd, 2H), 7.56 (m, 4H), 3.35 (s, 4H), 1.65 (broad s, H_2O); ^{13}C NMR ($CDCl_3$) δ 153.5, 145.0, 134.4, 133.9, 132.6, 132.3, 129.6, 129.1, 128.0, 126.7, 126.5, 126.0, 125.4, 29.3. Anal. Calcd for $C_{28}H_{18}N_2 \cdot 0.5CHCl_3$: C, 76.50; H, 4.14; N, 6.25. Found: C, 76.46; H, 4.26; N, 6.05.

3,3′:5,3″-Bis(dimethylene)-2,6-bis[2′-benzo[g]quinolyl]-pyridine (13). Following the same procedure as described for 11, a mixture of 3-amino-2-naphthaldehyde (85.5 mg, 0.5 mmol), 4,5-dioxo-1,2,3,4,5,6,7,8-octahydroacridine[7] (50 mg, 0.23 mmol), and saturated ethanolic KOH (0.2 mL) in EtOH (10 mL) was refluxed under Ar for 18 h. A brown residue (110 mg) was obtained and chromatographed on alumina (12 g), eluting with EtOAc/hexane (1:1) followed by EtOAc/MeOH (10:1) to give 80 mg (70%) of a brown yellow solid , mp > 300 °C: ^{1}H NMR ($CDCl_3$) δ 9.10 (s, 2H), 8.32 (s, 2H), 8.18 (m, 4H), 8.00 (m, 2H), 7.62 (s, 1H), 7.53 (m, 4H), 3.26 (t, 4H), 3.17 (t, 4H), 2.3 (broad s, H_2O); ^{13}C NMR could not be obtained due to low solubility; HRMS calcd for $C_{35}H_{23}N_3$ 485.18919, found 485.19021.

7,6-(2′,3′-Benzo[g]quinolino)tetracyclo[6.3.0.0^{4,11}.0^{5,9}]-undecan-2-one (15). A mixture of 3-amino-2-naphthaldehyde (500 mg, 2.9 mmol), tetracyclo[6.3.0.0^{4,11}.0^{5,9}]undecane-2,7-dione[8] (475 mg, 2.7 mmol), and 1 pellet of KOH, in EtOH (100 mL), was refluxed under Ar for 40 h. The solvent was evaporated and the crude residue was chromatographed on alumina (15 g), eluting with EtOAc/hexane (1:1) followed by EtOAc/hexane (2:1) to give 400 mg (47%) of a pale yellow solid, mp 254–256 °C: ^{1}H NMR ($CDCl_3$) δ 8.57 (s, 1H), 8.23 (s, 1H), 8.05 (m, 1H), 7.99 (m, 1H), 7.87 (s, 1H), 7.50 (m, 2H), 3.59 (m, 1H), 3.48 (m, 1H), 3.37 (broad s, 1H), 3.01 (broad s, 1H), 2.92 (m, 2H), 2.09 (m, 3H), 1.68 (d, 1H), 1.65 (broad s, H_2O); ^{13}C NMR ($CDCl_3$) δ 218.1 (CO), 170.4, 137.9, 133.5, 131.7, 130.0, 128.5, 127.8, 126.9, 126.1, 126.0, 125.8, (two aromatic carbons undetected), 57.7, 55.6, 54.0, 49.8, 47.6, 42.1, 41.0, 35.5. Anal. Calcd for $C_{22}H_{17}NO \cdot 0.5H_2O$: C, 82.50; H, 5.62; N, 4.38. Found: C, 82.48; H, 5.53; N 4.45.

2,3:7,6-Bis(2′,3′-benzo[g]quinolino)tetracyclo[6.3.0.0^{4,11}.0^{5,9}]-undecane (16). A mixture of 7,6-(2′,3′-benzo[g]quinolino)-tetracyclo[6.3.0.0^{4,11}.0^{5,9}]undecan-2-one (218 mg, 0.7 mmol) and 3-amino-2-naphthaldehyde (128 mg, 0.75 mmol) in freshly distilled toluene (20 mL) and saturated methanolic KOH (1 mL) was refluxed under Ar for 4 days, using a Dean–Stark water separator. The solvent was then removed and the crude residue was chromatographed on alumina (11 g), eluting with EtOAc/hexane (1:1) followed by EtOAc/hexane (2:1) to afford 90 mg (28%) of a white solid, mp > 300 °C: ^{1}H NMR ($CDCl_3$) δ 8.30 (s, 2H), 7.91 (s, 2H), 7.84, (m, 2H), 7.75 (m, 2H), 7.59 (s, 2H), 7.34 (m, 4H), 3.82 (broad s, 2H), 3.69 (broad s, 2H), 3.56 (broad s, 2H), 2.31 (quartet, 2H), 1.75 (broad s, H_2O); ^{13}C NMR ($CDCl_3$) δ 171.1, 143.5, 139.1, 133.2, 131.3, 128.7, 128.4, 127.7, 126.6, 125.8, 125.6,

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125.5, (1 aromatic carbon undetected), 57.8, 53.7, 49.8, 36.1. Anal. Calcd for $C_{20}H_{14}N_2 \cdot 1H_2O$: C, 85.34; H, 5.17; N, 6.03. Found: C, 85.59; H, 5.11; N, 5.99.

2,3-Trimethylenebenzo[*g*]quinoline (17). A mixture of freshly distilled cyclopentanone (21 mg, 0.25 mmol) and 3-amino-2-naphthaldehyde (46 mg, 0.27 mmol) in EtOH (8 mL) and saturated ethanolic KOH (0.3 mL) was refluxed under Ar for 15 h. The solvent was evaporated and the crude solid was chromatographed on alumina (5 g) eluting with EtOAc/hexane (1:2) to provide 35 mg (64%) of a light yellow solid, mp 181–184 °C: ^{1}H NMR ($CDCl_3$) δ 8.58 (s, 1H), 8.30 (s, 1H), 8.06 (m, 1H), 8.03 (s, 1H), 8.00 (m, 1H), 7.49 (m, 2H), 3.21 (t, 2H), 3.14 (t, 2H), 2.25 (quintet, 2H), 1.6 (broad s, H_2O); ^{13}C NMR ($CDCl_3$) δ 169.6, 135.5, 133.3, 131.4, 129.9, 128.4, 128.2, 127.9, 127.4, 126.1, 125.7, 125.5, 124.4, 34.9, 30.6, 23.7. Anal. Calcd for $C_{16}H_{13}N \cdot 0.2H_2O$: C, 86.25; H, 6.02; N, 6.29. Found: C, 86.33; H, 5.85; N, 6.14.

Acknowledgment. We are grateful to the Robert A. Welch Foundation, the National Science Foundation (CHE-8910991), and the University of Houston Energy Lab for financial support of this work. The NMR spectrometer was partially funded by NSF (CHE-8616352). E.T. acknowledges a bourse from the Region Rhône-Alpes.

Supplementary Material Available: ^{1}H NMR spectra of **1**, **5**, and **13**, ^{13}C NMR spectra of **1** and **5**, and a table giving aromatic proton chemical shifts of **16** and **17** (6 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.