Electrostatic Effects on the Population of Atropisomers of Charged and Dipolar Derivatives of 1,8-Di(2′-pyridyl)naphthalene

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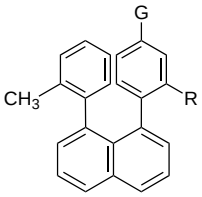
Dicationic 1′,1′-dimethyl (**6a**), dipolar 1′,1′-dioxide (**6b**), and 6′,6′-dipyridone (**7**) derivatives of 1,8-di(2′-pyridyl)naphthalene were prepared. Proton NMR failed to reveal the presence of individual *anti*-*syn* atropisomers over a wide range of temperatures. By contrast, the 1′,1″-dimethyl derivative of 1-(2′-pyridyl)-8-(3″-pyridyl)naphthalene (**8**), a positional isomer of **6a**, existed in DMSO-d_6 as a 2:1 mixture of *anti* to *syn* atropisomers at ambient temperatures. Electrostatic repulsion is believed to cause the *anti* atropisomer to be favored, especially in **6a** where the charged regions are closer together than in **8**, owing to the splayed-out arrangement of the rings. AM1 and PM3 computations confirm that the *anti* is highly favored over the *syn* isomer for **6a**, **6b**, and **7**.

Electrostatic effects provide the basis of noncovalent interactions present during molecular recognition in such diverse systems as proteins, nucleic acids, and host−guest pairs. Such interactions involve charged and dipolar groups, including π-stacked rings.[1,2]

Recent studies using π-cofacial 1,8-diarylnaphthalenes (**1**) have demonstrated that the electronic effects of substituents bonded to the benzene rings preferentially affect ground-state energies by means of Coulombic (electrostatic) interactions[3,4] and that electron-withdrawing groups lower the energy of the ground state, thereby enhancing the barrier to rotation.[5−8] Crystal structures show that the aryl rings in such naphthalenes are not parallel to each other but are tilted away in order to increase separation and thereby minimize electrostatic repulsion.[9,10] An *ortho* substituent is especially effective in inhibiting aryl ring rotation.[11]

We continue to use model compounds to explore the nature of such interactions using heteroaryl rings constrained to be cofacial in 1,8-disubstituted naphthalenes. These rings contain dipolar groups as well as positive charges. Simple dipyridyl derivatives of 1,8-disubstituted naphthalenes at ambient temperatures have chemical shift differences and barriers to rotation that are large enough to allow the ready observation of atropisomers. Thus, 1,8-di(3′-pyridyl)naphthalene (**2**)[12] and derivatives such as dimethyl diquaternized salt **3a,** di-*N*-oxide **3b**, and dipyridone **4**[13] show hindered rotation in a number of solvents. The *anti* isomer is moderately favored for all compounds at normal temperatures, and the *anti* to *syn* isomer ratio is slightly dependent on solvent polarity, the *syn* diastereomers tending to increase in abundance in more polar solvents.



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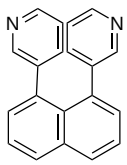
1b, R = CH_3



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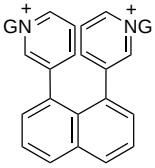
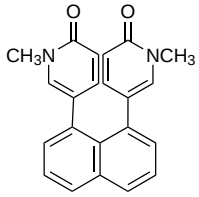


3a, G = CH_3
3b, G = O^-



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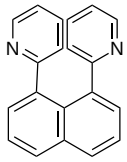

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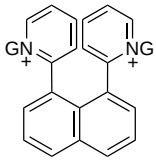
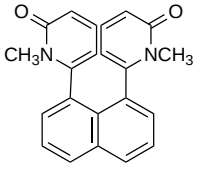


6a, G = CH_3
6b, G = O^-



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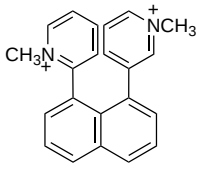

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By marked contrast, the 1,8-di(2′-pyridyl)naphthalene (**5**) isomer failed to demonstrate such atropisomerism at ambient temperatures. Only on cooling a sample in acetone-d_6 to −65 °C does the presence of another isomer become clearly apparent, now being present in a 3.3:1 ratio favoring the *anti* isomer.[14] Examples **2** and **5** show that the size of the rotational barrier is markedly

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diminished simply on moving the annular nitrogen atom from the 3′ to the 2′ position.

