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Diastereomers of a Cofacial Ternaphthalene and Two Azaternaphthalenes. Syntheses and Barriers to Isomerization

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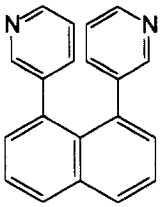
Abstract: The title compounds, a mixture of *anti* and *syn* diastereomers, were prepared by Pd-catalyzed coupling of areneboronic acids with hetaryl halides. Energy barriers for the interconversion of the diastereomers obtained by kinetic and computational studies show a dependence on the location of the annular nitrogen atom, the *ortho* providing a smaller barrier than the *meta* nitrogen atom. © 1997 Elsevier Science Ltd.

The position of the annular nitrogen atom in cofacial 1,8-dipyridyl naphthalenes has a large influence on the magnitude of the energy barrier to rotation about the pyridyl-naphthalene bond. When the nitrogen atom is located *meta* to the site of bonding as in **1**, *anti* and *syn* atropisomers are readily observed by proton magnetic resonance at ambient temperatures but the isomers interconvert too rapidly to allow them to be isolated in a pure form.[1] However, when the heteroatom is situated *ortho* as in **2**, interconversion of *anti* and *syn* forms is so rapid that atropisomers may only be observed by proton resonance at low temperatures.[2]

We report the preparation of azaternaphthalenes **3** and **4** having cofacial naphthalene and isoquinoline rings as well as the known ternaphthalene **5**[3] using a Pd-catalyzed cross-coupling method and examine their barriers to *anti*-*syn* interconversion, considerably larger than those found for **1** and **2**.

Rates of isomerization of the *anti* forms of **4** and **5** to an equilibrium mixture of *anti* and *syn* isomers show that both compounds have essentially the same rotational energy barrier, 27-28 kcal/mol. But **3** has a much lower barrier and could not be separated at room temperature into a pure diastereomer. The structure of *anti*-**4** was determined by an X-ray analysis.



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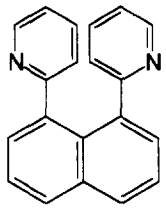

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Results

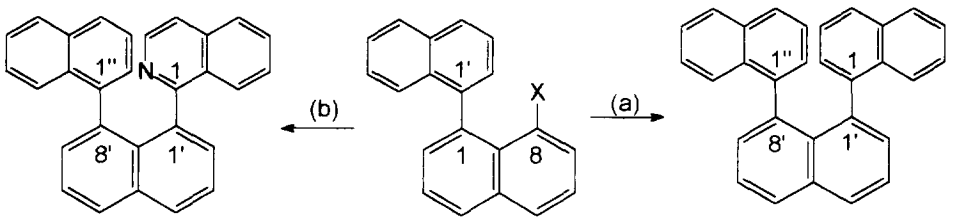
Syntheses. 8-Bromo-1,1'-binaphthyl (**6**) was easily formed by coupling (70%) 1,8-dibromonaphthalene[4] with 1-naphthaleneboronic acid[5] in aqueous carbonate under Suzuki's conditions using $Pd(PPh_3)_4$.[6] The coupling process was repeated making use of the same acid to give a superior synthesis (90%) of **5**.[7] Our conditions using aqueous carbonate are modeled after those employed in another coupling reaction of a naphthaleneboronic acid.[8]

Isoquinolyl **3** was made in two steps from **6** by first converting **6** to its di-*n*-butyl boronate ester **7** and then coupling **7** to 1-chloroisoquinoline(63% overall).

