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Conformational Studies by Dynamic NMR. 78.[1] Stereomutation of the Helical Enantiomers of Trigonal Carbon Diaryl-Substituted Compounds: Dimesitylketone, Dimesitylthioketone, and Dimesitylethylene

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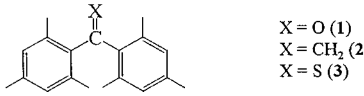
The free energies of activation for the enantiomerization of the title compounds ($Mes_2C{=}X$, Mes = 2,4,6,-trimethylphenyl) were determined by dynamic NMR to be 4.6, 6.5, and 9.2 kcal mol^{-1} for X= O, S, and CH_2, respectively. Single-crystal X-ray diffraction showed that the structure of dimesitylketone is that of a propeller (C_2 symmetry) with the mesityl rings twisted by 50° with respect to the plane of carbonyl. The same structure was predicted by molecular mechanics calculations, which also produced good agreement between computed and experimental barriers for a dynamic process where a disrotatory one-ring flip pathway reverses the helicity of the conformational enantiomers. Solid-state NMR spectra indicated that the enantiomerization barrier in the crystal must be much higher (at least 19 kcal mol^{-1}) than that in solution. Contrary to the case of dimesitylketone, the calculated barrier of dimesitylethylene agrees better with the experimental value if the enantiomerization process is assumed to be a conrotatory two-ring flip pathway.

Introduction

The stereomutation processes involving two phenyl rings bonded to the same sp^2-hybridized carbon have been theoretically analyzed in terms of pathways dubbed "ring-flip" mechanisms.[3−5] In particular, detailed computations are available for the simple cases of 1,1-diphenylethylene ($Ph_2C{=}CH_2$),[6,7] benzophenone ($Ph_2C{=}O$),[8,9] and diphenylketene ($Ph_2C{=}C{=}O$).[5,10,11] The calculations indicate that the threshold barriers for the stereomutation in these diphenyl derivatives have quite low activation energies that make impossible, in practice, the observation of these processes in solution by dynamic NMR spectroscopy. This circumstance has prevented an experimental verification of the computed values for these barriers. As reported in a variety of less symmetric molecules,[4,12−14] substitution of the phenyl rings with the bulkier mesityl groups increases substantially the interconversion barriers, so it would become possible, in principle, to detect experimentally such dynamic processes at least in the case of dimesitylketone, **1** (Chart 1), and 1,1-dimesitylethylene, **2**. Yet previously reported attempts[15,16] of observing these processes by NMR spectroscopy had failed, so the experimental barriers for the stereomutations occurring in **1** and **2** are still unknown. Since the latter compounds are the prototypes of the simplest sp^2-carbon-bonded diaryl derivatives where an experimental determination is likely to be feasible, we

Chart 1



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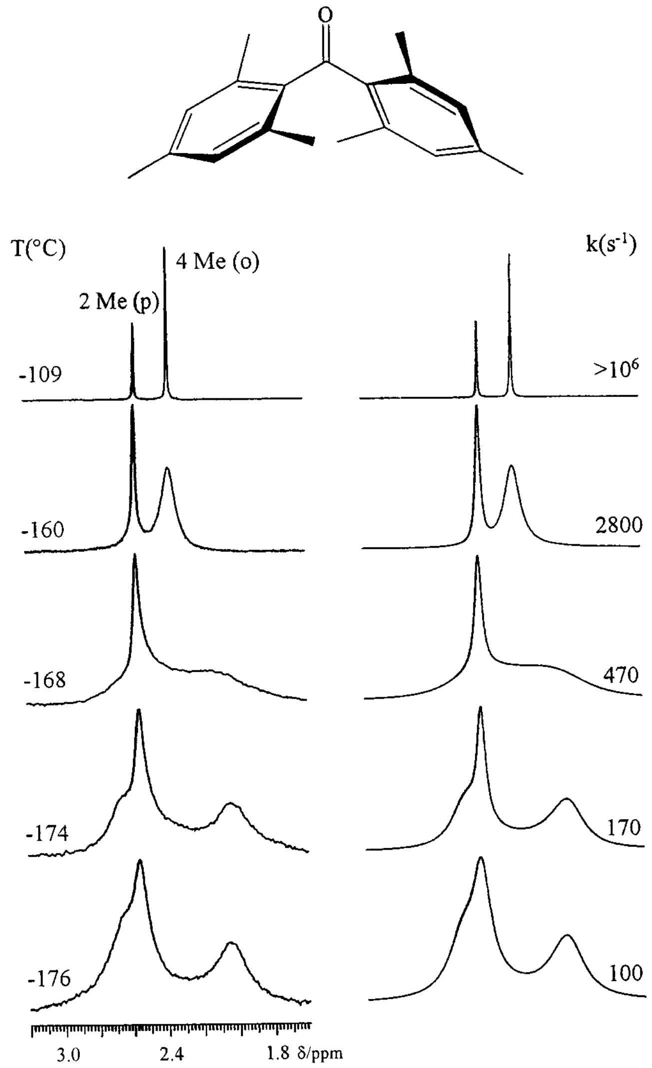


