JOC Article

Conformational Studies by Dynamic NMR. 90.[1] Structure and Stereodynamics of the Rotamers of Di- and Tri-α-naphthylphenyl Derivatives

Stefano Grilli, Lodovico Lunazzi, Andrea Mazzanti,* and Marco Pinamonti

Department of Organic Chemistry "A. Mangini", University of Bologna, Viale Risorgimento, 4, Bologna 40136, Italy

mazzand@ms.fci.unibo.it

Received April 15, 2002

The crystal structure of 1,3,5-tris(4-methylnaphth-1-yl)benzene, **1**, shows one naphthyl substituent in an *anti* relationship to the other two. On the other hand, low temperature (−70 °C) ^{1}H NMR spectra in solution show the presence of a second rotational conformer (rotamer) having all the three naphthyl substituents in a *syn* relationship. The interconversion barrier between the *anti* (77%) and *syn* (23%) rotamers of **1** was determined by line shape simulation of the temperature-dependent NMR spectra ($\Delta G^{\ddagger} = 12.1$ kcal mol^{-1}). In the analogous disubstituted *meta* and *para* derivatives, that is, 1,3- and 1,4-bis(4-methylnaphth-1-yl)benzene (**2** and **3**, respectively), the presence of both the *anti* and *syn* rotamers was also detected by low-temperature NMR spectroscopy. In the latter compounds, the proportions of the *anti* and *syn* forms are nearly equal, and the corresponding *anti* to *syn* interconversion barriers were found to be lower (11.4 and 11.1_5 kcal mol^{-1}, respectively) than those of the trisubstituted derivative **1**.

Stereomutations in aromatic derivatives substituted by two aryl groups have been increasingly investigated in recent times by NMR spectroscopy.[2,3] The interest for this type of compounds is due to their possible use in the field of molecular recognition.[4] A benzene ring, symmetrically substituted by three aromatic groups, should also undergo stereomutation processes detectable by NMR spectroscopy and be amenable to a quantitative investigation. Symmetrically substituted triarylmesitylenes could be separated as pairs of stable isomers, since the corresponding free energy of activation for their interconversion is about 30 kcal mol^{-1}.[5] On the other hand, a triarylbenzene having three appropriate substituents in a reciprocal *meta* relationship is expected to give rise to stereolabile isomers (rotational conformers) as a result of the lower interconversion barrier, since the methyl groups of the mesitylene moiety are absent.

One such compound is 1,3,5-tris(4-methylnaphth-1-yl)-benzene, **1**, which should display two possible rotational conformers (rotamers): one having the three naphthyl moieties in a *syn* relationship and the other having one of the three naphthyl groups in an *anti* relationship. Molecular mechanics computations indicate that in the isolated molecule the naphthyl substituents are orthogonal to the benzene ring, producing C_s symmetry for the *anti* conformer and C_{3v} symmetry for the *syn* conformer (Chart 1). Calculations also predict that these rotamers have essentially the same energy,[6] suggesting that their relative proportions should mainly depend on statistical considerations. Since each of the three naphthyl substituents can alternatively adopt an antiparallel relationship with respect to the other two, the *anti* conformer is 3-fold degenerate, so that the corresponding ratio is consequently expected to be 3:1.

However, single crystal X-ray diffraction (Chart 1) shows that only the *anti* rotamer is populated in the solid

(1) For Part 89, see: Gasparrini, F.; Grilli, S.; Leardini, R.; Lunazzi, L.; Mazzanti, A.; Nanni, D.; Pierini, M.; Pinamonti, M. *J. Org. Chem*. **2002**, *67*, 3089.

(2) Clough, R. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1976**, *98*, 1018. Mitchell, R. H.; Yan, J. S. H. *Can. J. Chem*. **1980**, *58*, 2584. Lai, Y.-H. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1667. Cosmo, R.; Sternhell, S. *Aust. J. Chem*. **1987**, *40*, 35. Cosmo, R.; Sternhell, S. *Aust. J. Chem*. **1987**, *40*, 1107. Lai, Y.-H.; Chen, P. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1665. Nagawa, Y.; Honda, K.; Nakanishi, H. *Magn. Reson. Chem*. **1996**, *34*, 78. Zoltewicz, J. A.; Maier, N. M.; Fabian, W. M. F. *J. Org. Chem*. **1996**, *61*, 7018. Zoltewicz, J. A.; Maier, N. M.; Fabian, W. M. F. *Tetrahedron* **1996**, *52*, 8703. Zoltewicz, J. A.; Maier, N. M.; Fabian, W. M. F. *J. Org. Chem*. **1997**, *62*, 3215. Zoltewicz, J. A.; Maier, N. M.; Fabian, W. M. F. *J. Org. Chem*. **1997**, *62*, 2763. Zoltewicz, J. A.; Maier, N. M.; Fabian, W. M. F. *J. Org. Chem*. **1998**, *63*, 4985. Cross, W.; Hawkes, G. E.; Kroemer, R. T.; Liedl, K. R.; Loerting, T.; Nasser, R.; Pritchard, R. G.; Steele, M.; Watkinson, M.; Whiting, A. *J. Chem. Soc., Perkin Trans. 2* **2001**, 459.