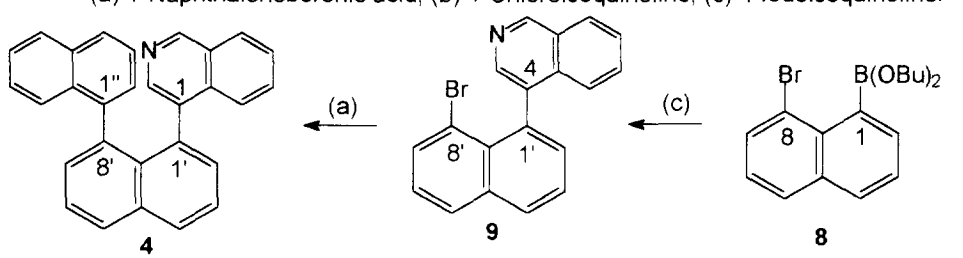
Isoquinolyl **4** was synthesized by a multistep sequence starting with the conversion of the 1,8-dibromide[4] to boronate ester **8** by low temperature lithiation followed by substitution with tri-*n*-butyl borate. This ester then was coupled to 4-iodoisoquinoline[9] in aqueous KOH along 4-(8'-bromo-1'-naphthyl)isoquinoline (**9**) (93%). This new bromide and 1-naphthaleneboronic acid in the presence of the phase transfer catalyst and aqueous KOH gave **4** (84%). A phase transfer catalyst has been employed in other Suzuki couplings.[10]

X-Ray Structure of Anti-4. The crystalline diastereomer has the *anti* structure and this confirmed the *anti* assignment given to its solution NMR spectrum. The 1,8-sigma bonds form an 8° dihedral angle with respect to each other due to out-of-plane deformations of the carbon atoms of the disubstituted naphthalene ring. The isoquinolyl and naphthyl rings are twisted 70.4° and 71.1°, respectively, with respect to the central naphthalene plane. These two rings are splayed out with a V-shaped pattern forming a 18° angle. The crystal is defined by a herring bone pattern with the disubstituted rings alternating in an "up-down" arrangement with adjacent molecules adopting a T-shaped stacked orientation. Among the several 1,8-cofacial structures determined by X-ray analysis[11] are those

of *cis*- and *trans*-1,8-bis(1'-pyrenyl)naphthalene where, as here, naphthalene-type rings interact on bond rotation.[16]



(a) 1-Naphthaleneboronic acid, (b) 1-Chloroisoquinoline, (c) 4-Iodoisoquinoline.



Equilibrium Composition of Atropisomers. Compounds **3-5** have complex spectra but a few signals do not overlap and allow the isomer ratio to be determined. For **5** in $CDCl_3$ the distinguishing multiplets at 6.33 and 6.70 ppm for the *anti* and *syn* isomers, respectively, gave an *anti*/*syn* equilibrium constant of 3.6 (74 C). For **4** the singlet peaks at 8.48 and 8.65 ppm associated with the *anti* and *syn* isomers, respectively, provided *anti*/*syn* equilibrium constants of 3.0 (25 C), 2.0 (75 C) and 1.8 (90 C) and an enthalpy (ΔH) of -1,660 cal/mol and an entropy (ΔS) of -3.4 eu, the latter small value being typical for a conformational change. For **3** at 20 C the multiplets at 6.27 and 6.64 ppm for the *anti* and *syn* isomers, respectively, afforded an equilibrium constant of 2.7. The *anti* isomer is favored for **3-5**.

Rates of Isomerization of 4 and 5. The rate of isomerization of the enriched *anti* diastereomers of **4** and **5** in $CDCl_3$ at 75 C was monitored by proton NMR.

The rate constant, $k_{a \rightarrow s}$, for **5** has the value of 3.08×10^{-4} sec^{-1} for a reaction approaching an equilibrium mixture, Eqn 1, with a final *anti* to *syn* ratio of 3.3. This constant has not been statistically corrected for the presence of two equivalent rotating rings. Using the equilibrium constant to provide mole fractions (see Experimental) and making the statistical correction, the rate constant in the forward *anti* to *syn*

direction, k_{as}, is 0.36 x 10^{-4} sec^{-1}, and in the reverse direction of *syn* to *anti*, k_{sa}, it is 1.18 x 10^{-4} sec^{-1}. The free energy ($\Delta G^{\ddagger}$) required to convert the *anti* to the *syn* form is 27 kcal/mol (75 °C), a considerably larger value than the 24.7 kcal/mol (*anti* to *syn*, 40 °C) found for 1,8-di(3-tolyl)naphthalene[13] where *ortho* methyl groups contribute significantly to the barrier and the *anti* to *syn* ratio is 3.2.

