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Unprecedented Detection of Enantiomerization π-Barriers Due to Restricted Aryl Torsion: Case of 1,8-Di-arylbiphenylenes

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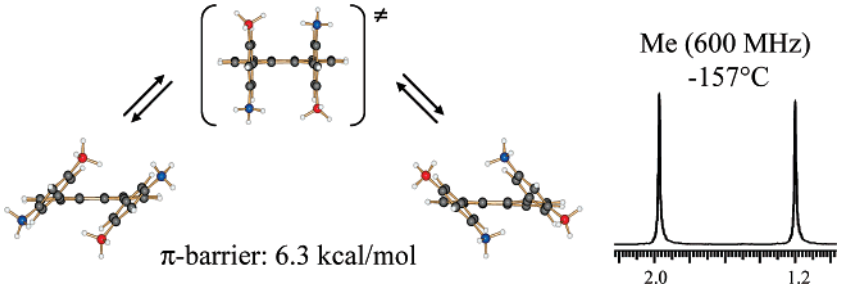

Dynamic NMR spectroscopy allowed, for the first time, the determination of the π-barriers responsible for the enantiomerization processes in derivatives bearing two aryl substituents bonded to a planar framework: this could be achieved in the case of 1,8-di-*m*-tolylbiphenylene (**1**) and 1,8-di-*m*-xylylbiphenylene (**2**). In derivative **1**, the three possible conformers predicted by DFT computations (anti-in, syn, and anti-out) were detected, and in addition, the steric barrier responsible for their interconversion could be measured. The barriers predicted by DFT calculations were found in satisfactory agreement with experimental data.

Introduction

When equal aryl substituents, lacking a local C_2 symmetry axis, are bonded in appropriate positions of planar frameworks (such as benzene,[2] naphthalene,[3] phenanthrene,[4] anthracene,[5] acenaphthene,[6] and acenaphthylene[7]), configurationally stable cis−trans isomers, or stereolabile syn−anti conformers, originate, depending on the extent of the steric hindrance. As pointed out by Clough and Roberts[3a] in the case of 1,8-di-*o*-tolylnaphthalene, the existence of cis and trans isomers is the consequence of the planes of the two tolyl substituents being twisted with respect to the plane of naphthalene, so that one methyl can stay either on the same or on the opposite side of the other methyl group. The trans to cis interconversion requires the passage through a transition state where one tolyl is coplanar with the naphthalene ring (steric barrier[8]), corresponding to a 180° rotation.[3a] It was also pointed out[3a] that the twisted disposition of the two tolyl substituents would make the cis form originate a pair of enantiomers that interconvert through a transition state where the tolyl groups are nearly orthogonal to the naphthalene ring (π-barrier[8]): this process corresponds to a torsion (also

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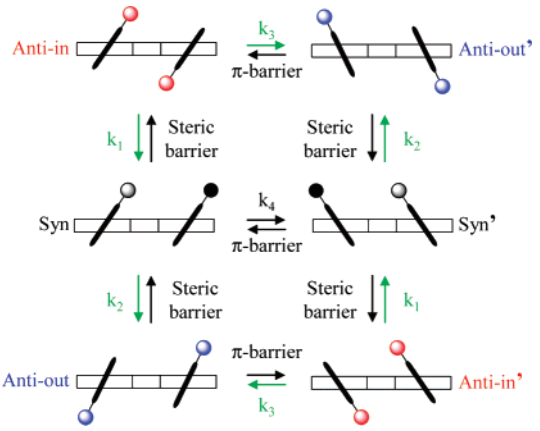
SCHEME 1. Representation of Conformers, Enantiomers, and Equilibrium Processes for 1[a]



[a] Circles represent the methyl: within each form, they have the same colors when enantiotopic (conformers anti) and different colors when diastereotopic (conformers syn). The primes indicate enantiomeric structures.

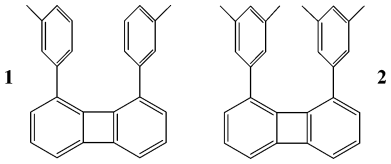
called flipping process[3a]) of approximately 90° (see Scheme 1, where an analogous case is described). In the case of the trans form, on the other hand, this nearly 90° torsion would create two conformers of different stabilities, identified as trans-in and trans-out.[9] Each of these conformers exists as a pair of enantiomers, but their enantiomerization requires passage through the cis isomer (i.e., the 180° rotation involving the steric barrier see also Scheme 1).