(3) Dell'Erba, C.; Gasparrini, F.; Grilli, S.; Lunazzi, L.; Mazzanti, A.; Novi, M.; Pierini, M.; Tavani, C.; Villani, C. *J. Org. Chem*. **2002**, *67*, 1663.

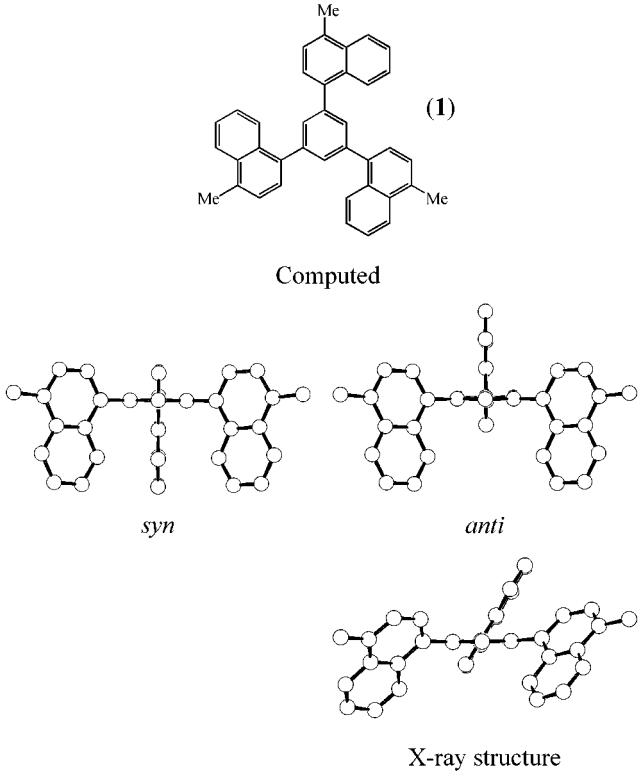
(4) Cozzi, F.; Cinquini, M.; Annunziata, R.; Dwyer, T.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 5729. Cozzi, F.; Cinquini, M.; Annunziata, R.; Siegel, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 5330. Cozzi, F.; Ponzini, F.; Annunziata, R.; Cinquini, M.; Siegel, J. S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1019. Chen, C.-T.; Chadha, R.; Siegel, J. S.; Hardcastle, K. *Tetrahedron Lett*. **1995**, *36*, 8403.

(5) Katz, H. E. *J. Org. Chem*. **1987**, *52*, 3932.

(6) The MMFF 94 force field, as implemented in the computer package PC-Model 7.5 (Serena Software, Bloomington, IN), indicates the *anti* conformer to be slightly more stable than the *syn* conformer ($\Delta E = -0.025$ kcal mol^{-1}). The same force field, as implemented in the program Titan (Wavefunction Inc., Irvine, CA), predicts the *syn* to be slightly more stable than the *anti* ($\Delta E = +0.046$ kcal mol^{-1}). The difference between these values is so small as to lie, in practice, within the approximations involved in the computer treatments of the MM parameters.

10.1021/jo0258195 CCC: $22.00
Published on Web 07/03/2002

CHART 1. Computed Structures for the Syn and Anti Rotational Conformers (top) and Experimental Observed Structure (bottom) of 1



state and that the crystal lattice makes the naphthyl groups deviate from orthogonality and adopt three different dihedral angles with respect to the benzene ring. The angle for the antiparallel naphthalene becomes −58.8°, and those for the two parallel naphthalene substituents become +55.3° and +45.3°, respectively. Derivative **1**, therefore, is a chiral object in the crystalline state (C_1, symmetry), and the four molecules contained in the centrosymmetric unit cell (see Experimental Section) correspond to two molecular pairs of opposite chirality (the dihedral angles for the enantiomeric form are +58.8°, −55.3°, and −45.3°, respectively).

