Polar−π and Cation−π Stabilizing Interactions between Constrained Cofacial Aromatic Rings Favoring the More Sterically Hindered Diastereomer

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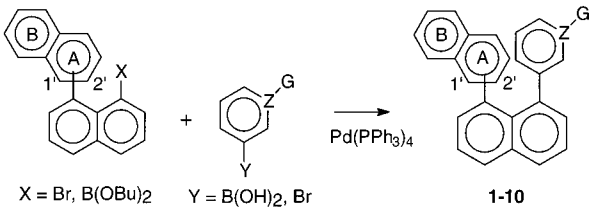
1,8-Diaryl cofacial naphthalenes[1−7] as well as cyclophanes[1] continue to be useful model compounds to study the interactions between aromatic rings held near or below van der Waals interatomic distances. In such naphthalenes, the two aromatic rings are held cofacial but are splayed out from each other and are able to rotate about the bonds attaching them to the rigid naphthalene frame, thereby giving rise to atropisomers.[4,8−10]They are readily prepared by a number of metal-catalyzed cross-coupling reactions.[11,12] Magnetic resonance[10,13−15] continues to offer a means of facile study of the consequences of $\pi-\pi$, π−dipole, and π−cation interactions, predominantly electrostatic in nature, on isomer populations.[16−22] Cation−π interactions play a role in molecular recognition and in substrate−protein binding.[23−28]

Scheme 1



We prepared two series of positional cofacial isomers and examined their syn−anti population ratios by proton NMR at 300 MHz at ambient temperatures. These include three additional 8-aryl-and 8-hetaryl-1,1′-binaphythyls to supplement our earlier study of such compounds[29] and seven new, isomeric 8-aryl- and 8-hetaryl-1,2′-binaphthyls (Scheme 1). The 8-arenes consisted of 3′-substituted benzenes and the 8-hetaryls contained a 3′-pyridyl ring. Arene substituents studied include methoxy (**1**, **2**), methylthio (**3**, **4**), dimethylsulfonio (**5**, **6**), dimethylamino (**7**), and trimethylammonio (**8**). The pyridyl ring existed either as the free base **9** or the *N*-methyl-quaternized ionic product **10**. Examples are given in Table 1. The results for these two series of neutral and ionic compounds allowed us to determine the influence of different groups and new geometries for the interacting cofacial rings on the preference for the more sterically hindered syn atropisomers induced by $\pi-\pi$, polar−π, or cation−π interactions.

Population ratios for the compounds are considered in pairs, each constitutional isomer of the pair having the same group at position 3′ of the arene while differing in the geometry of the cofacial 1′- or 2′-naphthyl ring. The syn diastereomer is defined as that rotational form having the group at position 3′ of the arene or hetarene directed toward the B-ring of the cofacial 1′- or 2′-naphthalene ring while the anti isomer is that structure having this group directed away from the B-ring of the naphthalene.

Results and Discussion

Syntheses. A common palladium-catalyzed cross-coupling approach was used to prepare all the cofacial compounds as in our earlier studies.[5,6,29] Usually, either an 8-bromo-1,1′-binaphthyl or an 8-bromo-1,2′-binaphthyl was coupled under Suzuki conditions[30−32] with a 3-substituted benzeneboronic acid or diethyl(3-pyridyl)borane in the presence of $Pd(PPh_3)_4$. An alternate route interchanged the positions of the bromo and boronic acid groups. Thus, 1,1′-binaphthy-8-boronic acid ester and