Whereas there are many reports[2−7] concerning the determination of cis−trans (or syn−anti) interconversion involving the steric barrier, never was the so-called π-barrier detected in this type of compound. This is due to the fact that such an enantiomerization barrier is expected to be very low,[2b,3a] thus usually not amenable to NMR observation. Here, we present two cases where, for the first time, such enantiomerization processes were observed and the corresponding π-barriers measured.

Results and Discussion

DFT computations[10] (at the B3LYP/6-31G(d) level) of 1,8-di-*m*-tolylbiphenylene (compound **1** in Chart 1) show, as anticipated, that there are three energy minima[11] corresponding to the mentioned anti-in, syn, and anti-out conformations. The

CHART 1



computed ground state energy for the anti-in conformation is 0.4 kcal mol^{-1} lower than that of the syn conformation and 0.7_5 kcal mol^{-1} lower than that of the anti-out (Figure 1). According to the DFT energies, the anti-in conformation should be therefore the most stable and the anti-out the least stable conformer,[12] with the syn having an intermediate stability.

As mentioned previously, these conformers interconvert according to the circuit displayed in Scheme 1. Within each of the two anti conformers, the hydrogens and carbons of one tolyl would always display NMR signals coincident (isochronous) with those of the other tolyl group, owing to the C_2 symmetry of these forms. In the syn conformer, on the other hand, these signals will be coincident only if the enantiomerization process (occurring via the 90° torsion involving the π-barrier) is fast. When this process is frozen, the signals of one tolyl group of the syn conformation will be different (anisochronous) with respect to those of the other, due to the C_1 symmetry: at the same time, distinct signals with different intensities should become observable for the anti-in and anti-out conformers (Scheme 1). The steric barrier computed[10] for the anti-in to syn interconversion was 6.3_5 kcal mol^{-1}, and that for the syn to anti-out interconversion was 5.9_5 kcal mol^{-1}, the difference being equal to the computed energy separation between the two corresponding ground states (i.e., 0.4 kcal mol^{-1} as in Figure 1).[13] The computed π-barriers for the exchange between the two enantiomers of the syn conformation, and that for the interconversion of the anti-in into the anti-out conformer, are 3.5 and 4.0 kcal mol^{-1}, respectively[14] (the corresponding

(9) This because the two methyl groups are directed either inward or outward with respect to the naphthalene moiety.[3a]

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(11) In a theoretical paper describing compounds analogous to **1**, only one of the two possible anti conformers was, inexplicably, considered (see: Bigdeli, M. A.; Moradi, S.; Nemati, F. *J. Mol. Struct. THEOCHEM* **2007**, *807*, 125−135).

(12) Greater stability of the anti−syn conformer might be due to the so-called CH−π interactions (see: Nishio, M.; Hirota, M; Umezawa, Y. *The CH/π Interaction: Evidence, Nature, and Consequences*; Wiley: New York, 1998.) that are possible in the anti-in but not in the anti-out. Also, the anti-out might be destabilized by the H/H repulsion between the methyl groups and the hydrogen protruding from the biphenylene ring, a situation that does not occur in the anti-in conformer.

(13) In Scheme 2, only one of the two possible transition states for the 180° rotation pathway (steric barrier) was reported (i.e., the one in which the tolyl plane, coplanar with that of biphenylene, places its methyl group opposite to the other tolyl, see TS-1 in Figure S-1 of the Supporting Information). In fact, the pathway for the alternative transition state (having the methyl on the same side of the other tolyl, see TS-1′ in Figure S-1 of the Supporting Information) has a higher energy (7.25 vs 6.35 kcal mol^{-1}) and therefore can be considered as forbidden. In the allowed pathway, only one of the two tolyl rings becomes, alternatively, coplanar with biphenylene, whereas the other remains close to its original position: the rotation processes of the tolyl substituents are thus independent of each other.