However, the existence of two rotamers (in a 77:23 ratio) was detected by ^{1}H NMR spectroscopy in a CD_2Cl_2 solution at −70 °C; in Figure 1, the spectral region for the hydrogens of the phenyl ring is reported. The *syn* structure could be unambiguously assigned to the less abundant (23%) rotamer, since its spectrum displays a single line corresponding to the three homotopic hydrogens of the rotamer with C_{3v} symmetry. The spectrum with a 77% intensity corresponds to the *anti* rotamer, since two groups of signals, with the expected 2:1 relative intensity ratio, are observed. The major signal is a doublet due to the pair of equivalent (enantiotopic) hydrogens coupled with the third hydrogen (J_{meta} = 1.5 Hz). The minor signal is a triplet due to the single hydrogen having the same J_{meta} coupling with the other two. The observed proportion slightly exceeds the exact 3:1 statistical distribution, indicating that in these conditions the *anti* is thermodynamically more stable than the *syn* rotamer, albeit by a very small amount ($\Delta G°$ is −0.04 kcal mol^{-1} at −70 °C). The same relative proportions[7] were observed when a solvent with a lower dielectric

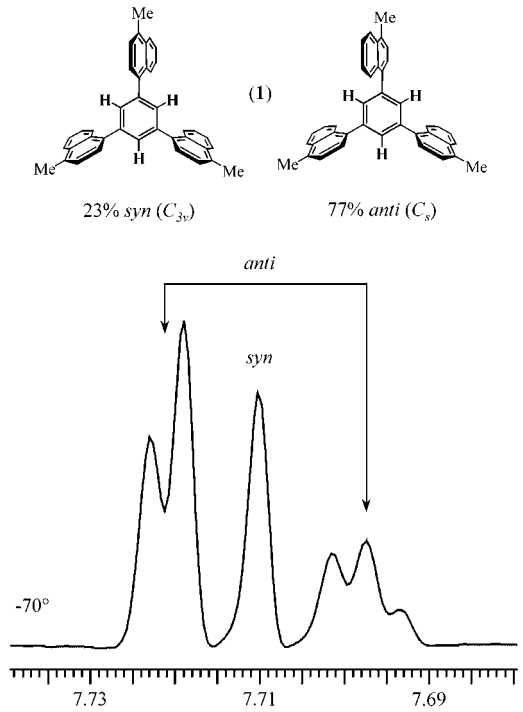


FIGURE 1. ^{1}H NMR (400 MHz) signals of the three phenyl hydrogens (as indicated in the formulas) of derivative **1** obtained in a CD_2Cl_2 solution at −70 °C.

TABLE 1. Dynamic NMR Parameters for Compounds 1−3

compd	$\Delta G^{\ddagger a}$	solvent	$\delta(anti)^b$	$\delta(syn)^b$	*anti*/*syn* ratio
1	12.2	CD_2Cl_2	8.113 and 8.203	8.279	3.35
1	12.0_5	toluene-d_8	8.603 and 8.696	8.796	3.35
2	11.4	toluene-d_8	8.506	8.563	1.22
3	11.1_5	toluene-d_8	8.475	8.617	1.13

[a] Free energy of activation (in kcal mol^{-1}) for exchanging the *anti* into the *syn* rotamer. [b] ^{1}H shifts (in ppm) of the doublet signals of the hydrogen in a *peri* relationship to the benzene ring at −70 °C.

constant (toluene-d_8) was used, indicating that the conformer ratio of this hydrocarbon is essentially independent of the solvent employed (Table 1).

At higher temperatures, these signals broaden and coalesce, eventually yielding a single sharp line for the three phenyl hydrogens of **1**, owing to the rapid rotation of the naphthyl substituents. Such a dynamic process was more conveniently investigated by monitoring the signals of the naphthyl hydrogens in the *peri* position to the benzene ring.

At ambient temperature, these hydrogens display a doublet signal due to the coupling (J = 8.4 Hz) with the naphthyl hydrogen in the *ortho*-like relationship.[8] As shown in Figure 2, such a doublet broadens on cooling and eventually splits into three distinct doublets at −70

(7) The nearly statistical distribution observed here is at variance with the observations reported for a number of 1,3,5-trineopentylbenzene derivatives, bearing however additional substituents in the 2,4,6-positions, where the conformers *syn* appear to be more stable than the *anti*. See: Nilsson, B.; Martinson, K.; Olsson, K.; Carter, R. E. *J. Am. Chem. Soc.* **1973**, *95*, 5615. Carter, R. E.; Nilsson, B.; Olsson, K. *J. Am. Chem. Soc.* **1975**, *97*, 6155. Carter, R. E.; Stilbs, P. *J. Am. Chem. Soc.* **1976**, *98*, 7515.