We now report our attempts to affect the magnitude of the rotational barrier in the 2′,2′ isomer by adding methyl and oxide groups to the nitrogen atom (*ortho* site). Included here are the syntheses and proton NMR spectra of the 2′,2′-dimethyl dication **6a,** the 2′,2′-di-*N*-oxide **6b**, and the dipyridone derivative **7** of the dimethyl dication. Also examined is the dimethyl dication of the isomer (2′,3″-dipyridyl)naphthalene (**8**), an important substrate with a substitution pattern intermediate between those of the 2′,2′ and 3′,3′ geometries. A classic example of the successful application of the *o*-methyl steric effect is found in the demonstration by proton NMR of the presence of *anti*-*syn* atropisomers of 1,8-di(2′-methylphenyl)naphthalene (**1b**, G = H) in $CDCl_3$ in a 3.2:1 ratio at ambient temperatures.[11] The two methyl groups increase the barrier to rotation about the phenylnaphthalene σ-bond by about 8 kcal/mol over that for the unsubstituted parent to 24.1 kcal/mol while, as others have reported, even larger alkyl groups on *meta* sites on the benzene ring are far less effective.[9,15]

Our new compounds provide a competition between steric hindrance to bond rotation, largely a transition-state effect and ground-state destabilization by means of electrostatic repulsion between charged and dipolar groups.

Results

Syntheses. The two dipyridyl materials **5** and **8** (as its unquaternized precursor) were prepared by Pd(0)-catalyzed cross-coupling reactions starting with 1,8-dibromonaphthalene[16] or its derivative; details appear elsewhere.[12,14]

Conversion of **5** to its monoquaternized derivative took place readily at room temperature with MeI. But diquaternization to give **6a** was quite difficult, in contrast to the facile conversion of the 3′,3′-isomer to its dication **3a**, the latter taking place at room temperature,[13] thereby indicating the presence of greater strain energy in **6a**. Diquaternization could be achieved by heating **5** with a large excess of MeI at 80 °C for 4 days or with neat methyl tosylate. Diquaternization to produce **8** using MeI at room temperature was unexceptional.

The mono- and di-*N*-oxides of **5** were prepared using *m*-chloroperbenzoic acid at room temperature. No difficulty was observed for di-N-oxidation to give **6b**. Preparation of the mono-*N*-oxide, by contrast, was not selective; the best method gave a mixture of starting material and the mono- and di-*N*-oxides.

Dication **6a** was easily converted to dipyridone **7** in aqueous alkali on oxidation with ferricyanide. The simplicity of the proton NMR, consisting of six peaks, is consistent with oxidation at the same position of each ring. Although isomeric structures are possible, the structural assignment can be made confidently from the coupling pattern, which shows a pair of doublets and an apparent triplet for the three pyridyl protons, thereby eliminating the possible oxidation at the 4′ position, the other likely reaction site.[17,18] This latter material would not show the apparent triplet, giving instead two doublets and a singlet.

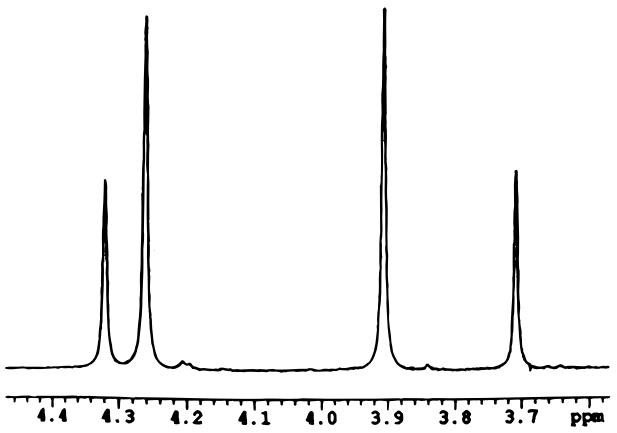

Figure 1. Partial ^{1}H NMR spectrum of 1-(1′-methyl-2′-pyridinium-2′-yl)-8-(1″-methyl-3″-pyridinium-3″-yl)naphthalene diperchlorate (**8**) in $CDCl_3$ at 19 °C showing just the *N*-methyl region. The smaller peaks are associated with the *syn* and the larger with the *anti* atropisomer. The lower field pair is due to the 1″ (*meta*) and the higher pair to the 1′ (*ortho*) *N*-methyl groups, respectively.