(14) Energy of the transition state for the enantiomerization (syn to syn interconversion, i.e., 90° torsion via π-barrier) is not necessarily equal to that for the interconversion of the two anti conformers: two different transition states thus imply two different π-barriers, as predicted by calculations (Table 1, Scheme 2, and Figure S-1). The pathways for the 90° torsion (π-barriers) take place through transition states where both the tolyl rings move away simultaneously from their original positions, reaching dispositions where both are tilted by the same dihedral angle with respect to biphenylene (see: TS-2 and TS-3 of Figure S-1 of the Supporting Information). The corresponding single imaginary normal modes involve the movement of both *m*-tolyl rings; accordingly, the 90° torsion processes should be considered examples of correlated motions. As a further indication, the computations show that situations where only one of the two tolyl groups has moved across to the nearly orthogonal position do not correspond to transition states.

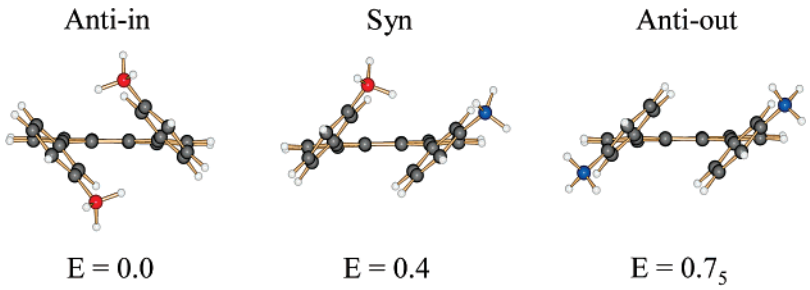
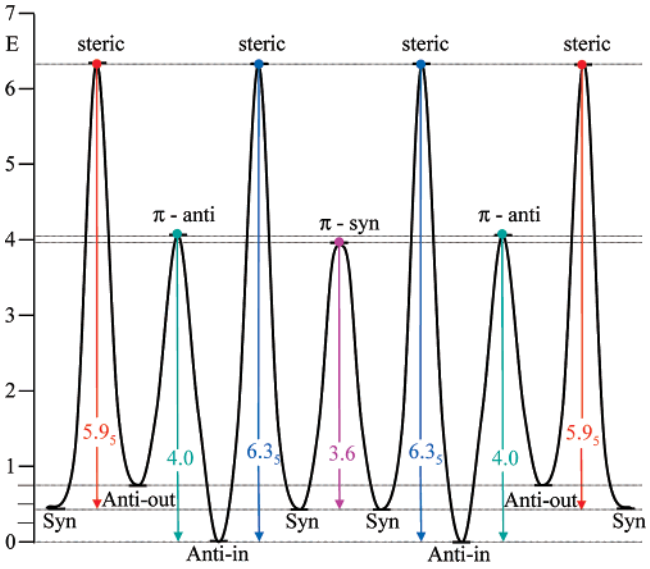


FIGURE 1. DFT computed structures of the three possible conformers of **1**, having dihedral angles of 44° between the planes of toluene and biphenylene (only one of the two enantiomers is displayed for convenience). Relative energies are in kcal mol^{-1}.

SCHEME 2. DFT Computed Energy Profile for Interconversion Pathways Occurring in 1[a]



[a] Energy values are in kcal mol^{-1}.

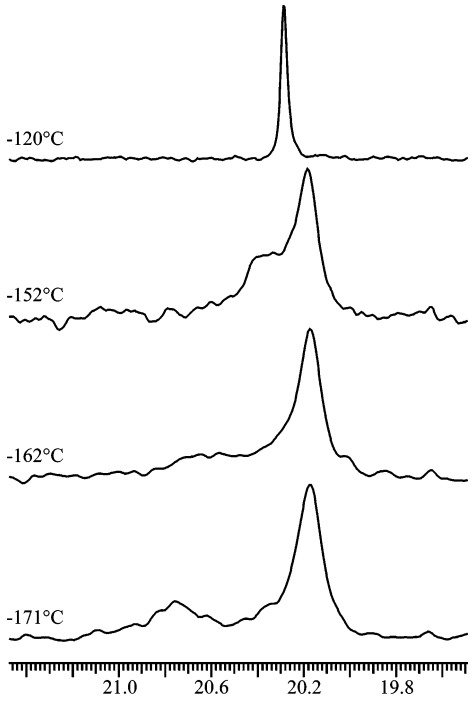


FIGURE 2. Temperature dependence of the methyl carbon signal (150.8 MHz in $CHF_2Cl/CHFCl_2$) of **1**.

computed transition states are shown in Figure S-1 of the Supporting Information). On this basis, one should first observe separate NMR methyl signals at low temperatures for the syn (in rapid exchange between the two enantiomeric forms) and for the anti conformers (in rapid exchange between the anti-in and the anti-out). On further lowering the temperature, one should then identify a pair of signals (with equal intensity) for the syn conformation and single signals (with different intensities) for the anti-in and anti-out conformers (see the pathway displayed in Scheme 2.)