(1) Boekelheide, V. *Top. Curr. Chem.* **1983**, *113*, 87−163.
(2) Iovine, P. M.; Kellett, M. A.; Redmore, N. P.; Therien, M. J. *J. Am. Chem. Soc.* **2000**, *122*, 8717−8727.
(3) Zoltewicz, J. A.; Maier, N. M.; Fabian, W. M. F. *J. Org. Chem.* **1997**, *62*, 3215−3219.
(4) Zoltewicz, J. A.; Maier, N. M.; Fabian, W. M. F. *J. Org. Chem.* **1997**, *62*, 2763−2766.
(5) Zoltewicz, J. A.; Maier, N. M.; Lavieri, S.; Ghiviriga, I.; Abboud, K. A.; Fabian, W. M. F. *Tetrahedron* **1997**, *53*, 5379−5388.
(6) Zoltewicz, J. A.; Maier, N. M.; Fabian, W. M. F. *J. Org. Chem.* **1996**, *61*, 7018−7021.
(7) Zoltewicz, J. A.; Maier, N. M.; Fabian, W. M. F. *Tetrahedron* **1996**, *52*, 8703−8706.
(8) House, H. O.; Koepsell, D. G.; Campbell, W. J. *J. Org. Chem.* **1972**, *37*, 1003−1009.
(9) Clough, R. L.; Kung, W. J.; Marsh, R. E.; Roberts, J. D. *J. Org. Chem.* **1976**, *41*, 3603−3609.
(10) Cosmo, R.; Sternhell, S. *Aust. J. Chem.* **1987**, *40*, 1107−1126.
(11) Clough, R. L.; Mison, P.; Roberts, J. D. *J. Org. Chem.* **1976**, *41*, 2252−2255.
(12) Diederich, F.; Stang, P. J. *Metal-Catalyzed Cross-Coupling Reactions*; Wiley-VCH: New York, 1998.
(13) House, H. O.; Campbell, W. J.; Gall, M. *J. Org. Chem.* **1970**, *35*, 1815−1819.
(14) Clough, R. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1976**, *98*, 1018−1020.
(15) Vögtle, F.; Wingen, R. *Tetrahedron Lett.* **1978**, 1459−1462.
(16) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525−5534.
(17) Hunter, C. A. *Chem. Soc. Rev.* **1994**, *23*, 101−109.
(18) Gallivan, J. P.; Dougherty, D. A. *Org. Lett.* **1999**, *1*, 103−105.
(19) Cozzi, F.; Cinquini, M.; Annunziata, R.; Dwyer, T.; Siegel, J. *J. Am. Chem. Soc.* **1992**, *114*, 5729−5733.
(20) Cozzi, F.; Cinquini, M.; Annunziata, R.; Siegel, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 5330−5331.
(21) Cozzi, F.; Ponzini, F.; Annuziata, R.; Cinquini, M.; Siegel, J. S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1019−1020.
(22) Cozzi, F.; Siegel, J. *Pure Appl. Chem.* **1995**, *67*, 683−689.
(23) Hunter, C. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1584−1586.
(24) Larsen, M.; Krebs, F. C.; Harrit, N.; Jorgensen, M. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1749−1757.
(25) Dougherty, D. A.; Lester, H. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2329−2331.
(26) Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303−1324.
(27) Gallivan, J. P.; Dougherty, D. A. *J. Am. Chem. Soc.* **2000**, *122*, 870−874.
(28) Gallivan, J. P.; Dougherty, D. A. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 9459−9464.
(29) Zoltewicz, J. A.; Maier, N. M.; Fabian, W. M. F. *J. Org. Chem.* **1998**, *63*, 4985−4990.
(30) Genet, J. P.; Savignac, M. *J. Organomet. Chem.* **1999**, *576*, 305−317.
(31) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147−168.
(32) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457−2483.

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Table 1. Chemical Shifts for Stereoisomeric Methyl Protons and Associated Isomer Quotients for Cofacial Compounds in Deuteriochloroform

compd	naphthyl	Z	G	low field, ppm	high field, ppm	(area high field)/ (area low field)
1	**1′**	C	OMe	3.63	3.09	1.2
2	**2′**	C	OMe	3.54	3.21	1.3
3	**1′**	C	SMe	2.35	1.95	1.0
4	**2′**	C	SMe	2.27	1.96	1.1
5[a]	**1′**	C	$+S(Me)_2$	3.31; 3.18[b]	2.98; 2.92[b]	2.3
6[a]	**2′**	C	$+(SMe)_2$	3.05; 3.01[b]	2.84; 2.34[b]	2.5
7A[d]	**1′**	C	$N(Me)_2$	2.78	2.30	1.5
7	**2′**	C	$N(Me)_2$	2.68	2.37	1.6
8A[c,d]	**1′**	C	$+N(Me)_3$	3.80	3.41	3.1
8[c]	**2′**	C	$+N(Me)_3$	3.64	3.29	2.8
9	**2′**	N	−	6.50[e]	6.25[e]	1.6
10A[c,d]	**1′**	+N	Me	4.30	3.95	2.2
10[c]	**2′**	+N	Me	4.38	3.94	1.5

[a] Triflate. [b] Diastereotopic methyl groups. [c] Iodide. [d] Reference 29. [e] Ring proton.