Variable-Temperature Proton NMR Spectra. The spectrum of the 2′,3″-dication **8** (tosylate, iodide, or perchlorate salt) in DMSO-d_6 clearly showed the presence of a mixture of *anti* and *syn* atropisomers in a 2 to 1 ratio at 19 °C. Two families of peaks were evident from their area ratios. The singlet signals for H2″ at δ 9.31 (*syn*) and δ 8.94 (*anti*) are especially conspicuous along with three multiplets centered at δ 8.8 for the *anti* and a pair of doublets at δ 8.25 for the *syn* isomers. Overlap is evident for the remainder of the aromatic portion of the spectrum. Two sets of nicely separated *N*-methyl peaks are present in a 2.1:1 ratio (DMSO-d_6), Figure 1. They may be assigned confidently by comparison with the shifts for **3a** (*m*-methyl: *anti* 4.29 and *syn* 4.26 ppm) and **6a** (*o*-methyl: 4.0 ppm), showing that the naphthyl ring provides additional shielding to the methyl groups closer to it as in **6a**. Because the shifts closely match, the lower field pair therefore may be assigned to the 1″ (*meta*) and the higher to the 1′(*ortho*) *N*-methyl group, respectively.

Heating **8** as its ditosylate in DMSO-d_6 to 100 °C failed to cause the *N*-methyl groups to coalesce, although the peaks did move closer together (1′-Me, $\Delta\delta$ ca. 1 Hz; 1″-Me, $\Delta\delta$ ca. 17 Hz), indicating some signal averaging but a condition below coalescence. Simply heating the compound in the NMR probe to 40 °C caused the *anti* to *syn* ratio to decrease to 1.7, indicating rapid ring rotation and equilibration.

No evidence was found for the existence of discreet forms of *anti* and *syn* diastereomers in any of several solvents above and below ambient temperature for those compounds derived from the 2′,2′-dipyridine with the possible exception of **7** in CD_3OD at −90 °C, where a small amount of the *syn* isomer may be present. These observations contrast with those for **2**−**4** where individual spectra are clearly apparent at ambient temperature.[12,13] There were some small changes in chemical shifts for a given sample among various solvents, however. Most spectra were recorded at 300 MHz, with some at 500 MHz in an attempt to increase any observable coalescence temperature.

Specifically, no significant change was found for 2′,2′ ditosylate **6a** in DMSO-d_6 at 20, 50, or 100 °C except for

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Table 1. Dipole Moments, *Anti/Syn* Ratios and Barriers to Rotation from the *Anti* to the *Syn* Isomer in DMSO at 25 °C as Computed by the AM1 and PM3 Semiempirical Methods

	dipole moment, μ[a]		[*anti*]/[*syn*]		kcal/mol	
Cpd	AM1	PM3	AM1	PM3	AM1	PM3
6a			7	42		
6b	1.66 (*A*)	2.41 (*A*)	627	35	17.3	20.1
	7.22 (*S*)	7.09 (*S*)				
7	8.55 (*A*)	8.19 (*A*)	30	9.0	23.1	23.4
	9.96 (*S*)	9.50 (*S*)				
8			1.2	1.2		
1b[b]			1.4	0.71	18.0	21.0

[a] *A* denotes the *anti* and *S* the *syn* isomers. [b] G = H.

upfield shifts in the position of the *N*-methyl peak appearing at 3.99, 3.96, and 3.93 ppm, respectively, where both the methyl groups of the tosylate anion and TMS served as shift references. No change was evident in a sample heated for 30 h at 80 °C in the same solvent, an experiment designed to allow isomer equilibration, if such an equilibration were slow. Lower temperatures were not pursued due to limited solubility in appropriate solvents.