The ^{13}C signal of the quaternary carbon of the four-membered ring, ortho to the tolyl substituent, broadens on cooling and splits, at −162 °C, into two lines, with an intensity ratio of about 35:65 (Figure S-2 of the Supporting Information). The spectral simulation provides a steric barrier of 6.2 ± 0.15 kcal mol^{-1} for the interconversion of the rapidly exchanging anti conformers (major line) into the rapidly exchanging syn enantiomers (minor line). Contrary to the prediction, however, the minor line does not split on further cooling because the difference between the shifts of the two expected diastereotopic carbons of the frozen asymmetric form syn is less than the line width.

This splitting, however, was observed in the case of the methyl carbon spectrum, where the corresponding single line first splits at −152 °C into a pair of partially overlapped signals of unequal intensity, separated by about 30 Hz (Figure 2), the major signal corresponding to the anti conformers and the minor, broader signal to the rapidly exchanging syn enantiomers. The latter signal broadens further on cooling, and at −171 °C splits into a pair of lines, one of which is invisible as it is overlapped by the major signal. This is proven by the fact that the visible downfield minor line is now separated from its major companion by 85 Hz and also by the observation that its relative intensity is approximately reduced by a factor of 2, whereas that of the major signal is correspondingly higher. The relative intensity of the syn conformation, in fact, has diminished (and that of the anti increased) because one of the two lines of the syn conformation is superimposed on that of the anti conformation. This feature thus indicates that, in addition to the steric barrier, also the mentioned π-barrier has been frozen. The spectrum does not display, however, a small line expected for the less stable anti-out conformer, either because of an insufficient signal-to-noise ratio or because this small line is hidden under one of the two observed lines (most likely the minor signal because it has a larger width than the major signal).

Likewise, the ^1H signal of the methyl groups (Figure 3) splits, at −141 °C, into two partially overlapped lines (a feature also observed in Figure 2 and Figure S-2 of the Supporting

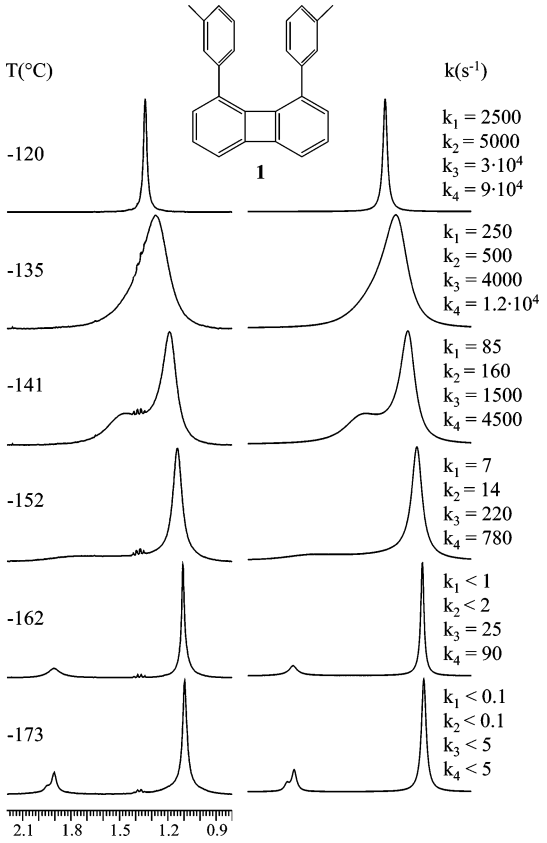


FIGURE 3. Temperature dependence (left) of the ^{1}H methyl signal of **1** (600 MHz in $CHF_2Cl/CHFCl_2$). On the right are shown the spectra simulated with k values employed, where k_1 interconverts the anti-in into the syn, k_2 the syn into the anti-out, k_3 the anti-in into the anti-out, and k_4 the syn into its enantiomeric form.