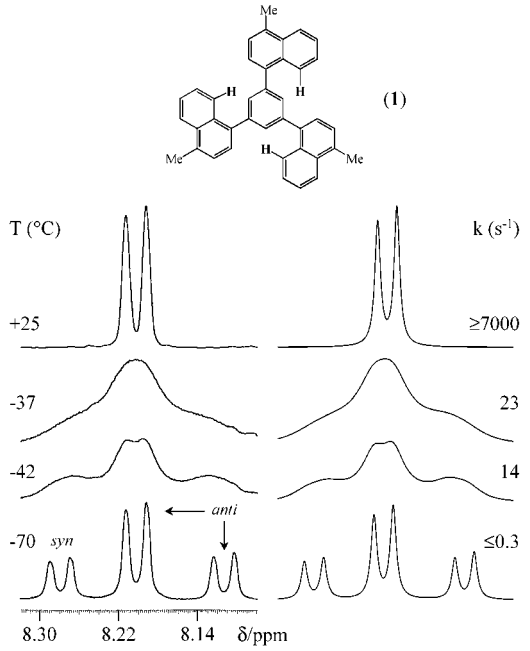
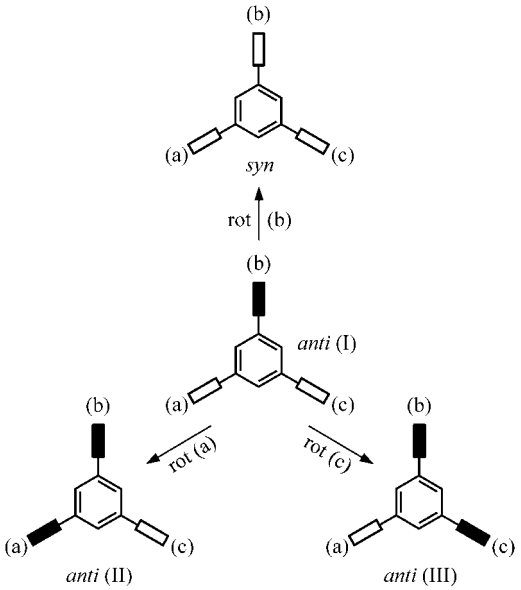


FIGURE 2. Selected examples of the temperature-dependent NMR signals (400 MHz in CD_2Cl_2) of the naphthyl hydrogens in the *peri* position to the benzene ring (as indicated in the formula) of derivative **1**. On the right are displayed the computer simulations obtained with the rate constants reported.

°C. The one at lower field (having a 23% proportion) is due to the three equivalent (homotopic) *peri* hydrogens of the conformer *syn*, and the other two doublets (that display a relative 2:1 intensity ratio and, as a whole, correspond to a 77% proportion) are due to the *anti* conformer, where two equivalent (enantiotopic) *peri* hydrogens are distinct from the third one (diastereotopic).

Line shape simulations performed at various temperatures yield a set of rate constants[9] for the exchange process: a few selected examples are reported in Figure 2. As shown in Scheme 1, the π rotation of the parallel naphthalene ring labeled a transforms the *anti* I into the degenerate *anti* II conformer and, at the same time, exchanges the shifts of the ring b with those of c. Likewise, rotation of the parallel ring c transforms the *anti* I into the other degenerate *anti* III conformer and exchanges the shifts of b with those of a. Only the rotation of ring b is effective in transforming the *anti* into the *syn* conformer; for this reason, a unitary transmission coefficient[10] was used in the Eyring equation to obtain

SCHEME 1. Top View of the Possible Conformations of 1 with the Connections Resulting from Rotations about the Naphthyl−Benzene Bonds[a]



[a] The full boxes represent the naphthyl rings lying above (and the empty boxes the rings lying below) the benzene plane. In this representation, an interchange of all the full with all the empty boxes, and *vice versa*, reproduces exactly the same conformer because this corresponds to a π rotation of the whole molecule about the appropriate axis on the benzene plane. Thus, *anti* I is identical to *anti* II and to *anti* III.

the free energy of activation required to achieve the *anti* to *syn* interconversion ($\Delta G^{\ddagger} = 12.2 \pm 0.1$ kcal mol^{-1}, as in Table 1). As often reported in the case of conformational processes, the corresponding $\Delta S^{\ddagger}$ value was found to be negligible (-2 ± 3 cal mol^{-1} T^{-1}) within the errors.[11] The same spectral features were also observed in toluene-d_8, where an essentially equal $\Delta G^{\ddagger}$ value ($12.0_5 \pm 0.1$ kcal mol^{-1}, as in Table 1) was obtained, indicating that the interconversion barrier, like the conformer ratio, is not appreciably affected by a change of the solvent.