The spectra of a solution of di-*N*-oxide **6b** in $CDCl_3$ were essentially the same at 20 and at −50 °C. Even at −90 °C in CD_3OD (500 MHz), there was no evidence of more than one component; the spectrum consisted of seven well-separated multiplets whose areas were in integral ratios.

There was no apparent change in the spectra of dipyridone **7** in $CDCl_3$ over the interval 40 to −40 °C. The spectrum of a sample in CD_3OD at −90 °C (500 MHz) was similar to that at ambient temperature, containing six clearly separated aromatic protons and a methyl singlet. However, three, new, small (about 5%) pyridone multiplets did appear, suggesting the presence of the *syn* isomer.

The monoquaternized and N-oxidized materials were not investigated extensively, both showing spectra consistent with the presence of a single substance in DMSO-d_6 at 20 °C. At 100 °C in the same solvent the mono-*N*-oxide appears to be homogeneous. Rotation of the unsubstituted 2′-pyridyl ring is expected to be so facile[14] that the observation of atropisomers will be difficult.

Semiemperical Computations. Table 1 summarizes for **6a**, **6b**, **7**, **8**, and **1b** (G = H) the results of AM1 and PM3 computations for the *anti*/*syn* ratio and the barrier to rotation from the *anti* ground state to the lower energy transition state, assuming the compounds are in DMSO. The dipole moments for di-*N*-oxide **6b** and dipyridone **7** also are included. These data show that for all the 2′,2′-dipyridyl derivatives the *anti* isomer is highly favored over the *syn* at equilibrium. Only in the case of the mixed dipyridyl **8** are the ground-state populations similar, being 1.2 by computation and 2 by observation. The distance between the nitrogen atoms in the *anti* diastereomer of **6a** is 4.4 (AM1) or 4.5 Å (PM3) and for the *syn* it is 3.9 (AM1) or 4.1 Å (PM3), quite similar values not much larger than the van der Waals contact distance of 3.4 Å between stacked benzene rings.[19,20]

The transition state for rotation has a pyridyl hydrogen and not the *N*-methyl group directed at the face of the adjacent pyridyl ring in an approximate T-shaped geometry. Having an *N*-methyl group move across the face of a pyridyl ring in the alternate transition state is a process prohibited by more than an additional 10 kcal/mol; these values are not included in Table 1. In the case of **8** each ring is expected to rotate at different rates and have different energy barriers. Rotation of the 3-pyridyl ring is expected for steric reasons to have the smaller barrier.

The dipole moments for **6b** and **7** are large, and as expected, the *syn* isomer has the larger value. While the difference between the *syn* and *anti* values is quite large for **6b**, the difference for **7** is almost negligible.

Computed and experimental results are available for **1b** (G = H). The rotational barrier is computed to be 18 (AM1) or 21 kcal/mol (PM3), Table 1, and the observed quantity is 24.1 kcal/mol.[11] The computed barriers are systematically low. The computed difference between the *anti-syn* ground-state energies is so similar (0.2 kcal/mol) that each method predicts the opposite result for the more stable form. The observed value is 0.7 kcal/mol.[11]

Discussion

o-Methylated pyridyl analogues **6a**, a dication, and highly dipolar **6b** and **7** do not show discreet *anti-syn* atropisomers when examined by proton NMR near room temperature. Compound **6b** at −90 °C in CD_3OD failed to demonstrate such isomerism, but **7** in CD_3OD may have provided a small amount of the *syn* isomer at this temperature, which is designed to freeze out isomers having a rotational barrier as low as 10 kcal/mol. Heating **6a** at 80 °C for 30 h failed to produce a change in its NMR spectrum. Under such conditions, isomers separated by a rotational barrier as high as 25 kcal/mol would be expected to equilibrate.