Information), with an approximate 35:65 ratio. On further cooling to −173 °C, this spectrum also shows that the minor broad signal of the syn conformer is split into a pair of widely separated lines: one (upfield) is again overlapped by the major signal of the anti-in conformer, whereas the other (downfield with respect to the two overlapped lines) is clearly visible. At this temperature, the ^{1}H spectrum exhibits an additional small methyl line (also involved in the exchange process), which is due to the least stable anti-out conformer. The shift of this small line is close to that of the downfield line of the syn because both these methyl groups point outward with respect to the biphenylene ring, thus experiencing similar environments. Indeed, the relative methyl shifts predicted by computations[10] agree with the experimental trend: the anti-in and upfield line of the syn conformation are predicted to be at 1.82 and 1.78 ppm, respectively,[15] and thus are close enough ($\Delta\nu = 0.04$ ppm) to overlap, as observed. The downfield line of the syn conformation and that of the anti-out conformation are predicted to be 2.40 and 2.52 ppm, respectively[15] (i.e., a difference ($\Delta\nu = 0.12$ ppm) compatible with the detection of two separate lines). The relative intensities of the lines in the −173 °C spectrum are about 5:15:(65 + 15), corresponding to a proportion of the three conformers approximately equal to 5:30:65, for the anti-out, syn, and anti-in conformations, respectively. The experimental relative $\Delta G°$ values are 0.51, 0.15, and 0 kcal mol^{-1}, a trend that parallels that of the corresponding DFT computed energies (0.75, 0.4, and 0 kcal mol^{-1}).

TABLE 1. Experimental and Computed Barriers (kcal mol^{-1}) for Interconversion Processes in 1

	steric barrier[a]	π-barriers[b]	
	anti-in to syn	anti-in to anti-out (π-anti)	enantiomerization (π-syn)
experimental	6.4	5.6	5.3
computed	6.3_5	4.0	3.5

[a] See ref 17. [b] See ref 18.

Since this spectrum displays lines for every one of the three species taking part in the exchange process, all the four rate constants (k_1, k_2, k_3, and k_4, as in Scheme 1) involved had to be used[16] for describing the line shape. Two constraints should be, however, taken into account: (i) the rate for the steric process transforming the anti-in into the syn conformation (k_1) must differ from the rate interconverting the syn into anti-out conformation (k_2) by an amount corresponding to the experimental $\Delta G°$ value of the anti-in and syn ground states (i.e., ca. 0.15 kcal mol^{-1} as mentioned previously) and (ii) the rate k_1 must yield a steric barrier equal, within experimental error, to that (6.2 ± 0.15 kcal mol^{-1}) determined from the signals shown in Figure S-2 of the Supporting Information. The rates used for the simulation of Figure 3 reproduce the experimental shape and also fulfill these constraints. The barriers derived from these rates are collected in Table 1, and as anticipated, the π-barriers were found to be lower than the steric barriers.

The interpretation proposed for these experiments implies that in a more symmetric compound, as 1,8-di-*m*-xylyl biphenylene (**2**), the steric barrier will be NMR invisible. In fact, the 180° rotation of one xylyl group (across the transition state where the xylyl groups are alternatively coplanar with the biphenylene ring) will reproduce the same conformer with identical chemical shifts (homomerization).[19] Therefore, if a dynamic process will

(15) Computed[10] shift differences of the methyl groups are quite close to the experimental differences, although their absolute values are consistently downfield by about 0.65 ± 0.1 ppm with respect to the corresponding experimental data. The previous assignment of the anti-in structure of **1** as more stable than the anti-out (based on the 0.75 kcal mol^{-1} lower computed energy, as in Figure 1) is further confirmed by the computed methyl shifts that are predicted to be upfield for anti-in (1.82 ppm) with respect to anti-out (2.52 ppm): such a computed difference (0.70 ppm) agrees with the difference (0.87 ppm) observed in the experimental spectrum, where the most intense signal is likewise upfield with respect to the least intense one (1.08 and 1.95 ppm, respectively, as in the −173 °C trace of Figure 3).

(16) Three rate constants (k_1, k_2, and k_3) are needed for describing the direct interconversion of the three conformers; the fourth (k_4) is needed for describing the direct interconversion of the two enantiomers within the syn conformation (see Scheme 1).

