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Unexpected Stereodynamic Consequences of the Restricted Rotations in *ortho*-Acyl- and *ortho*-Vinyl Biphenyls

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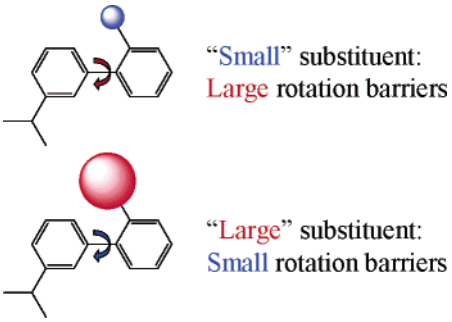

Surprisingly, the aryl−aryl rotation barriers of biphenyl derivatives ortho-substituted by the "small" HC═O and HC═CH_2 groups (10.0 and 8.4 kcal mol^{-1}, respectively) were found greater than those observed in biphenyls ortho-substituted by the "large" *t*-BuC═O and *t*-BuC═CH_2 groups (6.7 and 6.9 kcal mol^{-1}, respectively).

Introduction

The stereodynamic processes occurring in biphenyl derivatives bearing substituents in the ortho positions have been used to evaluate the steric properties of these groups. The Ar−Ar bond rotation barriers can be measured by variable-temperature NMR spectroscopy, and the corresponding values provide an indication on the hindrance exerted upon such a rotation by the various substituents.[2,3] The experimental results have been also supported by theoretical calculations.[3−5] Because indications on the steric effects of the acyl moieties were not reported in this series, we performed DFT calculations to predict the aryl−aryl rotation barriers for biphenyls substituted by RC═O groups in the ortho position. Surprisingly, in the case of the "small" HC═O, this barrier was calculated to be significantly greater than that for the "large" *t*-Bu−C═O group (Table 1). For such a reason, an experimental verification of this apparently contradictory result was undertaken.

TABLE 1. Computed and Experimental Barriers (±0.2 kcal mol^{-1}) for the Enantiomerization Process of the Ar−Ar Bond Rotation in Compounds 1−6

	compd					
	1 (R = H)	**2** (R = Me)	**3** (R = ^{i}Pr)	**4** (R = ^{t}Bu)	**5** (R = H)	**6** (R = ^{t}Bu)
exp	10.0	8.0	7.9	6.7	8.3	6.9
calcd	10.9	8.3	8.9	7.2	8.4	6.6

Results and Discussion

To measure by NMR the Ar−Ar rotation barrier of monosubstituted biphenyls, we introduced an isopropyl group to exploit the diastereotopicity of its methyls[3,6] under the mode of slow rotation around the biphenyl bond at an appropriate low temperature. In such a way, it was possible to infer the existence of the *M* and *P* chiral forms (stereolabile atropisomers) of Figure 1. Compounds **1**−**4** were accordingly synthetized, because the

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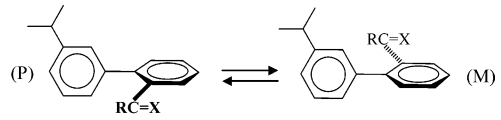

X = O; R = H (**1**); R = Me (**2**); R = Pr^i (**3**), R = Bu^t (**4**).

X = CH2; R = H (**5**); R = Bu^t (**6**).

FIGURE 1. *M* and *P* stereolabile enantiomers of compounds **1**−**6**.

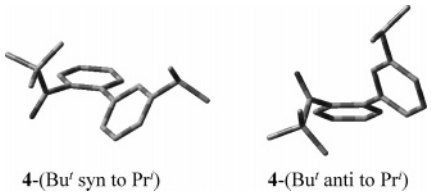

FIGURE 2. Computed structures of the two syn and anti stereolabile diastereoisomers of **4** (only one of the two possible enantiomers for each diastereoisomer is displayed).