1-bromo-3-methythiobenzene as well as *N*,*N*-dimethyl-3-bromoaniline were coupled using $Pd(PPh_3)_4$. The methylthio cofacial product then was S-methylated with methyl triflate while quaternization of the aniline and pyridine employed MeI.

Proton NMR Studies. Spectra for all the compounds were taken at probe temperature at 300 MHz using $CDCl_3$ as the solvent, previously found to give the largest difference between the populations of the syn and anti isomers,[29] the area of the methyl signal serving as the primary population reporter group. The chemical shifts of the methyl reporter groups for the 1,1′- and 1,2′-binaphthyl series are in general agreement, Table 1. In general, the aromatic region suffered from signal overlap and gave little information except in the case of the pyridyl ligand **9** that provided a larger separation in proton signal positions for this ring. Area ratios based on the signals for the methyl protons and also the ring protons of **9** are summarized in Table 1. As expected, the sulfonium salts demonstrated a pair of signals in equal areas for the two diastereotopic methyl groups in each of the syn and anti atropisomers for a total of four singlet signals. Results in Table 1 for compounds denoted by a number and also the letter **A** are from our earlier study.[29]

Syn/Anti Population Ratios. As in our[29] and other[10,13,14] studies, we assign in Table 1 the higher field singlet to the more shielded methyl group that is positioned over the cofacial 1′- or 2′-naphthyl B-ring in the more sterically hindered syn atropisomer. The preference for this more hindered diastereomer is small for the neutral compounds having a 3′-OMe (**1, 2**), a 3′-SMe (**4**), or a 3′-NMe_2 (**7, 7A**) group, the ratio being only slightly greater than one except for the SMe compound **3** in the 1′-naphthyl series where the value appears to be about one. There is no substantial difference in these population ratios between the 1′- and 2′-naphthyl constitutional isomers having $\pi-\pi$ and polar$-\pi$ interactions. However, when the substitutent at position 3′ has a positive charge as in **5, 6, 8**, and **8A**, the preference for the syn atropisomer increases noticeably, more than a factor of 2. When the positive charge is located on the ring as in the 1-(2′-naphthyl)-8-(3′-pyridylium) ion **10**, the value is 1.5, and this is smaller than that found earlier for the corresponding 1′-naphthyl structural isomer **10A** (2.2) under similar conditions. The largest preference was found for the ions with the largest group, trimethylammonio **8** and **8A**, where the *syn*/*anti* ratio is 2.8 to 1 and 3.1, respectively.

For the unquaternized 1-(2′-naphthyl)-8-(3′-pyridyl) **9**, the broadened multiplets at 6.25 and 6.50 ppm were in a 1.6 to 1 area ratio, respectively. The higher field more abundant signal is due to a ring proton, in contrast to the other substrates studied here where the higher field signals are due to methyl protons. These signals are easily identified as being due to the H-5′ pyridyl ring protons by their chemical shifts and by the presence of two large ortho coupling constants in each of the two atropisomers.[7] The higher field multiplet is associated with H-5′ which is directed over the B-ring of the naphthalene, and this is the anti isomer where the annular nitrogen atom of the pyridyl ring is directed away from the B-ring of its neighbor. With **9** the more highly populated atropisomer is anti as in classical studies. This result stands in contrast with those found for the other compounds in this study where the syn isomer is favored. Thus, the identity of the major diastereomer changes with the presence or absence of a positive charge, **10** versus **9**, interesting differences.