(17) Pathways for the anti-in to syn and for the syn to anti-out steric interconversion share the same transition state (see Scheme 2); thus, the corresponding $\Delta G^‡$ values (derived from the rate constants k_1 and k_2, i.e., 6.4 and 6.2 kcal mol^{-1}, respectively) differ solely by the $\Delta G°$ value between the ground states of anti-in and syn (experimental value 0.15 kcal mol^{-1}). Thus, in practice, there is only one steric barrier, corresponding to the higher of these two $\Delta G^‡$ values, i.e., 6.4 ± 0.15 kcal mol^{-1}, as in Table 1.

(18) Experimental $\Delta G^‡$ values of 5.6 and 5.3 kcal mol^{-1} (corresponding to π-anti and π-syn barriers of Table 1) derive from the two values of rate constants (k_3 and k_4) that have at least a 3:1 ratio (Figure 3). If equal values are assumed for these rates, a proper simulation could not be achieved. Since these rate constants are obtained from spectra taken at the very same temperature, their differences are certainly meaningful. Consequently, the small difference between the corresponding $\Delta G^‡$ values is also meaningful because they are not affected by the uncertainty on the temperature (errors due solely to the simulation are less than 0.1 kcal mol^{-1}, see: Bonini, B. F.; Grossi, L.; Lunazzi, L. *J. Org. Chem.* **1986**, *51*, 517−522). Of course, when comparing $\Delta G^‡$ values obtained from spectra taken at different temperatures, experimental errors of about ±0.15 kcal mol^{-1} should be taken into account.

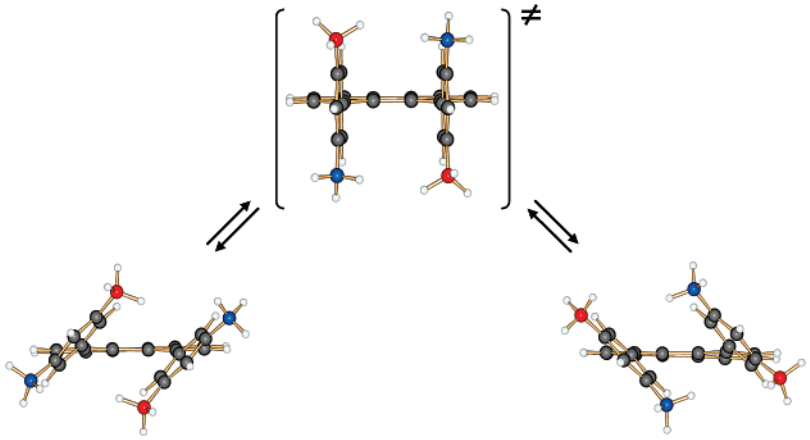


FIGURE 4. DFT computed structures (bottom) of the conformational enantiomers of **2** (having dihedral angles of 43° between the planes of xylene and biphenylene). They exchange their inner and outer methyl groups passing across the orthogonal transition state (top), having a computed relative energy of 4.6 kcal mol^{-1}, via a ∼90° torsion (π-barrier).

TABLE 2. Experimental and Computed Barriers (kcal mol^{-1}) for Interconversion Processes in 2

	steric barrier	π-barrier
experimental	not measurable[a]	6.3
computed	7.1	4.6

[a] NMR invisible owing to molecular symmetry (see text).

nonetheless be observed, one is led inexorably to assign it to the enantiomerization process involving the ∼90° torsion, via the π-barrier, as shown in Figure 4.

The steric barrier for the 180° rotation process of **2** can be only obtained, as mentioned, by means of theoretical methods (the DFT computed value is 7.1 kcal mol^{-1}, as in Table 2): these calculations also predict a π-barrier (4.6 kcal mol^{-1}, as in Table 2) that is at least 0.6 kcal mol^{-1} higher than the corresponding π-barriers computed for **1** (Table 1). This is due to the fact that in the computed transition state for the enantiomerization of **2** (Figure 4), the two xylyl rings are both exactly orthogonal to the biphenylene plane, whereas this is not the case for the tolyl groups in **1** (see Figure S-1 of the Supporting Information). The perfect orthogonality of the two xylyl rings eliminates any contribution of conjugation with biphenylene, as compared to the case of **1**, thus enhancing the energy of the transition state, hence the corresponding barrier. Since the π-barriers measured in **1** are 5.3−5.6 kcal mol^{-1} (Table 1), the corresponding barrier in **2** (which is computed to be 0.6 kcal mol^{-1} higher) is expected to become about 6 kcal mol^{-1}. Such a value is well within the range accessible to dynamic NMR experiments, particularly because computations[10] predict a shift separation for the ^{1}H lines of the methyl groups as large as 0.77 ppm. The calculations also indicate that the upfield line will correspond to that of the methyls in the inner position: in this situation, in fact, these groups can experience a shielding effect due to the aromatic ring currents.[20]