By contrast, di-*o*-tolyl **1b** (G = H) in $CDCl_3$, having methyl groups at *ortho* positions on the rotating aryl rings, shows *anti-syn* atropisomerism in a 3.2:1 isomer ratio at ambient temperatures.[11] Similarly, pyridyl dimethyl dication **8** with one *o*-methyl and one *m*-methyl group consists of an *anti-syn* mixture in a 2:1 ratio. In DMSO-d_6 rapid ring rotation does indeed take place with **8** at ambient temperatures as demonstrated by the decrease in this isomer ratio on heating a sample in the NMR probe.

Our computational results, Table 1, suggest that the *anti-syn* population is heavily biased to favor the *anti* diastereomer for all the 2′,2′-dipyridyl derivatives. Moreover, comparison of the chemical shifts for the *N*-methyl protons of **6a** and **8** in DMSO-d_6 supports this conclusion for **6a** when making the usual assumption that the observed chemical shift in a rapidly equilibrating system is a reflection of the population-weighted shifts of the individual components. Thus, the *N*-methyl protons of the 2′-pyridyl ring of **8** serve as a model to give the chemical shifts for both the *anti* and the *syn* *N*-methyl groups at an *ortho* position. The values for a solution of **8** as the ditosylate in DMSO-d_6 are 3.92 and 3.70 ppm at 20 °C and 3.89 and 3.73 ppm at 100 °C, respectively. For the ditosylate of **6a** in DMSO-d_6 the observed values are 3.99 ppm at 19 °C, 3.96 at 50 °C and 3.93 ppm at 100 °C. These values for **6a** are quite close to those for the *anti* *N*-methyl protons of **8**, confirming the position of the equilibrium as being weighted on the side of the *anti* diastereomer for **6a** even at the higher temperature. Moreover, the upfield shifts of 9 and 18 Hz on heating are consistent with the mixing-in of the higher field, higher energy *syn* isomer. And if the difference between

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the *anti* and *syn* intrinsic chemical shifts is similar for both **6a** and **8**, then about 27% (18 Hz/66 Hz at 300 MHz) of the *syn* isomer must be present at 100 °C.

Conclusions. Atropisomers of **6a**, **6b**, and **7** were not observed at ambient temperature because the equilibrium strongly favors the *anti* over the *syn* isomer. Although barriers to rotation are likely to be in a range that would allow the equilibrium to be frozen out at low temperatures, the skewed position of the equilibrium hinders the observation of the *syn* structure. Ring rotation merely results in the interconversion of the enantiomers of the dominant *anti* isomer, a degenerate process.

Electrostatic destabilization is more severe for both the *anti* and the *syn* forms in the 2′,2′ series of dipyridines than in the 3′,3′ series because the distances between the charges and the dipoles in the former are smaller. This is a consequence of the splayed geometry where the distance between the rings increases as atoms move away from the point of attachment to the naphthalene frame. The ground-state energy in the 2′,2′ series therefore is greater than in the 3′,3′ series. The energy provided by electrostatic repulsion is more than enough to overcome the steric barrier imposed by the *ortho* substituents on the pyridine rings to allow their rapid rotation.

Experimental Section

General NMR. Spectra were recorded at either 300 or 500 MHz. Coupling constants, *J*, are given in Hz. Sample temperatures were taken to be those given by the digital readout on the instrument and have an uncertainty of a few degrees, especially at the lowest temperatures.

1-(1′-Methylpyridin-1′-ium-2′-yl)-8-(2″-pyridyl)naphthalene Iodide. A mixture of 100 mg (0.354 mmol) of 1,8-di(2′-pyridyl)naphthalene[14] in 2 mL of $CHCl_3$ and 100 mg of methyl iodide was kept at rt in a sealed tube for 48 h. After solvent evaporation, the residue was stirred with ether to give a yellowish precipitate (110 mg, 0.259 mmol, 73%): mp 218−220 °C; ^{1}H NMR (DMSO-d_6) δ 8.88 (1H, d, J = 6.0), 8.40 (1H, dd, J = 2.1, 7.2), 8.29 (1H, dd, J = 1.2, 8.1), 8.1 (2H, m), 7.8 (4H, m), 7.71 (1H, td, J = 1.5, 7.5), 7.63 (1H, dd, J = 1.2, 7.8), 7.50 (2H, dd, J = 1.2, 7.8), 7.06 (1H, ddd, J = 1.5, 5.1, 6.3), 4.20 (3H, s). Anal. Calcd for $C_{21}H_{17}N_2I$: C, 59.43; H, 4.04; N, 6.60. Found: C, 59.88; H, 3.91; N, 6.51.