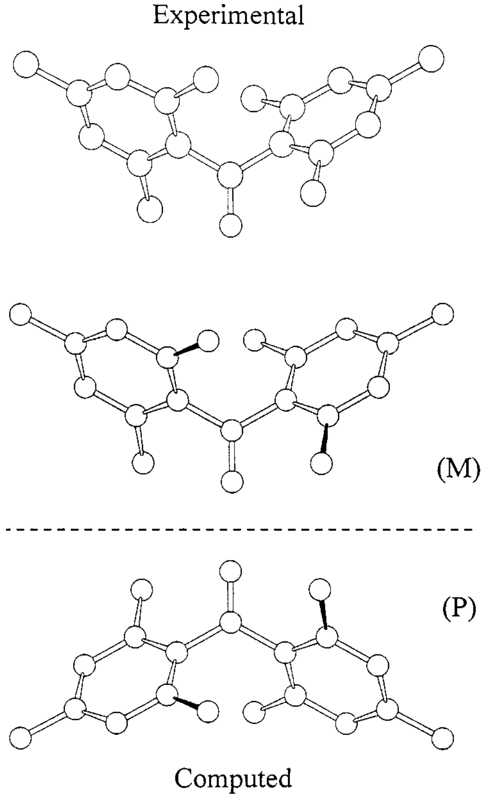
Figure 1. Temperature dependence of the ^{1}H NMR methyl signals (300 MHz) of dimesitylketone, **1**, in $CHF_2Cl/CHFCl_2$ 5:1 v/v (left). The simulated traces obtained with the rate constants are indicated (right).

have undertaken an investigation to fill this gap in our knowledge of such basic conformational processes. The study was also extended to dimesitylthioketone, **3**, which has the same symmetry of **1** but is more sterically hindered.

Results and Discussion

Dimesitylketone (1). From ambient temperature down to −110 °C, the 300 MHz ^{1}H NMR spectrum (in $CHF_2Cl/CHFCl_2$, 5:1 v/v) of **1** displays, in the aliphatic region, two lines with a 2:4 intensity ratio, corresponding to the two para and the four ortho methyl groups. The signal of the latter broadens significantly on cooling below −150 °C and decoalesces into a pair of equally intense lines below −170 °C, whereas the line of the para methyl groups remains a singlet which partly overlaps one of the two ortho lines (Figure 1). Even at −176 °C, the two lines for the ortho are broader than the single line for the para methyl groups, indicating that the motion responsible for the observed exchange process is not yet completely frozen in the NMR time scale. This interpretation was supported by the computer simulation displayed in Figure 1, which provided the rate constants at different temperatures, from which a free energy of activation ($\Delta G^\ddagger$) of 4.6 ± 0.1_5 kcal mol^{-1} was derived.[17] Analogous features should have been exhibited by the ^{13}C spectrum, but the poor solubility of **1** at such low temperatures prevented its observation. Also, we could not investigate the aromatic region of the ^{1}H spectrum because it was obscured by the intense signals of the solvent.

Scheme 1. X-ray Structure of Dimesitylketone, 1 (Top), and MM Calculated Structures (Bottom) of the Two M,P Enantiomeric Forms



The spectral multiplicity exhibited by the ^{1}H methyl signals is compatible with a conformation whereby the two mesityl rings are symmetrically twisted with respect to the carbonyl plane so that the ortho positions become diastereotopic, even though the para positions remain homotopic. The twisting of the two rings creates, in such a way, a helicity resembling that of a two-blade propeller. Such a conformation corresponds to the helical structure of **1**, which we obtained (Scheme 1) by single-crystal X-ray diffraction (although the structures of many diarylketones could be retrieved,[9] that of **1** was not available in the literature). The mentioned dihedral angles were found to be 50.2° and 50.8°, which means that they are equal within the experimental errors. As predicted, these values are larger than those measured in crystalline benzophenone (29.4 and 30.9°),[9,18] owing to the mesityl being bulkier than the phenyl rings. Also it was found that in the cell of **1**, there are two pairs of molecules ($Z = 4$, see Experimental Section) of opposite chirality, indicating that the crystals are heterochiral.

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[17] As often observed in conformational processes, the $\Delta G^\ddagger$ value was found essentially independent of temperature, thus indicating a $\Delta S^\ddagger$ value negligible within the experimental errors. See, for instance: Gur, E.; Kaida, Y.; Okamoto, Y.; Biali, S. E.; Rappoport, Z. *J. Org. Chem.* **1992**, *57*, 3689. Maeda, K.; Okamoto, U.; Toledano, O.; Becker, D.; Biali, S. E.; Rappoport, Z. *J. Org. Chem.* **1994**, *59*, 5473.