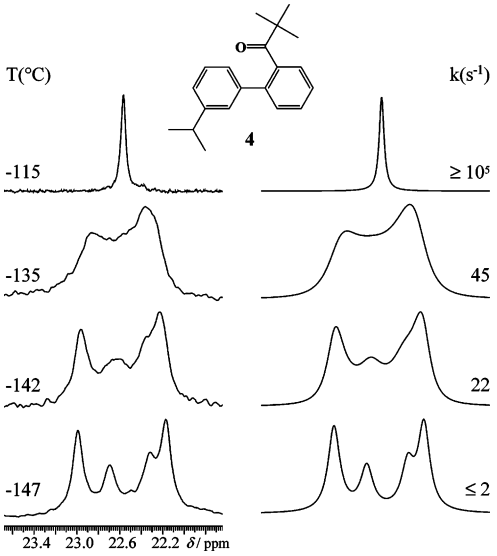

FIGURE 3. Left: temperature dependence of the ^{13}C isopropyl methyl lines of **4** (150.8 MHz in $CHF_2Cl/CHFCl_2$). Right: line shapes simulated with the rate constants reported.

meta isopropyl group is unlikely to interfere significantly with the mentioned rotation process.

The ^{13}C NMR spectrum (150.8 MHz) of **1** shows, for instance, that the single line of the methyl groups broadens on cooling and splits into a pair of equally intense lines separated by 10.3 Hz at −104 °C (Figure S1, Supporting Information). From the rate constant determined by complete line shape simulation, the free energy of activation ($\Delta G^{\ddagger}$ = 10.0 kcal mol^{-1}) for the Ar−Ar rotation is derived. As shown in Table 1, this value decreases with the increasing dimension of the R groups and reaches a value as low as 6.7 kcal mol^{-1} in the case of **4** (R = *tert*-butyl). This finding is in keeping with the theoretical predictions. In particular, the NMR experiments indicate that the HC═O group hinders the Ar−Ar bond rotation significantly more than does the *t*-Bu−C═O group: the amount of such an effect is almost equal to that anticipated by calculations (Table 1).

This unexpected result can be explained by taking into account that the HC═O moiety in **1** is essentially coplanar with the phenyl ring, as indicated by NMR studies on benzaldehydes[7] and ortho-substituted benzaldehydes,[8,9] and supported by our DFT calculations of **1**.[10] In such a situation, the HC═O group exerts a relatively large steric effect upon the transition state of the aryl−aryl bond rotation,[11] where the two aryl rings become coplanar to interconvert the *M* and *P* atropisomers of Figure 1.

In the case of **4**, on the contrary, the *t*-BuC═O moiety is almost orthogonal to the phenyl ring (the computed dihedral angle is 78°), and thus the hindrance exerted upon the aryl−aryl rotation is lower than in **1** and is also lower than in **2** and **3** because in these two compounds computations indicate that the Ph−C(O)R moieties deviate from coplanarity only by 24° and 36°, respectively. Because of the orthogonal arrangement of **4**, the restricted Ph−C(O)^{t}Bu bond rotation originates a second stereogenic axis, in addition to the Ar−Ar axis. This creates two stereolabile diastereoisomers that, according to computations, have equal energies (Figure 2).

The ^{13}C spectrum of **4** at −147 °C shows indeed that most of the signals split into pairs of lines, with a 65:35 intensity ratio.[12] For this reason, the isopropyl methyl carbons display four lines at this temperature (Figure 3) because each of the two diastereoisomers of Figure 2 exhibits two lines due to the diastereotopicity of the isopropyl methyl groups.

Simulation of the 65:35 pair of lines of one quaternary carbon allowed the barrier for the interconversion of the major into the minor diastereoisomer to be determined (6.6 kcal mol^{-1}). Because either the Ph−CO or the Ar−Ar bond rotation would allow this process to take place, one cannot indicate which of the two motions is responsible for the interconversion.