Case **1** is a prototypical example where one can show that the conformer ratio corresponds to a nearly statistical distribution and where it can be established which conformer exceeds the exact statistic expectation based on symmetry arguments. This finding is thus helpful for performing assignments in the case of analogous molecules where the difference in the symmetry of conformers is not detectable by NMR spectroscopy as, for instance, in the case of the corresponding disubstituted derivatives. When the two naphthyl substituents are in an *ortho* relationship, as in 1,2-bis(4-methylnaphth-1-yl)-benzene, the *anti* to *syn* interconversion barrier was found[3] to be high enough (19.5 kcal mol^{-1}) as to allow

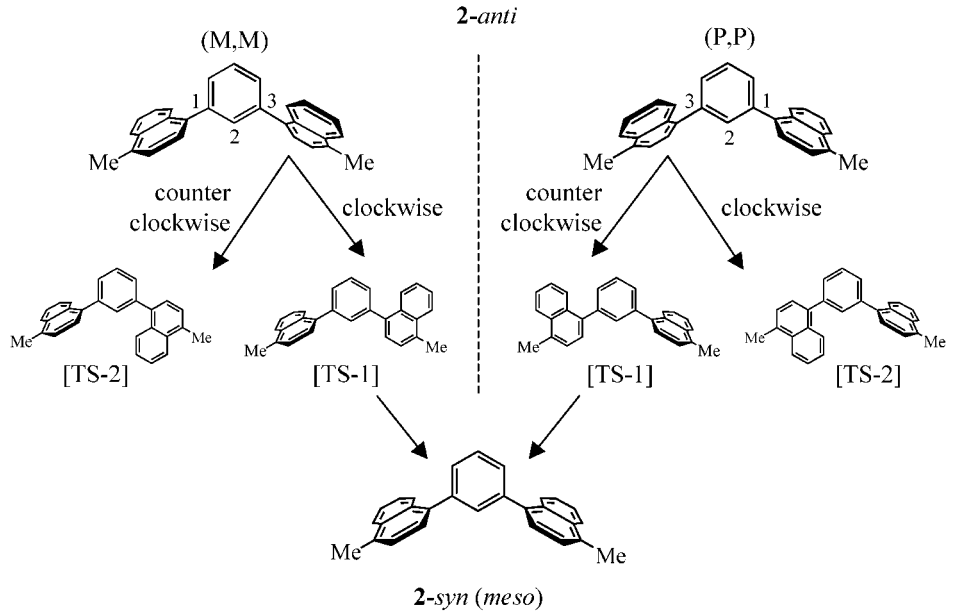
(8) The shift of the hydrogen *peri* to the phenyl ring was unambiguously assigned as follows. At higher resolution, the corresponding doublet signal (8.21 ppm) displays a further doublet splitting due to a *meta* coupling ($J = 1.6$ Hz), indicating that it belongs to either of the two α-hydrogens of the naphthyl ring. Irradiation of the Me line shows that the 8.21 ppm signal does not experience a NOE effect which, on the contrary, was detected for the signal (8.07 ppm) of the α-hydrogen *peri* to the methyl group.

(9) In principle, two different rates might be considered for the *anti* to *syn* and for the *anti* to *anti* interconversions (see Scheme 1). In practice, however, the spectra of Figure 2 could be perfectly simulated using the same rate constant for both processes. This means that the difference between these two rates is much too small to be detected, a result which is not unexpected, since the corresponding transition states are, predictably, extremely similar.

(10) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982; p 94.

(11) Hoogosian, S.; Bushweller, C. H.; Anderson, W. G.; Kigsley, G. *J. Phys. Chem.* **1976**, *80*, 643. Lunazzi, L.; Cerioni, G.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7484. Bernardi, F.; Lunazzi, L.; Zanirato, P.; Cerioni, G. *Tetrahedron* **1977**, *33*, 1337. Lunazzi, L.; Magagnoli, C.; Guerra, M.; Macciantelli, D. *Tetrahedron Lett.* **1979**, 3031. Anderson, J. E.; Tocher, D. A.; Casarini, D.; Lunazzi, L. *J. Org. Chem.* **1991**, *56*, 1731. Cremonini, M. A.; Lunazzi, L.; Placucci, G.; Okazaki, R.; Yamamoto, G. *J. Am. Chem. Soc.* **1992**, *114*, 6521. Borghi, R.; Lunazzi, L.; Placucci, G.; Cerioni, G.; Foresti, E.; Plumitallo, A. *J. Org. Chem.* **1997**, *62*, 4923.