Similarly, *anti*-**4** gave k_{obs} = 9.76 x 10^{-5} sec^{-1}. While the rotating rings are structurally different, they are expected to be approximately equivalent. Making the corrections (K 2.0) as for **5** gave k_{as} = 1.61 x 10^{-5}, k_{sa} = 3.27 x 10^{-5} sec^{-1} and $\Delta G^{\ddagger}$ = 28 kcal/mol (75 °C) for the *anti* to *syn* conversion. By comparison, the $\Delta G^{\ddagger}$ value for 1,8-di(1'-pyrenyl)-naphthalene[12] (75 °C, $CHCl_2CHCl_2$) is 28 kcal/mol.

$$k_{obs} = k_{as} + k_{sa} \qquad (1)$$

AM1 and PM3 Computations. The *anti/syn* ratio (DMSO solvent, 25°) was estimated reasonably well in most cases. For **5**, it was 3.3 to 1 by both AM1 and PM3. For **4**, the AM1 method gave an equimolar ratio but the PM3 method favored *anti* over *syn* by a factor of 1.6. And for **3** AM1 favored the *syn* isomer by a factor of 1.5; PM3 favored the *anti* by a factor of 1.6. Experimentally, the *anti* is the major isomer in all cases.

The computed enthalpy barrier to interconvert all three compounds was systematically low, being only about 20 kcal/mol by both methods for **4** and **5**, compared with the experimental free energy value of 27-28 kcal/mol at 75 °C. There is essentially no difference in the size of the barrier for the rotation of a 1-naphthyl or a 4-isoquinolyl ring.

Comparison of the computed and the observed crystal structure of *anti*-**4** revealed that the computed structure has more distortion. Thus, the true 8° dihedral bond angle at the 1,8 position was computed to be 15° (AM1) or 20° (PM3), the 18° V-splay angle was 30° (AM1) or 27° (PM3) and the observed torsional angle of 70.4° for the isoquinoly ring was 69.8° (AM1) or 97.2° (PM3) and the observed angle of 71.1° for the naphthyl ring was 70.5° (AM1) or 86.7° (PM3). Thus, the PM3 method gave larger deviations.

Discussion

Syntheses. Our use of the Suzuki method[6] of palladium-catalyzed cross-coupling of boronic acids in a mixed aqueous-organic medium became straightforward only when certain adaptations were made to overcome the hydrophobicity of the naphthalene and isoquinoline reactants. These included (1) the use of the higher boiling and more solubilizing 1,2-

dimethoxyethane (DME) in place of the usual THF solvent, an approach used by others,[8] and (2) often the addition of the phase transfer catalyst tetra-*n*-butylammonium halide[10,14] along with a change in the base from carbonate to KOH.[15] No attempt was made to learn whether both the transfer catalyst and the higher concentration of hydroxide ion were necessary but it is known that the "ate" complex formed on the addition of hydroxide ion to a boronic acid as required for ligand transfer to a palladium oxidative addition complex is subject to steric hindrance.[16] Moreover, the use of an ionizable boronic acid over a borane provided the advantage of water solubility. Carbocyclic boronic acids were favored over hetaryl counterparts because of their ease of preparation and purification. Hetaryl boranes were avoided because they often are oligomeric materials with limited solubility.[17-19] Our reaction conditions may well be useful to others preparing highly hydrophobic materials using the Suzuki method. A trial using a Stille route[20] on 4-(tributylstannyl)isoquinoline[21] and 1-bromonaphthalene failed.

Barriers to Bond Rotation. The computations show that the energetically preferred geometry for bond rotation in **3-5** has an approximate T-shaped *anti* transition state in which the smaller side of the rotating ring is directed at the face of its neighbor.

The free energy of activation for the conversion of the lower energy *anti* isomer to the transition state has essentially the same value of 27-28 kcal/mol for both **4** and **5**. This similarity is readily understandable because the separation between the splayed rings increases with added distance from the point of attachment to the naphthalene base and so the small change in size between a CH group and a nitrogen atom at a *meta* site is essentially inconsequential. Hence, rotation of the 1-naphthyl and 4-isoquinolyl rings proceeds with the same facility.