In Figure 3 it is shown, however, how the coalescence of the 1:1 isopropyl methyl lines is simultaneously accompanied by the coalescence of the corresponding 65:35 pairs of lines. A unique rate constant is thus sufficient to obtain a satisfactory simulation of the four lines merging into one,[13] and a single

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(10) It should be pointed out that the planarity of the Ph−CHO moiety would make observable, in principle, two rotational conformers (*E* and *Z*) as reported for the ortho-substituted alkyl benzaldehydes.[8,9] Even at −170 °C, however, the NMR spectra of **1** do not display evidence of such rotamers. DFT calculations indicate in fact that the *Z* rotamer of **1**, with the oxygen facing the *m*-isopropyl phenyl ring, is 2.4 kcal mol^{-1} less stable than the rotamer *E*. This is probably due to the repulsion between the lone pair electrons of the oxygen and the π-electrons of the *m*-isopropyl phenyl ring. This is supported by the calculations showing how the more stable conformer of **2** and **3** is again the *E* rotamer, where the oxygen points away from the *m*-isopropyl phenyl. The need of avoiding the electron repulsion is so strong as to exceed the larger steric effects experienced by the *E* with respect to the *Z* form in **2** and **3** (the computed energy differences are 1.5 and 2.1 kcal mol^{-1}, respectively). Such a large difference means that only the *E* rotamer is essentially populated in **1**−**3**, thus explaining why the effects of the restricted Ph−C═O rotation cannot be observed.

(11) In the transition state of the aryl−aryl bond rotation of **1**, the HC═O group, according to DFT calculations, remains nearly coplanar, and thus still able to conjugate, with the phenyl ring.

(12) The DFT computed energies for the two diastereomeric conformers are essentially equal (the difference is only 0.07 kcal mol^{-1}), and thus the different populations observed by NMR depend on the condensed phase. We arbitrarily identified the less hindered conformer (having the two substituents in an anti relationship) as the more populated form in solution.

(13) PC version of QCPE program no. 633, Indiana University, Bloomington, IN.

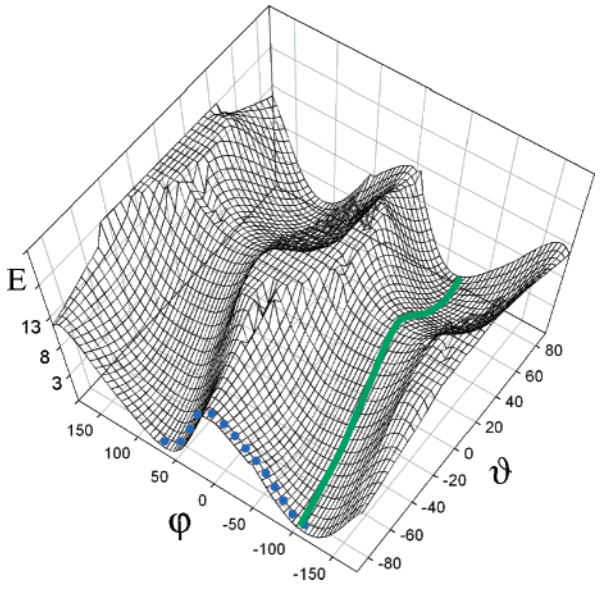

FIGURE 4. MM computed energy surface of **4** (E in kcal mol^{-1}) as a function of the Ph−CO (ϑ) torsion angle (green full line pathway) and Ar−Ar (φ) torsion angle (blue dotted line pathway).

value is accordingly obtained for the corresponding activation energy ($\Delta G^{\ddagger}$ = 6.7 kcal mol^{-1}, i.e., equal to that previously obtained by monitoring the two quaternary carbon lines). Within the experimental uncertainty, two distinguishable barriers could not be measured, and thus the Ar−CO^{t}Bu and the Ar−Ar bond rotations must have very similar barriers.[14]

An indication that this is indeed the case can be also inferred from a Molecular Mechanics[15] computation of the energy surface as a function of the Ph−CO (ϑ) and Ar−Ar (φ) torsion angles. As shown in Figure 4, the Ph−CO and Ar−Ar rotation pathways are independent of each other (the corresponding lines in fact run parallel[16] to the ϑ and φ axes), but the two transition states (E = 12.5 and 12.1 kcal mol^{-1}, respectively) have essentially the same energy (the DFT Ar−Ar rotation barrier of Table 1 differs from that of the MM method, due to the greater approximations of the latter approach).