SCHEME 2. Representation of the *anti* to *syn* Interconversion Pathway for the Rotamers of 2[a]



[a] In the M,M enantiomer, the rotating naphthalene ring in position 3 either moves toward H-2, reaching TS-2 by a counterclockwise pathway, or moves away from H-2, reaching TS-1 by a clockwise pathway. The reverse occurs in the P,P enantiomer.

the physical separation of the conformers on an enantioselective HPLC column cooled at −20 °C and the consequent unambiguous identification of the minor (38%) *syn* conformer (*meso*), due to its insensitivity to CD detection (the major, *anti* conformer, on the other hand, displayed the pair of CD peaks due to the separation of the two enantiomers[3]).

Also, the corresponding *meta* derivative, that is, 1,3-bis(4-methylnaphth-1-yl)benzene, **2**, should adopt an *anti* (racemic) and a *syn* (*meso*) conformation, as in Scheme 2; in this case, however, a physical separation was impossible because of the exceedingly fast interconversion rate. The symmetry groups of the *syn* and *anti* rotamers of **2** (C_s and C_2, respectively) imply the same line multiplicity, and having both the same 2-fold degeneracy,[12] they should display a 1:1 intensity ratio on a purely statistic ground. The NMR spectrum of **2** in toluene-d_8[13] shows, however, that one rotamer is present in a slight excess. In fact, the doublet signal of the naphthalene hydrogen in the *peri* position to the benzene ring splits, at −70 °C, into two doublets with a 55:45 intensity ratio.[14]

Since we had previously shown that the *anti* conformer is more stable than the *syn* conformer in derivative **1**, it seems reasonable to assign the *anti* structure also to the more abundant conformer of **2**. Furthermore, in the case of **1**, the signals of the hydrogen *peri* to the phenyl group were found at higher field in the *anti* with respect to the *syn* conformer, in both CD_2Cl_2 and toluene-d_8 solutions (Table 1). Likewise, the major doublet signal for the same hydrogen appears in **2** at higher field than the minor one. This independent criterion agrees in considering the *anti* as the more abundant conformer of **2**.[15] The line shape simulation of the mentioned signals of **2** yields an *anti* to *syn* interconversion barrier ($\Delta G^{\ddagger}$) of 11.4 ± 0.1 kcal mol^{-1}, as in Table 1; in this case, a transmission coefficient of $^1/_2$ had to be employed in the Eyring equation to account for the fact that rotation of either of the antiparallel naphthyl rings allows the interconversion from the *anti* to the *syn* rotamer.[16]

The barrier of **2** is lower than that of **1** in the same solvent (Table 1) by an amount which definitely exceeds the experimental errors. Such a difference can be rationalized by considering that the clockwise rotation of either of the two naphthyl rings in the M,M enantiomer leads to a transition state (TS-1 of Scheme 2) with a lower energy than that for the transition state (TS-2) encountered in a counterclockwise rotation, owing to the lesser steric interactions between the two naphthyl substituents. The same holds for a counterclockwise rotation of the enantiomer P,P (leading to an antipode of TS-1), with respect to a clockwise rotation (leading to an antipode of TS-2).

Contrary to the case of **1**, the naphthyl rings of **2** have pathways available (*via* TS-1) where the interactions

(12) Actually, only in the case of the *syn* (meso) conformer do we deal with a proper degeneration, since the degeneration of the *anti* (racemic) conformer is due to a pair of enantiomers (see Scheme 2).

(13) In the case of **2**, a CD_2Cl_2 solution could not be used because the signal of interest overlapped with that of another naphthalene hydrogen, thus preventing an accurate simulation of the corresponding line shape as a function of temperature.

(14) The same ratio was also observed for the methyl signals, as well as for the signals of the phenyl hydrogen in an *ortho* relationship to both the naphthyl groups.

(15) The MMFF 94 force field, as implemented in the computer package PC-Model 7.5 (Serena Software, Bloomington, IN), indicates the *syn* conformer to be slightly more stable than the *anti* conformer (ΔE = +0.038 kcal mol^{-1}). The same force field, as implemented in the program Titan (Wavefunction Inc., Irvine, CA), predicts the *anti* to be slightly more stable than the *syn* (ΔE = −0.133 kcal mol^{-1}). Again, the small differences are likely to be a consequence of the approximations involved in the computer treatments of the MM parameters.

(16) Casarini, D.; Lunazzi, L.; Foresti, E.; Macciantelli, D. *J. Org. Chem.* **1994**, *59*, 4637. Casarini, D.; Lunazzi, L. *J. Org. Chem.* **1996**, *61*, 6240. Casarini, D.; Lunazzi, L.; Mazzanti, A. *J. Org. Chem.* **1997**, *62*, 7592. Bonini, B. F.; Fochi, M.; Lunazzi, L.; Mazzanti, A. *J. Org. Chem.* **2000**, 65, 2596.