Actually, the ^{1}H methyl signal of **2** broadens on lowering the temperature and eventually decoalesces into a pair of equally

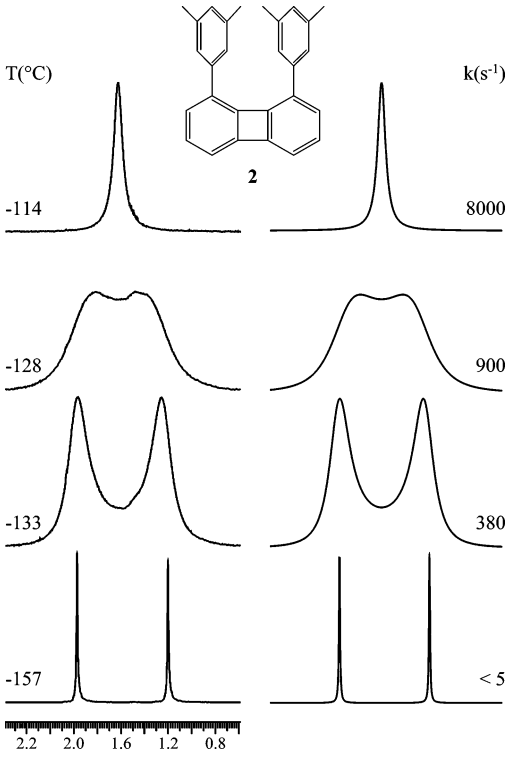


FIGURE 5. Temperature dependence (left) of the ^{1}H methyl signal of **2** (600 MHz in $CHF_2Cl/CHFCl_2$). On the right are shown the simulations obtained with the rate constants indicated.

intense sharp lines at −157 °C (Figure 5), separated by 0.775 ppm: a shift difference in excellent agreement with theoretical predictions. No other exchange processes were observed, as conceivable, on further cooling to −175 °C. Spectral simulations afforded rate constants corresponding to an enantiomerization π-barrier ($\Delta G^{\ddagger}$) of 6.3 kcal mol^{-1} (Table 2), in agreement with what was anticipated.

It can be concluded therefore that unambiguous evidence has been obtained for the hitherto unobserved enantiomerization

(19) When these types of situations are encountered in dynamic NMR processes, the effects of the higher barrier are invisible until also the lower barrier is frozen. See, for instance: (a) Jackson, W. R.; Jennings, W. B. *Tetrahedron Lett.* **1974**, *15*, 1837−1838. (b) Anderson, J. E.; Casarini, D.; Ijeh, A. J.; Lunazzi, L. *J. Am. Chem. Soc.* **1997**, *119*, 8050−8057. (c) Lunazzi, L.; Mazzanti, A.; Álvarez Muñoz, A. *J. Org. Chem.* **2000**, *65*, 3200−3206.

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π-barrier: this could be achieved in the case of derivatives bearing two equal aromatic substituents (*m*-tolyl or *m*-xylyl) bonded to the planar framework of biphenylene.

Experimental Section

Materials. 1,8-Dibromobiphenylene[21] and 1,3-dibromo-2-iodobenzene[22] were prepared according to the literature; 3-methylphenyl boronic acid and 3,5-dimethylphenyl boronic acid were commercially available.