The present explanation that the rotation barrier in **1** is larger than that in **4** implies that other derivatives, having analogous steric requirements, should also display the same trend. Thus,

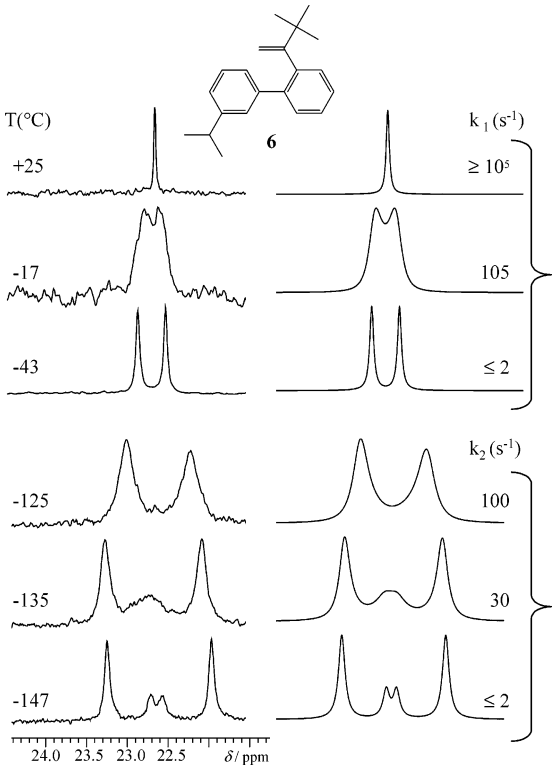

FIGURE 5. Left: temperature dependence of the ^{13}C isopropyl methyl lines of **6** (150.8 MHz). The top three traces are in CD_2Cl_2, and the bottom three traces are in $CHF_2Cl/CHFCl_2$. Right: line shapes simulated with the rate constant k_1 for the Ph−C(CH2)^{t}Bu bond rotation and k_2 for the Ar−Ar bond rotation.

for instance, biphenyls substituted in the ortho position by the R−C═CH_2 moiety should likewise exhibit an Ar−Ar rotation barrier that is larger for R = H than for R = *t*-butyl. To check this point, compounds **5** and **6** of Figure 1 were also investigated.

Styrene, contrary to benzaldehyde, is not planar, the dihedral angle between the phenyl and the vinyl plane lying in the 18°[17] to 27°[18] range (the Ph−C═CH_2 rotation barrier is predicted[18] to be much lower than that for benzaldehyde; thus it is NMR invisible). The Ar−Ar rotation barrier of **5** should be similar to that of **1**, albeit smaller, due to the deviation from the coplanarity of the styrene moiety. Actually the ^{13}C methyl line of **5** splits into a 1:1 pair at −125 °C (Figure S2, Supporting Information), and the corresponding $\Delta G^{\ddagger}$ value for the Ar−Ar bond rotation was found equal to 8.3 kcal mol^{-1}.[19]

In the case of **6**, the 1:1 splitting of the ^{13}C isopropyl methyl line appears at a quite higher temperature (−17 °C as in Figure 5), the barrier responsible for this process being 12.5 kcal mol^{-1}. On lowering the temperature to −147 °C, two pairs of 1:1 lines are observed in a 75 to 25 proportion,[20] (Figure 5), and the barrier measured for this second process is 6.9 kcal mol^{-1}. This means that the two rotation processes occur in subsequent steps, thus confirming that the equivalence of the two barriers in **4** was purely accidental.

(14) If the Ar−CO^{t}Bu rotation barrier of **4** had been larger than that for the Ar−Ar rotation, the isopropyl methyl line would first split into two with a 1:1 ratio. In fact, the slow rotation about the Ph−C(O)^{t}Bu bond would make the molecule chiral, the C(O)^{t}Bu moiety being orthogonal to the phenyl ring. For this reason, the isopropyl methyl groups would become diastereotopic, even in the presence of a fast Ar−Ar rotation. On the other hand, if the Ph−C(O)^{t}Bu rotation barrier had been lower than that for the Ar−Ar rotation, again the methyl line would first split into two, with a 1:1 ratio, because the slow Ar−Ar rotation would also make the molecule chiral. In both cases, only subsequently would four lines be detectable, that is, when also the second motion is frozen at a lower temperature, thus creating two chiral conformers. Because such a two-step process was not observed, in that the single signal splits directly into four, the two exchange pathways, leading to the coalescence of the 1:1 and of the 65:35 pairs of methyl lines, must occur almost simultaneously. This implies that the two barriers must be very similar, as proved by the fact that a single rate constant is sufficient for the simulation.