Conclusions

1,8-Disubstituted naphthalenes having two cofacial aromatic rings demonstrate either one of two preferred ground state syn or anti geometries due to restricted rotation about their substituent−naphthalene bonds. Two monocyclic aromatic rings, whether carbocyclic or heterocyclic, with uncharged or charged groups, adopt the expected classically favored anti geometry to minimize steric and electrostatic repulsive interactions between dipoles and/or charges.[2−7,16−22] The same is true for two cofacial 1- and 1′-naphthalene rings where again the less sterically hindered anti form is more abundant.[5] However, we find that when one of the cofacial aromatic rings is a fused bicyclic 1′-naphthalene[29] or a 2′-naphthalene ring and the other is a monosubstituted monocyclic ring, the syn diastereomer generally is favored in the ground state. Here favorable $\pi-\pi$, dipole$-\pi$, and charge$-\pi$ interactions between the two cofacial sites are large enough to overcome classically unfavorable interactions, even when one of the rings contains a site manifesting a considerable steric, repulsive, destabilizing interaction with its neighboring ring.

Experimental Section

General Methods. For flash chromatography, the crude coupled product was dissolved in a small amount of solvent and added to some silica gel. After removal of the solvent by

evaporation, the resultant powder then was added to the top of a silica gel column that then was eluted. Those compounds consisting of a mixture of syn−anti isomers in unequal amounts at probe temperature (ca. 20 °C) do not show integral peaks areas, and so areas are not reported for their NMR spectra.

1-(1′-Naphthyl)-8-(3′-methoxyphenyl)naphthalene (1). To a degassed solution of 70.9 mg (0.213 mmol) of 8-bromo-1-(1′-naphthyl)naphthalene[29] and 12.4 mg (0.0107 mmol, 5 mol %) of $Pd(PPh_3)_4$ in 5 mL of DME was added 35.6 mg (0.234 mmol) of 3-methoxyphenylboronic acid followed by 50 mg (0.49 mmol) of Na_2CO_3 in 2 mL of degassed water. The mixture was stirred at reflux under nitrogen for 3 h and then cooled to room temperature. The mixture was filtered and treated consecutively with CH_2Cl_2 (25 mL) and water (10 mL), and the aqueous layer was extracted with CH_2Cl_2 (2 × 25 mL). The combined organic phases were applied to a silica column equilibrated with hexanes/EtOAc (1:1). Elution with the same solvent gave 63.8 mg (0.177 mmol, 83%) of white crystals, mp144−145 °C. ^{1}H NMR ($CDCl_3$) δ 8.01 (2H, m), 7.70−7.10 (m), 6.71 (dd, J = 7.8, 8.1 Hz), 6.45 (dt, J = 1.5, 7.5 Hz), 6.32 (m), 5.95−5.99 (m), 5.87 (dd, J = 1.5, 2.4), 3.63 (Me), 3.09 (Me). Anal. Calcd for $C_{27}H_{20}O$: C, 89.97; H, 5.59. Found: C, 89.63; H, 5.61.

1-(2′-Naphthyl)-8-(3′-methoxyphenyl)naphthalene (2). To a degassed solution of 71.0 mg (0.213 mmol) of 8-bromo-1-(2′-naphthyl)naphthalene and 12 mg (0.011 mmol, 5 mol %) of $Pd(PPh_3)_4$ in 3 mL of DME was added 35.6 mg (0.234 mmol) of 3-methoxyphenylboronic acid followed by 50 mg (0.49 mmol) of Na_2CO_3 in 1 mL of degassed water. The contents of the sealed tube under nitrogen were magnetically stirred at 100 °C. After 30 min, to the black mixture was added an additional 6 mg of $Pd(PPh_3)_4$ and 4 mL of degassed DME−water (3:1). Further stirring, heating at reflux under nitrogen for 3 more hours, cooling, and filtering were followed by diluting with CH_2Cl_2 (25 mL) and then water (10 mL). After separating the phases, the water layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were chromatographed on a silica column equilibrated with hexanes/EtOAc (1:1) and eluted with the same solvent. Rechromatographing with hexanes by gravity gave 46.3 mg (12.8 mmol, 60%) of a yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.97 (d, 2H, J = 8.1 Hz), 7.70−7.22 (m), 7.08 (d, J = 8.4 Hz), 6.75−6.45 (m), 6.43 (s), 6.35 (s), 6.08 (m), 3.54 (Me), 3.21 (Me). Anal. Calcd for $C_{27}H_{20}O$: C, 89.97; H, 5.59. Found: C, 89.83; H, 5.77.