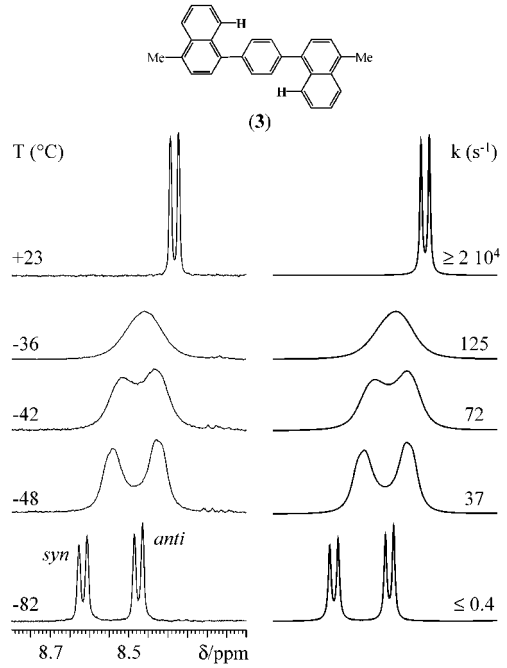


FIGURE 3. Selected examples of the temperature-dependent NMR signals (400 MHz in toluene-d_8) of the naphthyl hydrogens in the *peri* position to the benzene ring (as indicated in the formula) of **3**. On the right are displayed the computer simulations obtained with the rate constants reported.

with the second naphthyl substituent are smaller than those in the pathway (*via* a TS-2 type) followed by **1**, thus making the barrier of **2** lower than that of **1**.

Support to this interpretation is offered by the corresponding *para* derivative, that is, 1,4-bis(4-methylnaphth-1-yl)benzene, **3**.

The corresponding ^{1}H NMR spectrum in toluene-d_8 at −70 °C (Figure 3) shows that the upfield signal of the naphthalene hydrogen *peri* to the benzene ring is more intense (53%) than its downfield companion (47%), indicating that the degeneracy is lifted in favor of the *anti* conformer (Table 1).

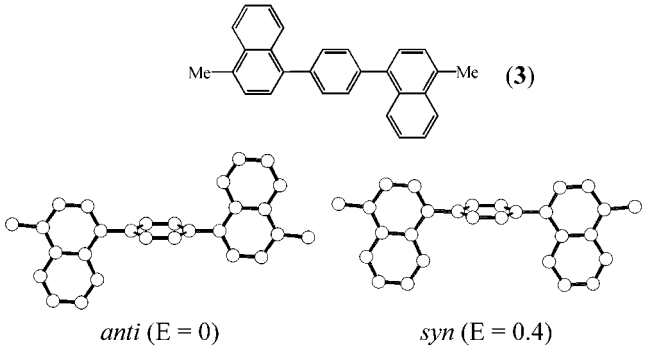
Molecular mechanics calculations indicate that the *anti* is slightly more stable than the *syn* conformer, the theoretical energy difference being −0.4 kcal mol^{-1} (Chart 2).

The rate constants, derived by line shape simulations, yield an interconversion barrier ($\Delta G^{\ddagger} = 11.1_5 \pm 0.1$ kcal mol^{-1}, when the $^1/_2$ transmission coefficient[16] is employed) which is essentially equal, within the experimental uncertainty, to that measured for **2**. The reason is that in derivative **3** both a clockwise rotation and a counterclockwise rotation lead to a transition state where there is little interaction with the second naphthyl ring; the transition state is, in fact, of the same type as that (TS-1 of Scheme 3) available to **2**.

Experimental Section

Materials. (A) 1,3,5-Tris(4-methylnaphth-1-yl)benzene (**1**) was prepared according to the procedure of Suzuki.[17] To a solution of 1,3,5-tribromobenzene (1 mmol in 5 mL of benzene)

CHART 2. MM Computed Structures for the *anti* (left) and *syn* (right) Rotamers of 3[a]



[a] Relative energies (E) in kcal mol^{-1} according to the MMFF 94 force field (as implemented in the computer package PC-Model 7.5, Serena Software, Bloomington, IN).