(15) MMFF force field as in PC model v 7.5, Serena Software, Bloomington, IN.

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(19) This barrier is close to that measured for **2** because MeC═O deviates from the coplanarity with the phenyl ring (24° according to our ab-initio calculations of **2**) essentially by the same amount as the C═CH_2 group. The two groups thus display an analogous steric effect upon the Ar−Ar rotation.

As discussed in ref 14, it is impossible to assign which rotation pathway corresponds to the measured barriers solely on experimental ground. Conventional wisdom clearly suggests, however, that the Ph−C(CH_2)^{t}Bu bond rotation of **6** should have a barrier larger than that of the Ph−C(O)^{t}Bu bond rotation of **4**. The C═CH_2 and C═O planes are orthogonal to the phenyl ring in both cases, but the steric hindrance of the former is obviously larger than that of the latter.[21] Consequently, the larger barrier (12.5 kcal mol^{-1}) should be assigned to the Ph−C(CH_2)^{t}Bu bond rotation. On the other hand, the Ar−Ar rotation should have similar barriers in both **4** and **6**, because the steric hindrance should be nearly the same, in that the *t*-BuC═O and *t*-BuC═CH_2 moieties are both orthogonal to their phenyl rings. Thus, the lower barrier of **6**, almost equal to that measured in **4** (Table 1), should be assigned to the Ar−Ar rotation. This assignment agrees with the results of DFT computations of **6** that indicate the Ph−C(CH_2)^{t}Bu bond rotation barrier to be larger (11.3 kcal mol^{-1}) than that for the Ar−Ar rotation (6.6 kcal mol^{-1}).

Conclusion

We have thus found at least two unusual examples where apparently bulkier substituents (i.e., the *t*-Bu−C═X groups in **4** and **6**) make the Ar−Ar rotation barriers lower than those occurring in apparently less crowded compounds (i.e., **1** and **5**, where the substituents are the "small" HC═X groups).

Experimental Section

Materials. 2-Bromobenzaldehyde and 2′-bromoacetophenone were commercially available and were used without further purification. 1-(2-Bromo-phenyl)-2,2-dimethyl-propan-1-one[22] and 3-isopropyl-phenylboronic acid[3b] were prepared according to the literature.

1-(2-Bromo-phenyl)-2-methyl-propan-1-one. To a solution of isopropylmagnesium bromide (0.5 M, obtained from 3.69 g of 2-bromopropane and 0.73 g of Mg turnings in 60 mL of anhydrous Et_2O) was slowly added, at 0 °C, a solution of *o*-bromobenzaldehyde (2.77 g in 40 mL of anhydrous Et_2O). After being stirred for 1 h, the solution was warmed to room temperature and quenched with aqueous NH_4Cl. The mixture was then treated with H_2O, extracted (Et_2O), and dried (Na_2SO_4). After the solvent was removed, the crude was purified by a silica gel chromatography column (petroleum ether/Et_2O 4/1) to give 1-(2-bromo-phenyl)-2-methyl-propan-1-ol. A solution of the alcohol (2.30 g, 10 mmol in 20 mL of CH_2Cl_2) was then treated with pyridinium chlorochromate (4.30 g, 20 mmol), monitoring the reaction by TLC. The reaction was complete in 3 h. After addition of 50 mL of Et_2O, the mixture was filtered on a short silica gel column and concentrated. The crude was purified by a silica gel chromatography column (petroleum ether/Et_2O 10:1) to obtain 1-(2-bromo-phenyl)-2-methyl-propan-1-one (2.05 g, overall yield 60%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.20 (6H, d, J = 6.8 Hz), 3.33 (1H, septet, J = 6.8 Hz), 7.26−7.29 (2H, m), 7.36 (1H, m), 7.59 (1H, m). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): δ 18.1 ($2CH_3$), 40.1 (CH), 118.6 (CH), 127.2 (CH), 128.1 (CH), 131.0 (CH), 133.4 (Cq), 142.0 (Cq), 208.6 (CO).