Clearly, **3** is different. The 1-isoquinolyl ring rotates easier than a 1-naphthyl ring here and even in the structurally less hindered but related 1'-naphthyl-1-isoquinoline, the latter as measured by its optical stability.[22] The favored orientation in the transition state has the nitrogen atom directed at the face of the monosubstituted naphthalene ring.

Because the analogous rotor 1,1'-binaphthyl with its barrier of 22.5 kcal/mol is reported to interconvert from *anti* to *syn* by a 2-step process,[23] a careful search was made of the transition state for **3** in which energies and geometries were examined every 2.5°. The resultant energy profile was flat, consistent with a concerted movement of the 1-

isoquinoly ring over the naphthalene base.

The decrease in the size of the rotational energy barrier found on moving an annular nitrogen atom from a *meta* to an *ortho* position in the simple dipyridyl systems **1**[2] and **2**[2] is found again in its benzologs. An annular nitrogen atom at an *ortho* site therefore is not conducive to chiral stability.

Experimental

General: Silica gel 230-425 mesh was used for flash chromatography. Proton NMR spectra were generally recorded at 19-20 ^{0}C at 300 MHz.

8-Bromo-1,1'-binaphthyl (6). To a degassed solution of 1.0 g (3.5 mmol) of 1,8-dibromonapththalene[4] and 0.120 g (0.105 mmol) of $Pd(PPh_3)_4$ in 10 mL of dimethoxyethane was added 0.66 g (3.5 mmol) of 1-naphthaleneboronic acid[5] followed by 3.5 mL of degassed 2N sodium carbonate. The mixture was heated at reflux with stirring under nitrogen for 4 h, the solvent was evaporated under reduced pressure and the residue was treated with a mixture of dichloromethane (50 mL) and water (25 mL). The organic layer was separated and the aqueous solution was extracted with dichloromethane (30 mL). The combined organic phase was dried and after the addition of 5 g of silica the solvent was removed under reduced pressure and the yellowish powder was dried under a vacuum at rt. The adsorbed material was applied to a silica column equilibrated with hexanes and eluted with the same solvent. Concentration gave 1.0 g of a yellowish oil, which crystallized on stirring in hexanes. The solid was dried at 100 ^{0}C in vacuo to give 0.82 g (25 mmol, 70%) of a yellow solid, recrystallized from hexanes, mp 118-120 ^{0}C. Anal. Calcd for $C_{20}H_{13}Br$: C, 72.09; H, 3.93. Found: C, 72.23; H, 3.96. ^{1}H NMR ($CDCl_3$) δ 7.94 (4H, m), 7.70 (1H, d, J = 7.2), 7.5 (5H, m), 7.27 (3H, m).

1,1':8',1''-Ternaphthalene[3] or 1,8-Bis(1'-napthyl)naphthalene (5). To a degassed solution of 150 mg (0.45 mmol) of 8-bromo-1,1'-binaphthyl **6** and 16 mg (0.013 mmol, 3 mol%) of $Pd(PPh_3)_4$ in 2 mL of dimethoxethane was added 85 mg (0.49 mmol) of 1-naphthaleneboronic acid,[5] followed by 50 mg (0.47 mmol) of Na_2CO_3 in 1 mL of water. After the mixture under nitrogen was stirred magnetically in a sealed tube at 100 ^{0}C for 45 min., it was diluted with 30 mL of dichloromethane and 10 mL of water. The organic phase was separated and the water layer was extracted with dichloromethane (10 mL). The combined organic layer was adsorbed onto 2 g of silica and chromatographed on silica using hexanes. After removal of the solvent 154 mg (0.40 mmol, 90%) of a slightly yellowish solid was obtained. ^{1}H NMR ($CDCl_3$) showed the presence of syn/anti isomers that matched the reported spectra.[3] Fractional crystallization from DME gave 46 mg (0.12 mmol) of the pure *anti* isomer, mp 176-177 ^{0}C lit[3] mp 173.3-174.2 ^{0}C. ^{1}H NMR ($CDCl_3$) δ 8.07 (2H, dd, J = 1.2 and 8.1), 7.57 (4H, m), 7.3 (8H, m), 7.06 (2H, d, J = 8.1), 6.46 (2H, dd, J = 1 and 6.9), 6.31 (2H, t, J = 8.1).