1-(1′-Naphthyl)-8-(3′-methylthiophenyl)naphthalene (3). A solution of 0.186 g (0.453 mmol) of di-*n*-butyl 1-(1′-naphthyl)-8-naphthaleneboronate in 7 mL of DME was added to 0.140 g (0.689 mmol) of 1-bromo-3-(methylthio)benzene (Lancaster), and after degassing, 26 mg (0.023 mmol, 5 mol %) of $Pd(PPh_3)_4$ followed by 70 mg (0.66 mmol) of Na_2CO_3 in 2 mL of degassed water was added. The mixture was heated at reflux with stirring under nitrogen for 5 h and then allowed to reach room temperature under nitrogen overnight. The solvent was removed, and the residue was diluted with a mixture of CH_2Cl_2 (25 mL) and water (10 mL). The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 25 mL). The combined organic phases were concentrated, and the residue was applied to a silica column equilibrated with hexanes and eluted with the same solvent. The pure fraction (identified by TLC) gave 0.128 g (0.340 mmol, 75%) of a white solid, mp 91−93 °C. ^{1}H NMR ($CDCl_3$) δ 8.01 (2H, m), 7.7−7.12 (m), 6.65 (m), 6.58 (m), 6.50 (dt, J = 2, 7.5 Hz), 6.25−6.13 (m), 2.35 (Me), 1.95 (Me). Anal. Calcd. for $C_{27}H_{20}S$: C, 86.13; H, 5.35. Found: C, 86.12; H, 5.97.

1-(2′-Naphthyl)-8-(3′-methylthiophenyl)naphthalene (4). To a degassed solution of 103 mg (0.309 mmol) of 8-bromo-1-(2′-naphthyl)naphthalene and 17.9 mg (0.015 mmol, 5% mol) of $Pd(PPh_3)_4$ in 5 mL of DME was added 50.8 mg (0.113 mmol) of the boroxine trimer of 3-(methylthio)benzeneboronic followed by 0.113 g (1.07 mmol) of Na_2CO_3 in 2 mL of degassed water. After 15 min, additional $Pd(PPh_3)_4$ was added, and stirring was continued for 3.25 more hours. The cooled mixture was diluted with CH_2Cl_2 (25 mL) and then with water (10 mL). The water layer was extracted with CH_2Cl_2 (2 × 25 mL). The combined organic phases were chromatographed on a silica column equilibrated with hexanes and eluted with the same solvent to give 47.0 mg (0.125 mmol, 40%) of a yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.97 (dd, J = 1.2, 8.4 Hz), 7.70−7.30 (m), 7.22 (m), 7.08 (m), 6.84−6.68 (m), 6.54−6.30 (m), 2.27 (Me), 1.96 (Me). Anal. Calcd for $C_{27}H_{20}S \cdot 0.4H_2O$: C, 84.51; H, 5.46. Found: C, 84.62, H, 5.90.

1-(1′-Naphthyl)-8-[(3′-dimethylsulfonio)phenyl]naphthalene Triflate (5). To a solution of 1-(1′-naphthyl)-8-[(3′-methylthio)phenyl]naphthalene 0.4 hydrate (10.0 mg, 0.0259 mmol) in dry hexanes (3 mL) was added at room-temperature methyl trifluoromethanesulfonate (0.05 mL, 0.45 mmol). The white precipitate was filtered and washed with hexanes and allowed to dry under reduced pressure. The yellowish precipitate then was dissolved in chloroform, and the organic phase was washed with aqueous 0.01 N K_2CO_3 and then with water until neutral. After drying over $MgSO_4$, the solvent was removed under reduced pressure to give 11.5 mg (0.019 mmol, 73%) of a yellowish solid, mp 127−130 °C. ^{1}H NMR ($CDCl_3$) δ 8.2−8.07 (m), 7.71−7.06 (m), 6.87 (m), 3.31 (Me), 3.18 (Me), 2.98 (Me), 2.92 (Me). Anal. Calcd $C_{29}H_{23}S_2F_3O_3 \cdot 3.5H_2O$: C, 57.70; H, 5.01. Found: C, 57.90; H, 4.79.