General Procedure for Compounds 1−4. To a solution of the appropriate *ortho*-bromo acylphenone (1 mmol in 6 mL of benzene) were added K_2CO_3 (2 M solution, 1.25 mL), 3-isopropylphenyl boronic acid (2.5 mmol, suspension in 4 mL of ethanol), and Pd(PPh_3)$_4$ (0.2 mmol) at ambient temperature. The stirred solution was refluxed for 2−3 h, the reaction being monitored by GC−MS. Subsequently, $CHCl_3$ and H_2O were added, and the extracted organic layer was dried (Na_2SO_4) and evaporated. The crude material was purified by chromatography on silica gel (hexane).

3′-Isopropyl[1,1′-biphenyl]-2-carbaldehyde (1). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ 1.28 (6H, d, J = 7.0 Hz), 2.97 (1H, septet, J = 7.0 Hz), 7.20−8.03 (8H, m), 9.98 (1H, s, CHO). ^{13}C NMR (150.8 MHz, $CDCl_3$, 25 °C, TMS): δ 23.9 (CH_3), 34.0 (CH), 126.2 (CH), 127.4 (CH), 127.5 (CH), 128.3 (CH), 128.4 (CH), 130.7 (CH), 133.4 (CH), 133.7 (q), 137.6 (q), 146.3 (q), 149.6 (q), 192.5 (CHO). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.45; H, 7.19.

1-(3′-Isopropyl[1,1′-biphenyl]-2-yl)-1-ethanone (2). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ 1.26 (6H, d, J = 7.0 Hz), 1.96 (s, 3H), 2.93 (1H, septet, J = 7.0 Hz), 7.17−7.54 (8H, m). ^{13}C NMR (150.8 MHz, $CDCl_3$, 25 °C, TMS): δ 24.0 (CH_3), 30.4 (CH_3), 34.1 (CH), 126.1 (CH), 126.3 (CH), 127.2 (CH), 127.3 (CH), 127.8 (CH), 128.7 (CH), 130.1 (CH), 130.6 (CH), 140.6 (q), 140.9 (q), 141.1 (q), 149.4 (q), 205.0 (C═O). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.41; H, 7.61.

1-(3′-Isopropyl[1,1′-biphenyl]-2-yl)-2-methyl-1-propanone (3). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ 0.80 (6H, d, J = 6.7 Hz), 1.26 (6H, d, J = 6.8 Hz), 2.41 (1H, septet, J = 6.8 Hz), 2.93 (1H, septet, J = 6.7 Hz), 7.15−7.49 (8H, m). ^{13}C NMR (150.8 MHz, $CDCl_3$, 25 °C, TMS): δ 18.7 (CH_3), 24.1 (CH_3), 34.2 (CH), 40.3 (CH), 126.0 (CH), 126.3 (CH), 127.3 (CH), 127.4 (CH), 128.0 (CH), 128.8 (CH), 130.1 (CH), 130.2 (CH), 140.1 (q), 140.6 (q), 140.9 (q), 149.4 (q), 212.9 (C═O). Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.27; H, 8.36.

1-(3′-Isopropyl[1,1′-biphenyl]-2-yl)-2,2-dimethyl-1-propanone (4). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 0.85 (9H, s), 1.25 (6H, d, J = 6.9 Hz), 2.91 (1H, septet, J = 6.9 Hz), 7.12−7.43 (8H, m). ^{13}C NMR (75.45 MHz, $CDCl_3$, 25 °C, TMS): δ 24.1 (CH_3), 27.4 (CH_3), 34.2 (CH), 45.0 (q), 125.8 (CH), 125.9 (CH), 126.8 (CH), 127.1 (CH), 128.1 (CH), 128.6 (CH), 128.8 (CH), 129.8 (CH), 138.5 (q), 141.0 (q), 141.3 (q), 149.2 (q), 216.8 (C═O). Anal. Calcd for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.50; H, 8.69.