were added K_2CO_3 (1 M solution, 3 mL), 4-methyl-1-naphthylboronic acid[18] (5 mmol, suspension in 7 mL of ethanol), and $Pd(PPh_3)_4$ (0.2 mmol) at room temperature. The stirred solution was refluxed for 4 h, the reaction being monitored by TLC (eluent petroleum ether/Et_2O 200:1). To the cooled solution was added a second amount of 4-methyl-1-naphthylboronic acid (5 mmol in 7 mL of ethanol), K_2CO_3 (1 M solution, 3 mL), and $Pd(PPh_3)_4$ (0.4 mmol). After refluxing for 4 h, $CHCl_3$ and H_2O were added and the extracted organic layer was dried (Na_2SO_4) and evaporated. The crude was purified by chromatography on silica gel (eluent petroleum ether/Et_2O 200:1) to yield 0.65 mmol (65%). Crystals suitable for X-ray diffraction were obtained by slow evaporation from absolute ethanol. Mp 194−195 °C; ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 2.74 (s, 9H, Me), 7.38−7.42 (m, 3H), 7.46−7.58 (m, 9H), 7.67 (s, 3H), 8.05−8.10 (m, 3H), 8.18−8.24 (m, 3H). Anal. Calcd for $C_{39}H_{30}$: C, 93.94; H, 6.06. Found: C, 93.89; H, 6.03.

(B) 1,3-Bis(4-methyl-1-naphthyl)benzene (**2**) was prepared starting from 1,3-dibromobenzene using the same procedure described above. Waxy solid; ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 2.73 (s, 6H, Me), 7.35−7.64 (m, 12H), 8.02−8.10 (m, 4H). Anal. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 93.78; H, 6.23.

(C) 1,4-Bis(4-methyl-1-naphthyl)benzene (3) was prepared from 1,3-dibromobenzene using the same procedure described above. Mp 213−215 °C (decomp); ^{1}H NMR (toluene-d_8, 400 MHz) δ 2.57 (s, 6H, Me), 7.23 (d, 2H, J = 7.2 Hz), 7.31−7.32 (m, 6H), 7.56 (s, 4H), 7.94 (d, 2H, J = 8.2 Hz), 8.18−8.23 (d, 2H, J = 8.1 Hz). Anal. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 93.84; H, 6.15.

X-ray Diffraction. Crystal Data of 1,3,5-Tris(4-methylnaphth-1-yl)benzene (1): $C_{39}H_{30}$ (498.63); monoclinic; space group $P2(1)_c$; Z = 4, a = 18.9269(33) Å, b = 8.4832(14) Å, c = 16.7259(28) Å, β = 97.366(10) Å, V = 2663.4(8) Å^3, D_c = 1.244 g cm^{-3}, $F(000)$ = 1056, μ_{Mo} = 0.070 mm^{-1}, T = 293 K; crystal size 0.3 × 0.3 × 0.05 mm. Data were collected using a graphite monochromated Mo Kα X-radiation (λ = 0.710 73 Å) in the range 1.08° < θ < 24.99°. Of 19 516 reflections collected, 4681 were found to be independent (R_{int} = 0.0924), 2330 of which were considered as observed [$I > 2\sigma(I)$], and used in the refinement of 356 parameters, leading to a final R_1 of 0.0643 and a R_{all} of 0.1438. The structure was solved by direct methods and refined by full-matrix least squares on F^2, using SHELXTL 5.1 program packages. In refinements, weights were used according to the scheme $w = [\sigma^2(F_o^2) + (0.0965P)^2 + 0.0000P]^{-1}$ where $P = (F_o^2) + 2F_c^2/3$. The hydrogen atoms were located by geometrical calculations and refined using a "riding" method. wR_2 was equal to 0.1735. The

(17) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513.

(18) Prepared according to: Thompson, W. J.; Gaudino, J. *J. Org. Chem.* **1984**, *49*, 5237.

goodness of fit parameters *S* was 0.912. The largest difference between peak and hole ranged from 0.21 to −0.21 e Å^{-3}. Crystallographic data (excluding structure factors and including selected torsion angles) have been deposited with the Cambridge Crystallographic Data Center, CCDC number 186 660.

NMR Measurements. Line shape simulations were obtained by means of a PC version of the DNMR6 computer program.[19] The probe temperatures were accurately calibrated by substituting the samples with a Ni/Cu thermocouple before acquiring the spectra. We also verified that, within ±0.1 kcal mol^{-1}, the same $\Delta G^{\ddagger}$ values were obtained when making use of two spectrometers (operating either at 300 or at 400 MHz) having probes with different calibration curves.

(19) QCPE program no. 633, Indiana University, Bloomington, IN.

Acknowledgment. One of the authors (M.P.) thanks CINMPIS for a fellowship, and a research fund for young researchers (University of Bologna) is also acknowledged (by S.G.). L.L. and A.M. received financial support from MURST, Rome (national project "Stereoselection in Organic Synthesis") and from the University of Bologna (Funds for selected research topics 2001−2002).

JO0258195