1-(2′-Naphthyl)-8-[(3′-dimethylsulfonio)phenyl]naphthalene Triflate (6). To a solution of 1-(2′-naphthyl)-8-[(3′-methylthio)phenyl]naphthalene 0.4 hydrate (17 mg, 0.044 mmol) in dry hexanes (3 mL) was added at room-temperature methyl trifluoromethanesulfonate (0.1 mL, 0.9 mmol). The hexane phase was removed, and the remaining phase was washed twice with hexanes. The combined hexanes phases were concentrated, the yellowish precipitate was dissolved in chloroform, and K_2CO_3 was added. After being dried over Na_2SO_4, the solvent was removed to give 18 mg (0.033 mmol, 75%) of a yellowish product, mp 123−125 °C. ^{1}H NMR ($CDCl_3$) δ 8.05 (t, J = 8 Hz), 7.8−7.0 (m), 3.05 (Me), 3.01 (Me), 2.84 (Me), 2.34 (Me). Anal. Calcd for $C_{29}H_{23}S_2F_3O_3 \cdot 0.5HOSO_2CF_3$: C, 57.74; H, 4.27. Found: C, 57.55; H, 3.85. Mass spectrum (positive FAB): m/z 391.1531 ($C_{28}H_{23}S$, 391.1520).

Di-*n*-butyl 1-(2′-Naphthyl)-8-naphthaleneboronate. A magnetically stirred solution of 1-bromo-8-(2′-naphthyl)naphthalene (100 mg, 0.300 mmol) in 30 mL of dry THF under nitrogen was cooled to −74 °C, and 1.8 N *n*-BuLi (hexane) (0.20 mL, 0.36 mmol) was added dropwise, keeping the temperature below −70 °C. The green-brown solution was stirred for 30 min at this temperature, and then tri-*n*-butyl borate (0.10 mL, 0.37 mmol) was added slowly by syringe keeping the temperature below −70 °C. The mixture was allowed to reach room temperature gradually (12 h). After quenching with 15 mL of saturated NH_4NO_3 and separating the phases, the organic layer was extracted with ether (3 × 20 mL) and dried with Na_2SO_4. Evaporation of the organic solvent gave a yellow oil which was preadsorbed onto 0.5 g of silica and purified by flash chromatography first using hexanes as eluent and then increasing the polarity to 20% ethyl acetate. Flash chromatography was performed again to the preadsorbed mixture onto 0.5 g silica using hexanes/EtOAc (4:1) to give 53 mg (0.13 mmol, 41%) of a yellow oil. Anal. Calcd for $C_{28}H_{31}BO_2 \cdot H_2O$: C, 78.51; H, 7.76. Found: C, 78.44; H, 7.72. 1,2′-Binaphthyl (27.7 mg, 0.11 mmol, 37%) mp 74−76 °C (lit.[33] mp 79−81 °C) was also obtained as a side product by washing the column with the same eluent.

1-(2′-Naphthyl)-8-[3′-(*N*,*N*-dimethylamino)phenyl]naphthalene (7). To a degassed solution of 40 mg (0.093 mmol) of di-*n*-butyl 1-(2′-naphthyl)-8-naphthaleneboronate and 5.4 mg (0.0047 mmol, 5 mol %) of $Pd(PPh_3)_4$ in 5 mL of DME was added 26.9 mg (0.134 mmol) of *N*,*N*-dimethyl-3-bromoaniline followed by a degassed solution of 130 mg (3.61 mmol) of KOH and 2.4 mg (0.0074 mmol) of tetra-*n*-butylammonium bromide in 2 mL of water. The mixture was stirred at reflux under nitrogen for 3 h, cooled to room temperature and diluted with CH_2Cl_2 (20 mL) and water (10 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 15 mL). The combined organic phases were added to 0.5 mg silica, concentrated, and applied to a silica column equilibrated with hexanes. Elution with EtOAc in hexanes (0−6%) gave 30 mg (0.073 mmol, 79%) of a yellowish oil. ^{1}H NMR ($CDCl_3$) δ 7.97 (2H, m), 7.68−7.24 (m), 7.04 (d, J = 8.1 Hz), 6.74 (t, J = 7 Hz), 6.47 (m), 6.16 (m), 5.92 (d, J = 7.2 Hz), 5.81 (m), 2.68 (Me), 2.37 (Me). Anal. Calcd for $C_{28}H_{23}N \cdot 2H_2O$: C, 82.12; H, 6.64; N, 3.42. Found: C, 81.95; H, 6.25; N: 3.60.