General Procedure for Compounds 5 and 6. To a cooled (0 °C) solution of 3′-isopropyl[1,1′-biphenyl]-2-carbaldehyde (**1**) (224 mg, 1 mmol in 10 mL of *n*-hexane) was added 0.94 mL (1.5 mmol) of methyl-lithium (1.6 M in Et_2O). When the addition was terminated, the reaction was refluxed for 2 h and then quenched with water (15−20 mL). The mixture was extracted with Et_2O, dried (Na_2SO_4), and the solvent removed at reduced pressure, and 192 mg (0.8 mmol) of pure 1-(3′-isopropyl-biphenyl-2-yl)-ethanol was obtained. The crude was treated with P_2O_5 (0.50 g, 3.52 mmol in $CHCl_3$), and the solution was allowed to warm for 1 h. The product was extracted with Et_2O, dried (Na_2SO_4), and the solvent removed at reduced pressure to obtain 154 mg (0.7 mmol, 70%) of **5**. The same procedure was used to obtain **6** starting from **4** (yield 65%).

3-Isopropyl-2′-vinyl-1-1′-biphenyl (5). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 1.28 (6H, d, J = 7.0 Hz), 2.95 (1H, septet, J = 7.0 Hz), 5.17 (1H, dd, J = 10.9, 1.3 Hz), 5.69 (1H, dd, J = 17.5, 1.3 Hz), 6.73 (1H, dd, J = 17.5, 10.9 Hz), 7.15−7.67 (8H, m). ^{13}C NMR (75.45 MHz, $CDCl_3$, 25 °C, TMS): δ 24.2 (CH_3), 34.3 (CH), 114.0 (CH), 125.3 (CH), 125.8 (CH), 127.4 (CH), 127.5 (CH), 127.8 (CH), 128.0 (CH), 128.3 (CH), 130.2 (CH), 136.3 (CH), 140.1 (q), 140.6 (q), 140.9 (q), 148.7 (q). Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.78; H, 8.35.

2-[1-(*tert*-Butyl)vinyl]-3′-isopropyl-1-1′-biphenyl (6). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ 0.76 (9H, s), 1.24 (6H, d, J = 6.8 Hz), 2.82 (1H, septet, J = 6.8 Hz), 5.06 (1H, d, J = 1.7 Hz),

(20) At −147 °C, many other ^{13}C lines of **6** split into two signals with a 75:25 proportion, due to two diastereomeric conformers being created by two stereogenic axes. The major spectrum has been arbitrarily assigned to the less hindered conformer, that is, that with the two substituents in an anti relationship.

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5.36 (1H, d, $J = 1.7$ Hz), 7.11−7.33 (8H, m). ^{13}C NMR (150.8 MHz, $CDCl_3$, 25 °C, TMS): δ 24.2 (CH_3), 30.4 (CH_3), 34.3 (CH), 36.8 (q), 115.2 (CH), 125.8 (CH), 126.2 (CH), 126.8 (CH), 127.6 (CH), 128.0 (CH), 129.0 (CH), 130.1 (CH), 131.0 (CH), 140.8 (q), 142.0 (q), 142.8 (q), 148.0 (q), 158.5 (q). Anal. Calcd for $C_{21}H_{26}$: C, 90.59; H, 9.41. Found: C, 90.55; H, 9.44.

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 DEPT and bi-dimensional experiments (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 some C_6D_6 for locking purpose and condensing therein the gaseous CHF_2-Cl 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. The temperatures were calibrated by substituting the sample with a Cu/Ni thermocouple before the measurements.

Calculations. Computations were carried out at the B3LYP/6-31G(d) level by means of the Gaussian 03 series of programs[25] (see Supporting Information); the standard Berny algorithm in redundant internal coordinates and default criteria of convergence were employed. The energy values are not ZPE corrected. Harmonic vibrational frequencies were calculated for all of 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.

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Supporting Information Available: Variable-temperature NMR spectra of compounds **1** and **5**. Computational details, ^{1}H and ^{13}C NMR spectra, combustion data, and HPLC traces of compounds **1**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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