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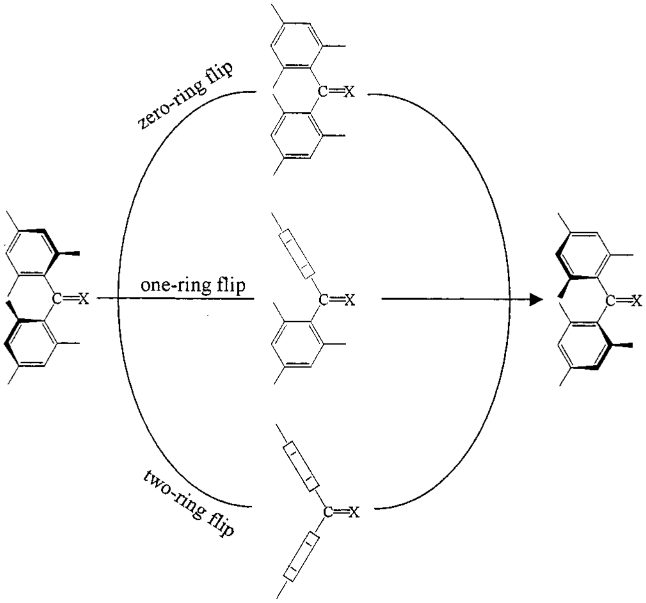
In the computed[19] ground state conformation of **1**, both the Ar−CO dihedral angles are equal to 49°, and the near identity of the value measured in the crystal with that calculated for the isolated molecule makes very plausible that in solution these dihedral angles are about 50° also. Such a conformation (C_2 symmetry point group) is chiral, so the measured barrier of 4.6 kcal mol^{-1} corresponds to an enantiomerization process which interconverts the M and P antipodes displayed in Scheme 1.

The interconversion process observed in **1** might occur, in principle, either via independent rotation of each ring or via rotation of the two rings in unison (correlated rotation);[4] when available, the latter pathway is energetically favored.[3b,5,20] That the motion observed in **1** is actually a correlated process (cog wheel effect) also emerges from the comparison with the rotation pathways occurring in phenyl mesityl ketone (MesPhC=O, where Mes = 2,4,6-trimethylphenyl). Even though the latter is a less crowded molecule (the situation is somewhat midway between that of benzophenone and dimesitylketone), the corresponding interconversion barriers were found[21] much higher than the 4.6 kcal mol^{-1} measured for **1**. This apparent paradox can be understood by considering that the two aromatic rings adopt a different disposition there with respect to the carbonyl moiety (the mesityl is orthogonal, the phenyl coplanar), leading to an achiral conformation (C_s symmetry) where the two rings are able to rotate almost independently of each other. For this reason, each ring exhibits a barrier to rotation (10.6 and 9.1 kcal mol^{-1} for mesityl and phenyl,[21] respectively) higher than that of **1**.

In a correlated process, the two rings of the propeller can be compared to a macroscopic two-toothed gear which may undergo either a conrotatory or a disrotatory motion.[3d,5] Such a correlated process can be described by "ring-flip" mechanisms leading to reversal of the helicity. In the case of **1**, the n-ring flip mechanisms may occur either via a disrotatory motion (when $n = 1$) or via a conrotatory motion (when $n = 2$) of the mesityl rings that, in so doing, pass through a plane orthogonal to that of the C=O moiety. The different sense of rotation leads to different shapes of the transition states for these two pathways (Scheme 2).[8,9] When $n = 1$, one ring is orthogonal and the other parallel to the carbonyl plane (gear meshing, C_s symmetry), with a degenerate situation subsequently occurring when the two rings reverse their disposition.[9] When $n = 2$, both rings become simultaneously orthogonal to the carbonyl plane, leading to a transition state having a C_{2v} symmetry (gear clashing). On the other hand, a zero-ring flip mechanism ($n = 0$) corresponds to a conrotatory motion involving the passage of both the mesityl rings through a plane coincident with that of carbonyl.[5,7,12,13] Detailed theoretical analysis of the three possible processes ($n = 0$, 1, 2 as in Scheme 2) had been reported for benzophenone using ab intio (at the STO-3G level)[8] and MM2 (85)[9] methods. In both cases the zero-ring flip appeared to be less plausible than the other two mechanisms because the corresponding transition state resulted to have the highest energy.[22] In the present case, this pathway would be NMR invisible[5,13] since it does not exchange the diastereotopic environments of the two ortho methyl groups within each ring and thus cannot account for the observed coalescence of the corresponding signals.[14] Nonetheless this "NMR silent" process might correspond to the threshold barrier for the enantiomerization of **1** if the corresponding barrier had a value lower than the 4.6 kcal mol^{-1} experimentally measured. This circumstance, however, seems even less likely to occur than in the case of benzophenone, since it would require a nearly planar transition state (Scheme 2), hardly believable to occur in **1**, due to the greater bulkiness of the mesityl with respect to the phenyl ring. The choice of the pathway responsible for the observed process is thus restricted to the one- and the two-ring flip mechanism.

Scheme 2. Schematic Representation of the Transition States for the Zero-, One-, and Two-Ring Flip Pathways that Interconvert the Enantiomeric Propeller Conformers of 1−3 (X = O, S, CH$_2$)



The calculations performed for benzophenone indicated a clear preference for the one-ring with respect to the two-ring flip pathway, the corresponding barriers being 1.3 vs 6.0 kcal mol^{-1} (STO-3G)[8] and 1.4 vs 6.8 kcal mol^{-1} (MM2), respectively.[9] In the case of 2,2′,6,6′-tetramethyl benzophenone, calculations had also suggested a preference for the one-ring flip mechanism, although the barrier of 2 kcal mol^{-1} computed for this pathway[16b] was much too low to be compatible with the experimental value presently obtained for **1**.