Di-*n*-butyl 1-(1'-Naphthyl)-8-naphthaleneboronate (7). A magnetically stirred solution of 780 mg (2.34 mmol) of 8-bromo-1,1'-binaphthyl (**6**) in 30 mL of tetrahydrofuran under nitrogen was cooled to -75 ^{0}C and

tri-*n*-butyl borate was added slowly by syringe keeping the temperature below -70 ^{0}C. The mixture was allowed to reach rt gradually (12 h). After quenching with satd. NH_4NO_3 (30 mL), the mixture was extracted with ether (2x40 mL). Drying (Na_2SO_4) and removal of the solvent under reduced pressure yielded 1.26 g of a yellowish oil that was used directly in the next step. Purity was confirmed by gc-ms analysis that showed the presence of just one product. ^{1}H NMR ($CDCl_3$) δ 7.92 (4H, m), 7.4 (9H, m), 3.5 (2H, m), 2.4 (2H, m), 1.35 (4H, m), 0.8 (10H, m).

2-Aza-1,1':8',1''-ternaphthalene (3). A mixture of 1.26 g of crude butyl naphthaleneboronate **7** with 450 mg (2.75 mmol) of 1-chloroisoquinoline[8] and 100 mg (0.087 mmol) of $Pd(PPh_3)_4$ was dissolved in 7 mL of DME. After adding an aqueous solution of 560 mg (10 mmol) of KOH and 60 mg (0.16 mmol) of tetra-*n*-butylammonium iodide, the heterogeneous mixture was degassed by bubbling nitrogen. The mixture was heated at reflux for 5 h under nitrogen, then cooled and diluted with dichloromethane (50 mL). The layers were separated and the aqueous phase was extracted with dichloromethane (20 mL). The combined organic phase was dried and adsorbed onto 3 g of silica, which then was applied to a silica column equilibrated with hexanes-ethyl acetate (4/1). Elution with this solvent gave 568 mg (1.5 mmol, 63% based on starting bromide over the two steps) of product as a slightly yellow solid, mp 148-150 ^{0}C, consisting of an *anti*/*syn* mixture (2.7/1). Recrystallization from several solvents failed to change the ratio. Anal. Calcd. $C_{26}H_{20}IN$: C, 91.31; H, 5.02; N, 3.67. Found: C, 91.14; H, 5.21; N, 3.64. ^{1}H NMR ($CDCl_3$, mixture of *anti* and *syn*) δ 8.21 (d, J = 6), 8.10 (m), 7.56 (m), 7.36 (m), 7.0 (m), 6.75 (d, J = 6), 6.64 (t, J = 8), 6.51 (d, J = 7.4), 6.27 (t, J = 8).

Di-*n*-butyl 8-Bromo-1-naphthaleneboronate (8). A solution of 2.0 g (7.0 mmol) of 1,8-dibromonaphthalene[4] in THF was cooled under nitrogen to -60 ^{0}C (dry ice-acetone) and 2.8 mL of 2.5 N n-BuLi in hexanes (7.5 mmol) was added over 10 min and the yellow solution was stirred for 1 h at this temperature. The mixture was cooled to -70 ^{0}C and 2 mL (1.7 g, 7.4 mmol) of tri-*n*-butyl borate was added over a period of 5 min. After stirring for 0.5 h at -70 ^{0}C the mixture was gradually warmed to rt. A small amount of a white precipitate was formed. After 3 h the mixture was quenched with 30 mL of saturated NH_4NO_3, the phases were separated and the organic layer was concentrated under reduced pressure. The brown oil was purified by chromatography on silica gel eluting with ethyl acetate-hexanes (0 to 5%) followed by Kugelrohr distillation under vacuum to give 2.02 g (5.57 mmol, 79%) of a colorless oil that was pure by gc-ms analysis. This material was used directly to make **9**. ^{1}H NMR ($CDCl_3$) δ 7.82 (3H, m), 7.54 (2H, m), 7.30 (1H, m), 3.85 (2H, m), 3.70 (2H, m), 1.57 (4H, m), 1.40 (4H, m), 0.90 (6H, m).