General Procedure for 1 and 2. To a solution of 1,8-dibromobiphenylene (0.062 g, 0.2 mmol, in 2 mL of benzene), K_2CO_3 (2 M solution, 1.0 mL), 3-methylphenyl boronic acid (0.070 g, 0.5 mmol, suspension in 2 mL of ethanol), and $Pd(PPh_3)_4$ (0.046 g, 0.04 mmol) were added at room temperature. The stirred solution was refluxed for 2−3 h, the reaction being monitored by GC-MS. After cooling to room temperature, a second amount of 3-methylphenyl boronic acid (0.070 g, 0.5 mmol, suspension in 2 mL of ethanol) and $Pd(PPh_3)_4$ (0.046 g, 0.04 mmol) was added, and the solution refluxed again for 2 h. Subsequently, $CHCl_3$ and H_2O were added, and the extracted organic layer was dried (Na_2SO_4) and evaporated. The crude product was prepurified by chromatography on silica gel (hexane/Et_2O 20:1) to obtain 0.052 g (75%) of **1**. Compound **2** was obtained following the same procedure, using 3,5-dimethylphenyl boronic acid (0.055 g, 69%). Analytically pure samples of **1** and **2** were obtained by semipreparative HPLC on a C_{18} column (5 μm, 250 mm × 10 mm, 5 mL/min, ACN/H_2O 95:5 v/v for **1**, ACN/H_2O 90:10 v/v for **2**).

1,8-Di-(3-methylphenyl)-biphenylene (1). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ 1.88 (6H, s), 6.65 (2H, bs), 6.67 (2H, d, J = 4.3, 3.2 Hz), 6.85−6.86 (4H, m), 6.91 (6H, m). ^{13}C NMR (150.8 MHz, $CDCl_3$, 25 °C, TMS): δ 21.0 (CH_3), 115.4 (CH), 124.2 (CH), 127.5 (CH), 127.8 (CH), 128.6 (CH), 129.3 (CH), 129.4 (CH), 133.0 (q) 137.4 (q), 137.7 (q), 148.1 (q), 151.4 (q). HRMS-(EI): *m*/*z* calcd for $C_{26}H_{20}$ 332.1565; found 332.1566.

1,8-Di-(3,5-dimethylphenyl)-biphenylene (2). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ 1.97 (12H, s), 6.61 (4H,bs), 6.65 (2H, dd, J = 5.6, 2.0 Hz), 6.74 (2H, bs), 6.82−6.86 (4H, m). ^{13}C NMR (150.8 MHz, $CDCl_3$, 25 °C, TMS): δ 20.9 (CH_3), 115.3 (CH), 125.9 (CH), 128.5 (CH), 128.8 (CH), 129.4 (CH), 133.0 (q) 137.2 (q), 137.7 (q), 148.1 (q), 151.3 (q). HRMS(EI): *m*/*z* calcd for $C_{28}H_{24}$ 360.1878; found 360.1873.

NMR Spectroscopy. The spectra were recorded at 600 MHz for ^{1}H and 150.8 MHz for ^{13}C. The assignments of the ^{13}C signals were obtained by bi-dimensional experiments (edited-gHSQC[23] and gHMBC[24] sequences). The samples for obtaining spectra at temperatures lower than −100 °C were prepared by connecting to a vacuum line the NMR tubes containing the compound and a small amount of C_6D_6 (for locking purposes) and condensing therein the gaseous CHF_2Cl and $CHFCl_2$ (4:1 v/v) under cooling with liquid nitrogen. The tubes were subsequently sealed in vacuo and introduced into the precooled probe of the spectrometer. Temperature calibrations were performed immediately before the experiments, using a Cu/Ni thermocouple immersed in a dummy sample tube filled with isopentane, and under conditions as nearly identical as possible. The uncertainty in the temperatures was estimated from the calibration curve to be ±2 °C. The line shape simulations were performed by means of a PC version of the QCPE program DNMR 6 no. 633, Indiana University, Bloomington, IN.

Calculations. Computations were carried out at the B3LYP/6-31G(d) level by means of the Gaussian 03 series of programs[10] (see Supporting Information): the standard Berny algorithm in redundant internal coordinates and default criteria of convergence were employed. The reported energy values are not ZPE corrected. Harmonic vibrational frequencies were calculated for all the stationary points. For each optimized ground state, the frequency analysis showed the absence of imaginary frequencies, whereas each transition state showed a single imaginary frequency. Visual inspection of the corresponding normal mode was used to confirm that the correct transition state had been found. NMR chemical shift calculations were obtained with the GIAO method at the B3LYP/6-311++G(2d,p)//B3LYP/ 6-31G(d) level. TMS, calculated at the same level of theory, was used as a reference to scale the absolute shielding value.

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Supporting Information Available: DFT computed transition states of **1**, ^{13}C VT-NMR of **1**, ^{1}H and ^{13}C NMR spectra and HPLC traces of **1**−**2**, chemical shift calculations and computational data of **1**−**2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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