We thus calculated (MMFF-94 force field)[19] the potential energy map for dimesitylketone as a function of the dihedral angles made by the mesityl rings with the carbonyl plane. The motion of one ring always entails the motion of the second one, indicating, as anticipated, that independent rotation is an unrealistic model and that the mesityl substituents experience a correlated rotation process (cog wheel effect). In agreement with the qualitative prediction, the zero-ring flip process turned out to have a barrier (42.4 kcal mol^{-1}) much

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(19) The MMFF-94 force field, as implemented in the PC Spartan-Pro 1.1 computer package, was used.

(20) Cremonini, M. A.; Lunazzi, L.; Placucci, G.; Okazaki, R.; Yamamoto, G. *J. Am. Chem. Soc.* **1990**, *112*, 2915.

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(22) The MM2 approach showed that the ring frame of each phenyl group of benzophenone is distorted from planarity by as much as 18° (leading to a C_2 symmetry rather than to the expected C_{2v} symmetry) in order to relieve the strain of the coplanar transition state.[9]

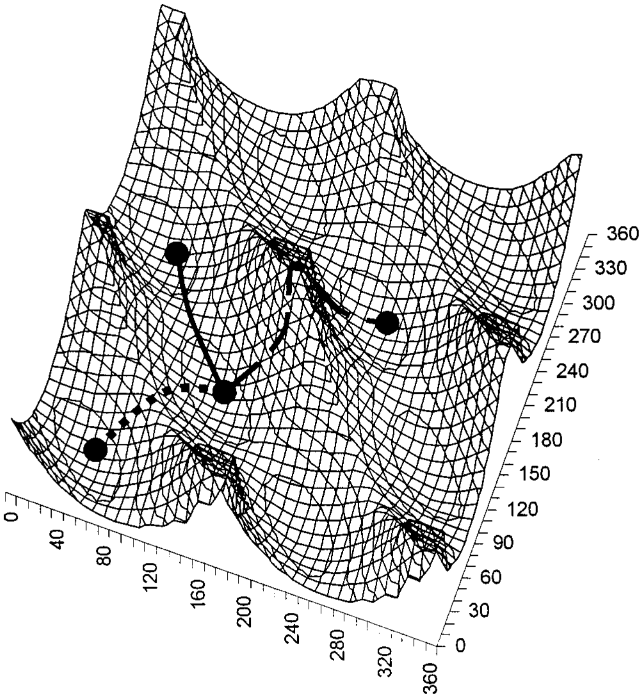

Figure 2. Potential energy map of dimesitylketone, **1**, computed as a function of the two Ar−CO dihedral angles. The circles correspond to the enantiomeric propeller conformers in the ground state. The full line, the dotted line, and the broken line indicate the one-ring flip ($n = 1$ with a barrier of 5.4 kcal mol^{-1}), the two-rings flip ($n = 2$, with a barrier of 17.0 kcal mol^{-1}), and the zero-ring flip ($n = 0$, with a barrier of 42.4 kcal mol^{-1}) pathways, respectively.

Table 1. Computed Barriers (kcal mol^{-1}) for the *n*-Ring Flip Pathways of 1 and 2[a]

	computed			
compound	$n = 0$	$n = 1$	$n = 2$	experimental
1 (X = O)	42.4	5.4	17.0	4.6
2 (X = CH$_2$)	66.7	12.3	10.7	9.3

[a] The experimental $\Delta G^{\ddagger}$ values are also reported.

higher than that computed for the same process in benzophenone (either 15.0[8] or 7.5[9] kcal mol^{-1}), with the ring frame of the mesityl groups being even more distorted (by 32°) from planarity[22] to relieve the greater strain of the corresponding transition state. In Figure 2 is reported the tridimensional picture of the map where it can be also seen how the barrier for the two-ring flip (17.0 kcal mol^{-1}) is much higher than that for the one-ring flip pathway (5.4 kcal mol^{-1}).[23] Not only does the latter process appear to be energetically favored but the corresponding barrier matches very satisfactorily to that experimentally determined, the difference being less than 1 kcal mol^{-1} (Table 1).

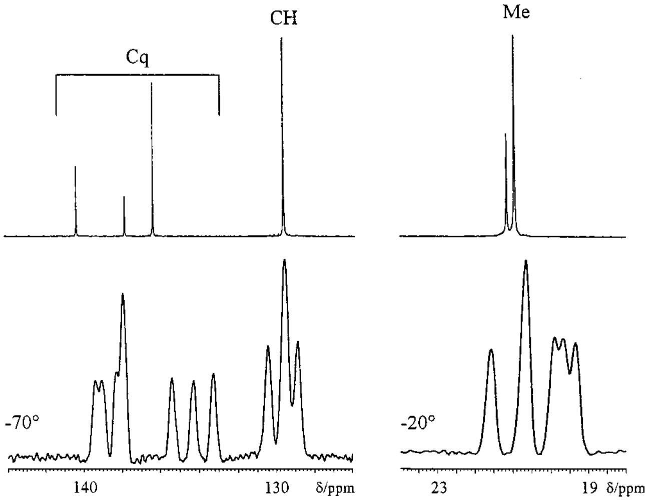

Figure 3. ^{13}C NMR spectrum of dimesitylketone, **1**, in a CD$_2$Cl$_2$ solution at −70 °C (top). The corresponding ^{13}C NMR CPMAS solid-state spectrum (75.4 MHz) at the temperatures indicated is reported (bottom). The signal of the carbonyl carbon is not displayed.