Conversion of 4-Bromoisoquinoline to 4-Iodoisoquinoline. The following is a superior preparation of the known iodo compound.[9] To a solution of 9 mL (22 mmol) of n-BuLi (2.5 N in hexane) in 80 mL of THF at -70 ^{0}C under nitrogen was added 2.08 (10 mmol) of 4-bromoisoquinoline in 15 mL of THF at such a rate that the temperature never exceeded -65 ^{0}C. The mixture was stirred for 30 min at -70 ^{0}C and 5.4 g (22 mmol) of I_2 in 16 mL of THF was added over 15 min keeping the temperature below -65 ^{0}C. The brownish suspension was

stirred for 1 h at -70 ^{0}C and allowed to warm gradually to rt. After dilution with ether (80 mL), the mixture was washed with 5% (3x100 mL) sodium metabisulfite The organic phase was dried (Na_2SO_4) and evaporated under reduced pressure to give a brownish solid that was purified on silica using ethyl acetate in hexanes (15 to 20%) to give 1.98 g (7.76 mmol, 77%) of a yellow solid. Recrystallization from hexanes gave 1.63 g (6.39 mmol, 63%) of slightly yellow needles, mp 94-96 ^{0}C. ^{1}H NMR ($CDCl_3$) showed different shifts for H3: bromo 8.72, iodo 8.95 ppm.

4-(8'-bromo-1'-naphthyl)isoquinoline (9). To a mixture of 724 mg (2.00 mmol) of bromo boronate ester **8**, 561 mg (2.20 mmol) of 4-iodoisoquinoline,[9] 140 mg (0.087 mmol, 6 mol%) of $Pd(PPh_3)_4$ and 4 mL of dimethoxyethane degassed by bubbling nitrogen was added 500 mg (8.92 mmol) of KOH and 100 mg (0.21 mmol) of tetra-*n*-butylammonium bromide in 2 mL of degassed H_2O. After heating at reflux under nitrogen for 2 h, chromatography on silica using 15-30% ethyl acetate in hexanes yielded 623 mg (1.86 mmol, 93%) of slightly yellow needles, mp 164-166 ^{0}C, after recrystallization from ethyl acetate. Calcd. for $C_{19}H_{12}BrN$. C, 68.28; H, 3.62; N, 4.19. Found: C, 67.97; H, 3.66; N, 4.12. ^{1}H NMR ($CDCl_3$) δ 9.32 (1H, s), 8.48 (1H, s), 8.0 (3H, m), 7.72 (1H, d, J = 7.5), 7.57 (4H, m), 7.29 (2H, m).

3-Aza-1,1':8',1''-Ternaphthalene (4). A mixture of 300 mg (0.90 mmol) of 4-(8'-bromo-1'-naphthyl)isoquinoline (**9**), 170 mg (0.99 mmol) of 1-naphthaleneboronic acid[5] and 62 mg (0.054 mmol, 6 mol%) of $Pd(PPh_3)_4$ in 4 mL of DME was degassed by bubbling nitrogen. A solution of 225 mg (4.00 mmol) of KOH and 43 mg (0.13 mmol) of tetra-*n*-butylammonium bromide in 3 mL of water was added and the resultant mixture was heated at reflux with stirring under nitrogen for 1.5 h. The mixture was cooled and partitioned between dichloromethane/water (50 mL/30 mL). The organic layer was adsorbed onto silica and chromatographed on a silica column preconditioned with ethyl acetate/hexanes (1/1) to yield 320 mg of a colorless glass that crystallized on stirring with hexanes. After drying in vacuo at 100 ^{0}C, 307 mg (0.80 mmol, 84%) of a white solid was recovered, consisting of a mixture of *anti* and *syn* isomers (*anti*/*syn* = 2.75), mp 200-201 ^{0}C. The material was purified from traces of Pd by sublimation (210 ^{0}C/0.5 mm Hg) and recrystallized from EtOH to give 92 mg of pure anti isomer, mp 205-207 ^{0}C. The isomer ratio did not change when the material was dried at 100 ^{0}C in vacuo. Anal. Calcd. $C_{29}H_{19}N$: C, 91.31; H, 5.02; N, 3.67. Found: C, 91.10; H, 4.80; N, 3.68. *Anti*: ^{1}H NMR ($CDCl_3$) δ 8.44 (1H, s), 8.11 (2H, t, J = 6.6), 7.6 (4H, m), 7.51 (1H, s), 7.45 (3H, m), 7.3 (3H, m), 7.19 (2H, m), 7.10 (1H, d, J = 8.4), 6.48 (1H, d, J = 6.3), 6.32 (1H, t, J = 8.1).