1,8-Bis(1′-methyl-2′-pyridinium-2′-yl)naphthalene Diiodide. (6a) To 100 mg (0.354 mmol) of 1,8-di(2′,2′-pyridyl)-naphthalene[14] in 2 mL of MeOH was added 0.5 mL (766 mg, 5.39 mmol) of methyl iodide. The sealed tube was heated at 80 °C for 4 d; the contents were diluted with MeOH (3 mL) and filtered and the solvent concentrated to a yellow powder, which contained about 20% of the monoquaternized material along with the dimethyl product. Recrystallization from MeOH/ether and then MeOH/EtOH gave 75 mg (0.13 mmol, 37%) of yellow needles: mp > 220 °C. Anal. Calcd for $C_{22}H_{20}N_2I_2$: C, 46.65; H, 3.56; N, 4.95. Found: C, 46.57; H, 3.41; N, 4.84.

1,8-Bis(1′-methyl-2′-pyridinium-2′-yl)naphthalene Ditosylate. (6a) A mixture of 100 mg (0.350 mmol) of 1,8-di-(2′,2′-dipyridyl)naphthalene[14] and 300 mg (1.61 mmol) of methyl *p*-toluenesulfonate was heated under nitrogen in a sealed tube for 10 h at 130 °C. After the mixture was cooled, the solid was washed with acetone (3 × 10 mL). The solid was recrystallized from methanol/acetone/ether to give 170 mg (0.26 mmol, 73%): mp 206−208 °C; ^{1}H NMR (DMSO-d_6) δ 8.94 (2H, d, J = 6.0), 8.53 (2H, dd, J = 1.5, 7.8), 8.29 (2H, t, J = 7.8), 8.01 (2H, d, J = 7.8), 7.9 (6H, m), 7.47 (4H, d, J = 7.8), 7.11 (4H, d, J = 7.8), 4.00 (6H, s), 2.28 (6H, s). Anal. Calcd for $C_{36}H_{34}N_2O_6S_2$: C, 66.04; H, 5.23; N, 4.28. Found: C, 66.08; H, 5.28; N, 4.21.

1,8-Di(2′-pyridyl)naphthalene 1′-Oxide Hydrate. To an ice-cold solution of 180 mg (0.64 mmol) of 1,8-di(2′-pyridyl)-naphthalene[14] in 15 mL of $CHCl_3$ was added 100 mg of *m*-chloroperbenzoic acid (71%, 0.41 mmol). After the solution was allowed to stand at 0 °C for 14 h, the solvent was removed, and the resultant yellowish oil was purified on a silica gel column using methanol in ethyl acetate (10−50%) to yield 80 mg (0.28 mmol, 44%) of starting material, 84 mg (0.28 mmol, 44%) of the 1′-oxide and 23 mg (0.073 mmol, 11%) of the di-*N*-oxide. An analytical sample was recrystalized from EtOAc to give a colorless solid: mp 209−210 °C; ^{1}H NMR (DMSO-d_6) δ 8.16 (3H, m), 7.65 (3H, m), 7.51 (1H, t, J = 7), 7.44 (3H, m), 7.22 (1H, d, J = 7.5), 7.08 (1H, t, J = 7.8), 6.98 (2H, m). Anal. Calcd for $C_{20}H_{14}N_2O\cdot0.25H_2O$: C, 79.32; H, 4.82; N, 9.25. Found: C, 79.11; H, 4.69; N, 9.25.