At any temperature[24] between +25 and −100 °C, the ^{13}C NMR CP-MAS solid-state spectrum of **1** (Figure 3, bottom) is quite different from that observed in solution in the same range (Figure 3, top). In particular, the six methyls do not yield two but five lines, the eight quaternary aromatic carbons yield seven rather than three, and the four CH carbons yield three instead of one (Table 1). Only the carbonyl carbon displays a single signal both in the solid state and in solution, and this proves that the increased multiplicity cannot be due to the molecule existing in two different solid phases,[25] as also confirmed by a DSC determination (see Experimental Section). The interpretation of the solid-state spectra of **1** requires that a number of possible situations be analyzed. (i) If the two rings rotate rapidly (fast enantiomerization) and the elements of molecular symmetry coincide with those of the crystals (site symmetry equal to molecular symmetry), the multiplicity would be the same as that observed in solution, which is obviously not the case here. (ii) If the two rings rotate rapidly but the elements of molecular symmetry do not coincide with those of the crystals (site symmetry different from molecular symmetry), the signals of one ring would be distinguishable from those of the other. As an example, the six methyl carbons would yield four lines (intensity ratio 1:1 for the para and 2:2 for the ortho positions), so this model does not fit the observed multiplicity either. (iii) If the two rings do not rotate rapidly and site symmetry is the same as molecular symmetry, we should have a single line for the carbons lying in the same plane of carbonyl (i.e., C=O, C ipso, C para, and Me para) but a pair of lines of double intensity for the methyl and for the quaternary ring carbons in position ortho as well as for the CH carbons in position meta. The six methyl carbons, for instance, would yield only three lines (intensity ratio 2:2:2), a feature again in contrast with the experimental observation. (iv) Finally, if the two rings do not rotate rapidly (which means that two stable enantiomers are present in the solid state) and, in addition, site symmetry is not coincident with molecular

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[23] We checked that the computational approach used here[19] yielded results in agreement with those previously reported[8,9] when applied to benzophenone. For the latter, we calculated dihedral angles for the ground state equal to 35° and barriers equal to 1.6, 7.4, and 10.6 kcal mol^{-1} for the one-, two-, and zero-ring flips, respectively.

[24] Owing to the temperature dependence of the chemical shifts, some accidentally coincident lines could be resolved at different temperatures for different types of carbons.

[25] If this was the case, a single carbon like that of CO would exhibit two lines with an intensity proportional to the ratio of the two phases. See for instance: Aliev, A. E.; Harris, K. D. M.; Apperley, D. C. *J. Chem. Soc., Chem. Commun.* **1993**, 251. Riddell, F. G.; Bernath, G.; Fülöp, F. *J. Am. Chem. Soc.* **1995**, *117*, 2327. Bauer, M.; Harris, R. K.; Rao, R. C.; Apperley, D. C.; Rodger, C. A. *J. Chem. Soc., Perkin Trans. 2* **1998**, 475.

Table 2. Comparison of the Multiplicity of the ^{13}C NMR Spectrum of 1 in Solution (CD_2Cl_2) and in the Solid State at −70 °C^a

signal	δ (ppm) in solution	δ (ppm) in solids
CO	202.8	204.0
C(quat)	140.9 [2], 137.8 [2], 136.3 [4]	139.4, 139.0, 138.3, 137.9 [2], 135.3, 134.3, 133.2
CH	129.7 [4]	130.4, 129.5 [2], 128.8
Me	21.1 [2], 20.9 [4]	21.7, 20.8 [2], 20.0, 19.8, 19.4

^{a} The shifts of the Me signals in the solids are given at −20 °C, since at this temperature these lines overlap less than at −70 °C. The numbers of the corresponding carbons are indicated in brackets.

symmetry, each individual carbon is expected to give a single line. This model agrees with the experiment although, owing to the large number of lines (there are 19 diastereotopic or constitutionally heterotopic carbons in the crystal), some of them are accidentally coincident. In particular, there are two coincident lines for the quaternary, CH, and methyl carbons, yielding, as a whole, 16 resolved signals (Table 2), 15 of which are shown in Figure 3 (the CO line lies outside the displayed range). This model agrees with the result of the X-ray diffraction which shows how the 2-fold symmetry axis of the molecule does not coincide with any element of symmetry of the crystal.