Proton NMR Kinetic Studies at 75 ^{0}C of the Isomerization of *Anti* to an Equilibrium Mixture of *Anti* and *Syn* Ternaphthalenes in $CDCl_3$. The rate constant was obtained by using the standard first order equation correcting for the approach to equilibrium concentrations where either the logarithm of the quantities ([*anti*] -[*anti*$_e$]) or ([*syn*$_e$] - [*syn*]) was fitted to a linear regression equation. The e subscript denotes the equilibrium intensities. A single kinetic run was made for each substrate.

The equilibrium constant, K = ([*anti*]/[*syn*]), obtained at the end of the run, was used to convert the

equilibrium intensities. A single kinetic run was made for each substrate.

The equilibrium constant, K = ([*anti*]/[*syn*]), obtained at the end of the run, was used to convert the observed rate constant, k_{obs}, into its component rate constants. Thus, k_{obs} x (1/(1 + K)) = k_{as} and k_{obs} x (K/(1 + K)) = k_{sa}.

Starting from pure *anti*-**5** the high field portion of the spectrum was repeatedly and automatically scanned from δ 7.1 to 6.2. The appearance of the *syn* peak at δ 6.70 as well as the disappearance of the *anti* multiplet at δ 6.35 were monitored (K = 3.3). The reaction of **5** was followed for four half-lives; results agreed to within 5%.

The singlet peaks of *anti*-**4** at 8.72 (*syn*), 8.54 (*anti*) and 7.95 (*syn*) ppm were monitored (K = 2.0). Each gave a k_{obs} that was averaged giving a deviation of 18% over 2.5 half-lives. The small change in concentrations due to K being equal to 2 is the likely reason for the large uncertainty.

The $CDCl_3$ was dried by passing it through a short column of neutral alumina.

Crystal Structure of Anti-4. The crystal was obtained by a slow evaporation of an ethanolic solution. Orthorhombic, $P2_12_12_1$, a = 11.5633(3) C, b = 12.3842(4) C, c = 13.8615(4) C, V = 1985.0(1) C^3, Z = 4, $D_{calc.}$ = 1.276 g cm^{-3}, Mo K" (8 = 0.71073 C), T = 173 K. The structure was solved by the Direct Methods in *SHELXTL5*,[24] and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their parent atoms; 348 parameters were refined in the final cycle of refinement using 3723 reflections with I > 2F(I) to yield R_1 4.16% and wR_2 of 8.14%, respectively. Refinement was done using F^2.

Semiemperical Computations. A general description of our computations using AM1[25] and PM3[26] methods has appeared.[1] In determining whether the transition state for **3** leads to the *syn* and *anti* minima in a concerted or a stepwise process, an intrinsic reaction coordinate calculation was done starting from the transition state. Calculations were made proceeding along both directions of the normal mode belonging to the negative eigenvalue of the force constant matrix. The potential energy curve in the vicinity of the transition state was very flat and no additional minima could be detected except for those of the *syn* and *anti* forms. Rotation therefore does not seem to proceed stepwise.

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