(33) Dobbs, T. K.; Hertzler, D. V.; Keen, G. W.; Eisenbraun, E. J.; Fink, R.; Hossain, M. B.; Helm, D. vd. *J. Org. Chem.* **1980**, *45*, 4769−4774.

1-(2′-Naphthyl)-8-[3′-(trimethylammonio)phenyl]naphthalene Iodide (8). To 17 mg (0.042 mmol) of 1-(2′-naphthyl)-8-[3′-(*N*,*N*-dimethylamino)phenyl]naphthalene in 2 mL of chloroform was added 0.05 mL (0.8 mmol) of iodomethane. After standing for 24 h at room temperature, the solvent was removed, and the yellowish solid was suspended in ether and filtered. The collected precipitate was washed with ether and dried to give 18.7 mg (0.0345 mmol, 82%) of a yellowish solid, mp 119−121 °C. ^{1}H NMR ($CDCl_3$) δ 8.07 (2H, t, J = 8 Hz), 7.75−7.24 (m), 7.03 (m), 6.92 (m), 3.64 (Me), 3.29 (Me). Anal. Calcd for $C_{29}H_{26}IN\cdot1.5H_2O$: C, 64.21; H, 5.39; N, 2.58. Found: C, 64.07; H, 5.31; N: 2.21.

1-(2′-Naphthyl)-8-(3′-pyridyl)naphthalene (9). To a degassed solution of 100 mg (0.300 mmol) of 8-bromo-1-(2′-naphthyl)naphthalene and 17 mg (0.013 mmol, 5 mol %) of $Pd(PPh_3)_4$ in 2 mL of DME was added 48 mg (0.33 mmol) of diethyl(3-pyridyl)borane followed by 50 mg (0.47 mmol) of Na_2CO_3 in 1 mL of water. The mixture was magnetically stirred in a tube sealed under nitrogen at 100 °C for 2 h. The cooled mixture was diluted with 50 mL of CH_2Cl_2 and 100 mL of water. The organic phase was separated, and the water layer was extracted with CH_2Cl_2 (10 mL). The combined organic phases were chromatographed on silica using hexanes/EtOAc (1:1) to give 84.2 mg (0.254 mmol, 85%) of a yellow oil which after standing in hexanes in a freezer for 3 days gave white crystals, 73.8 mg (0.223 mmol, 74%), mp 86−88 °C. ^{1}H NMR ($CDCl_3$) δ 8.34 (s), 7.99 (td, J = 1.2, 6.6 Hz), 7.79 (m), 7.70−7.30 (m), 7.20−6.97 (m), 6.50 (m), 6.25 (m). Anal. Calcd for $C_{25}H_{17}N\cdot0.25H_2O$: C, 89.39; H, 5.25; N, 4.17. Found: C, 89.40, H, 5.24; N, 4.20.

1-(2′-Naphthyl)-8-(1′-methyl-3′-pyridylium)naphthalene Iodide (10). To a solution of 12.6 mg (0.0381 mmol) of 1-(2′-naphthyl)-8-(3′-pyridyl)naphthalene in 0.5 mL of methanol was added 0.050 mL (0.11 g, 0.80 mmol) of CH_3I. Concentration of the mixture after 24 h at room temperature gave a yellow oil that subsequently crystallized. Recrystallization from ethanol/water gave 5.1 mg (0.011 mmol, 29%) of yellow crystals, mp193−194 °C. ^{1}H NMR ($CDCl_3$) δ 8.54 (s), 8.44 (s), 8.19 (m), 8.14 (dd, J = 2.1, 7.5 Hz), 8.08 (dd, J = 1.2, 8.1 Hz), 7.84−7.48 (m), 7.36 (m), 7.19 (m), 7.01 (m), 4.38 (Me), 3.94 (Me). Anal. Calcd for $C_{26}H_{20}NI$: C, 65.97; H, 4.26; N, 2.97. Found: C, 66.34; H, 4.49; N, 3.08.

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