Although less likely, an alternative explanation might be also advanced to account for the three pairs of coincident lines mentioned above. If the rotation of one mesityl ring is assumed to be fast in the NMR time scale (thus yielding two isochronous lines for the corresponding CH, ortho methyl, and ortho quaternary carbons) whereas the rotation of the other is assumed to be slow, then the 16 observed lines would be the consequence of a time-averaged symmetry rather than the result of a fortuitous degeneracy. To help in deciding which of these two alternatives applies, the CP-MAS spectrum of 2,2′,6,6′-tetramethyl benzophenone was obtained. The presence of four rather than six methyl groups should make an accidental degeneracy less likely to occur than in the case of **1**. Indeed, four methyl lines were identified (if one ring had been rotating rapidly, only three lines should have been observed) thus proving that the four ortho positions are diastereotopic in the crystal, as expected for a structure which is chiral in the NMR time scale, even at ambient temperature.

The solid state ^{13}C NMR spectrum of **1**, taken at a temperature as high as 110 °C, still exhibits the same spectral multiplicity without any evidence of an exchange process yet taking place. This indicates, therefore, that the enantiomerization barrier in the crystal must be larger than about 19 kcal mol^{-1} with a difference, with respect to the one measured in solution (4.6 kcal mol^{-1}), which by far exceeds the differences between the barriers measured in the solid and liquid phases for other interconverting conformers and enantiomers.[26]

1,1-Dimesitylethylene (2). Whereas the ^{1}H NMR line width of the para methyl groups of **2** is not affected by temperature changes, that of the ortho methyls broadens on cooling and splits into a pair of equally intense lines, like in the case of **1**, but at a considerably higher temperature (−110 °C in CD_2Cl_2/CHF_2Cl 1:1 v/v). Consequently, a larger free energy of activation (9.2 ± 0.15 kcal mol^{-1}) was obtained by line shape simulation for the corresponding dynamic process (Table 1). The temperature dependence of the methyl ^{13}C NMR signals also displays a similar trend, but in addition, the ^{13}C NMR spectra show how the three lines of the eight quaternary aromatic carbons become four at −110 °C (Table 3). This is because the pair of carbons in positions 1,1′ and 4,4′ of the mesityl rings displays sharp signals at any temperature, being unaffected by the internal motion, whereas the four carbons in positions 2,6,2′,6′ display two anisochronous lines at −110 °C, due to the pairs 2,2′ and 6,6′ becoming diastereotopic at this temperature. Likewise, the single line of the four CH aromatic carbons in positions 3,3′,5,5′ splits into two at the same low temperature (Table 3).[27]

In the propeller structure observed in the crystal,[28] the dihedral angles between the mesityl and ethylene planes are equal to 50° and 58° (the slight deviation from equivalence being possibly the consequence of crystal lattice effects). The most stable conformation we computed[19] for **2** predicts both these angles to be 57°; the close correspondence of the values measured in the crystal with those calculated for the isolated molecule makes the idea that the dihedral angles of **2** should also be about 55° in solution (C_2 symmetry) plausible.

That in solution the conformation is indeed dissymmetric can be made evident by a NMR spectrum taken in a chiral environment at a temperature where the interconversion of the two enantiomers is sufficiently slow. Since past attempts of differentiating analogous enantiomers by means of paramagnetic chiral lanthanide shift reagents were unsuccessful,[29] we performed the experiment using a diamagnetic chiral solvating agent (CSA). As shown in the bottom trace of Figure 4, one of the two ortho methyl signals of **1** (that at 1.75 ppm) splits into two when the 400 MHz ^{1}H spectrum is obtained at −110 °C in the presence of a molar excess (100:1) of an enantiopure Pirkle's alcohol.[30] Although in these conditions all the lines of one enantiomer should be, in principle, distinguishable from those of the other, the corresponding shifts were in practice too close to be resolved, except in the reported case where the separation ($\Delta\nu$ = 3 Hz) happened to exceed the line width. This experiment thus convincingly confirms that the conformation adopted by 1,1-dimesitylethylene in solution is chiral.

The potential energy map computed for **2** yields, as predictable, a barrier for the zero-ring flip pathway (66.7 kcal mol^{-1}) higher than that of **1**, owing to the larger steric hindrance of the CH_2 with respect to the CO moiety. On the contrary, it was not predictable to find the computed barrier for the one-ring flip (12.3 kcal mol^{-1}) higher than that for the two-ring flip (10.7 kcal mol^{-1}) pathway, the latter also agreeing better with the experimental value (Table 1). Opposite to the case of **1**, the computed barriers of **2** are quite close to each other, so the assignment of the two-ring flip as the preferred

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[26] Casarini, D.; Foresti, E.; Lunazzi, L.; Mazzanti, A. *Chem.—Eur. J.* **1999**, *5*, 3501. Lunazzi, L.; Mazzanti, A.; Casarini, D.; De Lucchi, O.; Fabris, F. *J. Org. Chem.* **2000**, *65*, 883. Casarini, D.; Lunazzi, L.; Mazzanti, A.; Simon, G. *J. Org. Chem.* **2000**, *65*, 3207.

[27] Owing to the poor solubility of **1** below −160 °C, the corresponding ^{13}C spectrum could not be obtained in the temperature range where the dynamic process is expected to be detectable.

[28] Data retrieved from the Cambridge Crystallographic Data Center according to ref 7.

[29] Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 477.

