Supporting Information

Synthesis and Stereodynamics of Highly Constrained

1,8-Bis(2,2'-dialkyl-4,4'-diquinolyl)naphthalenes (2)

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1. Isomerization reaction of **8** and **9** and mathematical treatment.

1.1. Isomerization study of 1,8-bis(2,2'-diphenyl-4,4'-diquinolyl)naphthalene, **8**.

The isomerization was performed in a closed vessel designed for high-pressure experiments using a concentration of 1 mg/mL of **8** in hexanes/EtOH = 85:15 at 97.8 °C and monitored by HPLC. The vessel was submerged in an ethylene glycol bath and the temperature was measured using a calibrated digital thermometer. The samples were cooled to room temperature prior to analysis by HPLC using a (*R,R*)-Whelk-O 1 column (4.6 x 250 mm) and hexanes/EtOH = 85:15 as the mobile phase (chromatographic enantioselectivity factor, α = 1.14). Individual response factors of the *anti*- and *syn*-isomers of **8** purified by preparative HPLC or crystallization were determined for quantitation. The individual response factors in hexanes/EtOH = 85:15 at 254 nm were calculated as 2256 A units/ug (*anti*-**8** and 862 A units/ug (*syn*-**8**).

time (min)	%anti	%syn
0	86.8	13.2
30	68.7	31.3
60	62.8	37.2
85	59.6	40.4
134	56.5	43.5
215	54.4	45.6
at equilibrium	54.1	45.9

1.2. Isomerization study of 1,8-bis(2,2'-diisopropyl-4,4'-diquinolyl)naphthalene *N,N'*-dioxide **9**.

The *syn/anti*-isomerization of **9** was measured at a concentration of 1 mg/mL in deuterated DMSO using NMR spectroscopy at 56.9 °C. The temperature of the sample was allowed to equilibrate for 10 min prior to the first NMR experiment. The NMR temperature was measured following a procedure reported by Merbach.¹

time (min)	%anti	%syn
0	92.9	7.1
21	92.4	7.6
60	91.9	8.1
92	91.5	8.5
122	91.2	8.8
240	90.8	9.2
at equilibrium	90.6	9.4

1.3. Reaction kinetics of a reversible first-order reaction via an intermediate.

$$\frac{dx}{dt} = -2k_2(S_0 + x) + 2k_1(A_0 - x) \quad (2)$$

where $A_0 = [\text{anti} - \mathbf{8a}]_0 = [\text{anti} - \mathbf{8b}]_0$

$S_0 = [\text{syn} - \mathbf{8}]$

$x = A_0 - A_t$ (concentration of A at time t)

k_1 = rate constant for *anti* - to *syn* - interconversion

k_2 = rate constant for *syn* - to *anti* - interconversion

at equilibrium $\frac{dx}{dt} = 0$

$$\begin{aligned} \frac{dx}{dt} &= -2k_2S_0 - 2k_2x + 2k_1A_0 - 2k_1x \\ &= -2x(k_2 + k_1) - 2k_2S_0 + 2k_1A_0 \end{aligned} \quad (3)$$

$$C_1 = -2(k_2 + k_1); \quad C_2 = -2k_2S_0 + 2k_1A_0 \quad (4)$$

$$\frac{dx}{dt} = C_1x + C_2 \quad (5)$$

at $t_0 = 0$; $x_0 = 0$

$$\int_0^{x_t} \frac{dx}{C_1x + C_2} = \int_0^t dt \quad (6)$$

Integration of both sides of equation 6 gives :

$$\frac{1}{C_1} \{ \ln(C_1x_t + C_2) - \ln C_2 \} = t \quad (7)$$

$$\ln \left(\frac{C_1x_t + C_2}{C_2} \right) = C_1t$$

$$\frac{C_1x_t + C_2}{C_2} = e^{C_1t}$$

$$x_t = \frac{C_2}{C_1} e^{C_1t} - \frac{C_2}{C_1} \quad (8)$$

Incorporation of equation 4 into 8 yields :

$$x_t = \frac{-2k_2S_0 + 2k_1A_0}{-2(k_2 + k_1)} e^{-2(k_2 + k_1)t} + \frac{2k_1A_0 - 2k_2S_0}{2(k_2 + k_1)} \quad (9)$$

2. Crystallography of **8**.

Single crystal X-ray diffractions of **8** were collected at -86 °C using a Siemens platform diffractometer with graphite monochromated Mo-K α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined with full-matrix least-squares/difference Fourier analysis using SHELX-97-2 software. Non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were placed in calculated positions and refined with a riding model. Data were corrected for the affects of absorption using SADABS.

Table 1. Crystal data and structure refinement for the single crystals of **8**.

empirical formula	C ₄₀ H ₂₆ N ₂
formula weight	534.66
Temperature/K	187(2)
wavelength	0.71073 Å
crystal system	monoclinic
space group	C2/c
unit cell dimensions	a = 18.885(2) Å b = 10.3754(0) Å c = 16.739(1) Å α = 90° β = 123.79(1)° γ = 90°
volume	2725.8 Å ³
Z	4
density (calculated)	1.303 g cm ⁻³
absorption coefficient	0.076
F(000)	1120
crystal size	0.30 x 0.10 x 0.10 mm
theta range for data collection	2.35-27.99
index ranges	2.35-28.22
reflections collected	3186
independent reflections	2477
completeness to theta = 27.00°	0.968
Absorption correction	0.9925
max. and min. transmission	1.000 0.837
refinement method	SHELXL-97 (Sheldrick, 1997)
data / restraints / parameters	3186/191/0
goodness-of-fit on F ²	1.135
final R indices [I>2sigma(I)]	0.0509
R indices (all data)	0.0678
largest diff. peak and hole	0.251, -0.208

3. NMR Spectra of 3.

3.1. ^1H NMR

3.2. HMQC

3.3. HMBC

4. NMR Spectra of 9.

4.1. ^1H NMR

4.2. HMQC

4.3. HMBC

5. NMR Spectra of 15.

5.1. ^1H NMR

5.2. HMQC

5.3. HMBC

6. NMR Spectra of 16.

6.1. ^1H NMR

6.2. HMQC

6.3. HMBC

(1) C. Ammann, P. Meier, A. E. Merbach, *J. Magn. Reson.* **1982**, *46*, 319-321.