1,8-Di(2′-pyridyl)naphthalene 1′,1″-Dioxide Hydrate. (6b) To a solution of 100 mg (0.35 mmol) of 1,8-di(2′-pyridyl)-naphthalene[14] in 2 mL of $CHCl_3$ was added 300 mg of *m*-chloroperbenzoic acid (71%, 1.23 mmol). After 14 h at rt, the solvent was removed under reduced pressure, and the solid residue was purified by column chromatography on alumina using EtOAc/MeOH (9/1). Drying in vacuo at 100 °C gave 95 mg (0.30 mmol, 84%) of an off-white solid: mp > 220 °C; ^{1}H NMR ($CDCl_3$ at −20 °C) δ 8.06 (2H, dd, J = 1.5, 8.2), 7.76 (4H, m), 7.61 (2H, t, J = 6.9), 7.31 (2H, dd, J = 1.5, 7.2), 7.21 (2H, td, J = 1, 7.5), 6.90 (2H, ddd, J = 2.1, 6.6, 7.5); (CD_3OD at −90 °C) δ 8.23 (2H, d, J = 8), 7.88 (2H, dd, J = 2, 8), 7.83 (2H, d, J = 6), 7.73 (2H, t, J = 7), 7.60 (2H, t, J = 7), 7.45 (2H, d, J = 7), 7.23 (2H, td, J = 2, 8). Anal. Calcd for $C_{20}H_{14}N_2O_2\cdot0.25H_2O$: C, 75.34; H, 4.58; N, 8.79. Found: C, 75.50; H, 4.56; N, 8.59.

Bis(1′-methyl-6′-pyridon-2′-yl)naphthalene (7). To 410 mg (0.62 mmol) of 1,8-di(1′-methylpyridinium-2′-yl)naphthalene ditosylate was added in portions a saturated solution of $K_3Fe(CN)_6$ in 20 mL of H_2O and 2 mL of 50% NaOH. After being stirred at rt for 14 h, the mixture was extracted with chloroform (3 × 30 mL); the extracts were dried ($MgSO_4$) and evaporated. The crystalline residue was purified by column chromatography on neutral alumina using 20% MeOH in EtOAc. Drying in vacuo at 100 °C gave 97 mg (0.28 mmol, 45%) of a yellowish solid. An analytical sample was recrystallized from ethanol: mp >220 °C; ^{1}H NMR (DMSO-d_6 at 19 °C) δ 8.23 (2H, d, J = 7.8), 7.71 (2H, t, J = 7.8), 7.51 (2H, d, J = 6.9), 7.16 (2H, dd, J = 6.9, 9.0), 6.09 (4H, dd, J = 6.6, 9.0), 2.91 (6H, s); (CD_3OD at −90 °C) minor peaks appeared at 7.39 (2H, dd, J = 4.5, 6), 6.41 (2H, d, J = 6), 6.26 (2H, d, J = 4.5). Anal. Calcd for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18. Found: C, 77.16; H, 5.23; N, 8.12.

1-(1′-Methyl-2′-pyridinium-2′-yl)-8-(1″-methyl-3″-pyridinium-3″-yl)naphthalene Diperchlorate (8). A mixture of 50 mg (0.18 mmol) of 1-(2′-pyridyl)-8-(3″-pyridyl)naphthalene,[14] 1 mL of $CHCl_3$, and 0.10 mL (1.6 mmol) of CH_3I was allowed to stand at rt for 48 h. Removal of the solvent under reduced pressure gave an oil that solidified on stirring with ether. This hygroscopic solid (70 mg) in 2 mL of MeOH was converted into its diperchlorate salt following the addition of 0.10 mL of 70% $HClO_4$. The resultant white solid was recrystallized from water−glacial acetic acid to give 49 mg (0.097 mmol, 54%): mp >220 °C; ^{1}H NMR (DMSO-d_6 at 19 °C), areas do not necessarily appear in integral ratios due to the presence of *anti* and *syn* forms in unequal amounts, δ 9.31 (s), 8.94 (s), 8.88 (d, J = 6), 8.83 (t, J = 5.4), 8.77 (d, J = 6.3), 8.5 (m), 8.28 (d, J = 7.8), 8.21 (d, J = 7.8), 7.9 (m), 7.66 (m), 4.36 (s), 4.30 (s), 3.94(s), 3.73 (s). Anal. Calcd for $C_{22}H_{20}Cl_2N_2O_8$: C, 51.68; H, 3.94; N, 5.48. Found: C, 51.53; H, 3.82; N, 5.39.

Semiempirical Computations. Details appear in our previous publications.[12,13]

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