[30] R-*l*-1-(9-anthryl)-2,2,2,-trifluoroethanol as in the following: Pirkle, W. H. *J. Am. Chem. Soc.* **1966**, *88*, 1837.

Table 3. Comparison of the Multiplicity of the ^{13}C NMR Spectrum of 2 at Two Different Temperatures in Solution (CHF_2Cl/CD_2Cl_2) and in the Solid State[a]

signal	δ (ppm) at +25 °C in solution	δ (ppm) at −110 °C in solution	δ (ppm) at −110 °C in solids
C(quat)	144.2, 138.8 [2], 136.7 [4], 136.2[2]	143.2, 138.4 [2], 137.2 [2], 136.5 [2], 136.4 [2]	141.5, 139.5, 137.6, 136.1, 135.1 [3], 134.6, 134.0
CH	138.7 [4]	129.5 [2], 129.1 [2]	130.3, 129.1 [3]
CH_2	124.5	124.8	124.5
Me	21.7 [4], 21.1 [2]	21.9 [2], 20.1 [2], 19.9 [2]	23.2, 21.8, 21.1, 20.6, 19.6 [2]

[a] The numbers of the corresponding carbons are indicated in brackets.

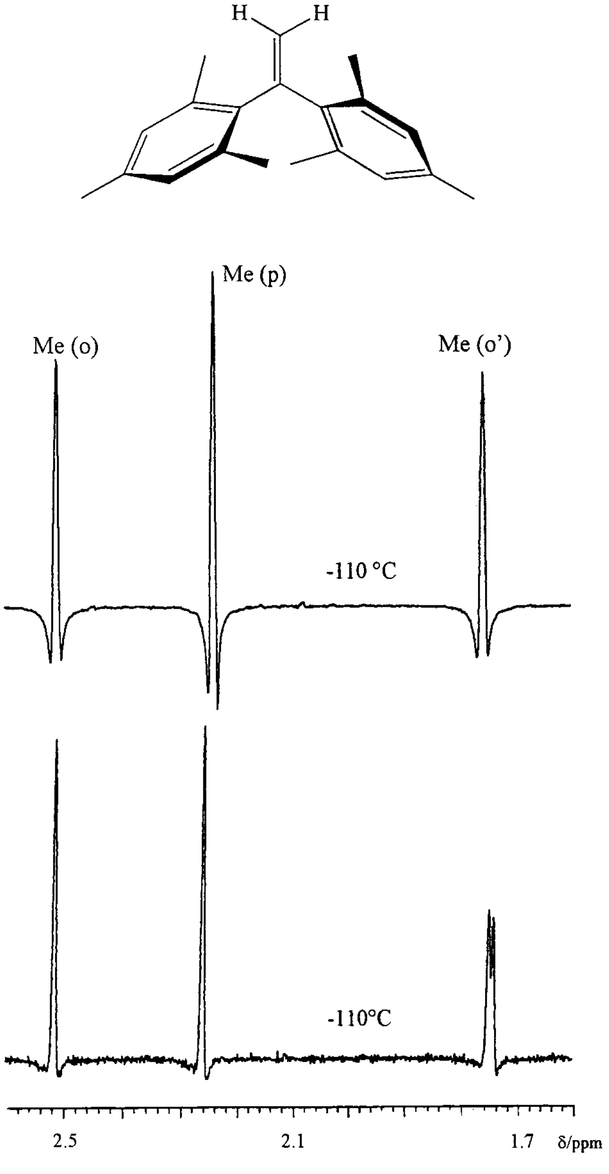

Figure 4. ^1H NMR methyl signals (400 MHz) of 1,1-dimesitylethylene, **2** (in CD_2Cl_2/CHF_2Cl 1:1 v/v), at −110 °C displaying one line for the para (2.25 ppm) and two lines for the diastereotopic ortho substituents (1.75 and 2.52 ppm) (top). The same spectral region in a chiral environment (also at −110 °C) exhibiting a 3 Hz splitting for the line at 1.75 ppm, due to the two conformational enantiomers becoming NMR detectable in these conditions, is displayed (bottom).

pathway has an inherently lower degree of confidence. Independent calculations based on an alternative force field (MMX)[31] also suggest that in **2** the one-ring flip mechanism has a higher barrier than the two-ring flip mechanism.[32] In the less hindered 1,1-diphenylethylene ($Ph_2C{=}CH_2$), the enantiomerization barriers had been computed to be 1.2, 3.0, and 12.9 kcal mol^{-1} for the one-, two-, and zero-ring flip pathways, respectively,[5,7] the same trend being also predicted by the present approach.[19] Thus, in diphenylethylene, the threshold barrier corresponds to a mechanism (one-ring flip) different from that of dimesitylethylene **2**, the switch from the one-ring to the two-ring flip pathway being a consequence of the highly hindered situation occurring in **2**. An additional factor might be also considered to play a role. In the one-ring flip process of dimesitylketone, an Ar−CO conjugation occurs between the carbonyl and the ring coplanar to it. This conjugation is not so effective in the transition state of the one-ring flip of 1,1-dimesitylethylene (Ar−CO conjugation is larger than Ar−C═C conjugation) thus contributing to making the two-ring flip the lowest energy pathway.

The solid-state spectrum of **2** shows, at any temperature, more lines than observed in solution at ambient temperature; their number even exceeds the greater number of lines detected in solution at low temperature (Table 3). This result is only compatible with a situation whereby site symmetry and molecular symmetry are different, an observation which agrees with the result of the X-ray diffraction, where the symmetry axis of the $P2_1/c$ space group is not coincident with the C_2 molecular symmetry axis of **2**.[7,28] Furthermore, to account for the observed number of lines, it is also required that the twisted mesityl rings do not experience a rapid rotation process in the NMR time scale, similar to the case of dimesitylketone **1**. The latter observation confirms that the enantiomerization barrier in the solid must be much higher than in solution.

Dimesitylthioketone (3). The enantiomerization barrier measured for **2** is larger than that of **1**, owing to the larger steric requirements of the ═CH_2 with respect to the C═O moiety. It is thus conceivable to expect for the barrier of dimesitylthioketone **3** a value between those of **1** and **2**, since the C═S moiety has an intermediate dimension. Indeed the ^1H NMR spectrum of **3** displays two lines for the ortho methyl groups at a temperature (−140 °C) higher than that of **1** but lower than that of **2**. Line shape simulation yielded, accordingly, an intermediate $\Delta G^{\ddagger}$ value equal to 6.5 kcal mol^{-1}.

The solid state ^{13}C NMR spectrum at ambient temperature shows again many more lines (17 as a whole) than

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[31] Use was made of the MMX force field, as implemented in the PC Model computer program, Serena Software, Bloomington, IN.

[32] When applied to dimesitylketone, **1**, the MMX computation[31] yielded barriers of 5.0 and 8.5 kcal mol^{-1} for the one-ring and two-ring flip mechanisms, respectively. In the case of 1,1-dimesitylethylene, **2**, the trend was reversed since the barriers were computed to be 9.3 and 7.7 kcal mol^{-1} for the one- and two-ring flip mechanisms, respectively. However, the computed difference between the two pathways still remains quite small, so it cannot be excluded that other types of calculations might lead to an opposite assignment.

Table 4. Comparison of the Multiplicity of the ^{13}C NMR Spectrum of 3 in Solution ($CDCl_3$) and in the Solid State at Ambient Temperature[a]

signal	δ (ppm) in solution	δ (ppm) in solids
CS	244.8	244.5
C(quat)	147.6 [2], 138.6 [2], 135.3 [4]	148.1, 146.8, 139.6 [2], 138.6, 137.8, 134.3, 132.6
CH	130.1 [4]	132.0, 130.9, 129.1, 128.3
Me	21.9 [4], 21.0 [2]	24.6, 23.6, 22.3 [2], 20.8, 19.3

[a] The numbers of the corresponding carbons are indicated in brackets.

the seven lines detected in solution (Table 4). In this case, four lines are displayed by the four CH carbons, thus unambiguously showing that the four meta positions are diastereotopic in the crystalline state. As a consequence, the lines with a double intensity observed for the quaternary and for the methyl carbons (Table 4) are undoubtedly due to accidental coincidences.

Conclusions

It has been demonstrated that two equivalent mesityl rings bonded to a trigonal carbon adopt, in solution, a chiral propeller-like conformation, equal to that determined by X-ray diffraction in the crystalline state. According to MM calculations, the two helical enantiomers interconvert through a one-ring flip pathway in the case of dimesitylketone but through a two-ring flip pathway in the case of 1,1-dimesitylethylene, the computed barriers (5.4 and 10.7 kcal mol^{-1}) being in good agreement with those experimentally determined (4.6 and 9.2 kcal mol^{-1}, respectively). An intermediate value (6.5 kcal mol^{-1}) was measured for the enantiomerization barrier of dimesitylthioketone. The solid-state NMR spectra indicate that these barriers are much higher in the crystal, but only their lower limit (19 kcal mol^{-1}) could be ascertained.

Experimental Section

Materials. Dimesitylketone, 1.[33] To a cooled (-78 °C) solution of mesityllithium, prepared by addition of butyllithium (11 mmol) to a solution of mesityl bromide (2.39 g, 12 mmol in 40 mL of THF), a solution of mesitylaldehyde (1.48 g, 10 mmol in 10 mL of THF) was added. After 30 min, the solution was allowed to warm and was quenched with aqueous NH_4Cl. The product was extracted with Et_2O and dried (Na_2SO_4), and the solvent was removed at reduced pressure. The crude was washed with pentane to give 2.42 g (90%) of pure dimesitylcarbinol. Oxidation with pyiridinium chlorochromate (2.90 g, 13.5 mmol in 50 mol of CH_2Cl_2) at room temperature, followed by filtration on silica, yielded 2.30 g (96%) of almost pure dimesitylketone, purified by crystallization (methanol). Crystals suitable for X-ray analyses were obtained by slow crystallization in methanol. Mp 138−140 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C, TMS): $\delta = 2.13$ (s, 12H, Me), 2.26 (s, 6H, CH_3), 6.82 (s, 4H, CH). ^{13}C NMR (100.6 MHz, $CDCl_3$, 22 °C, TMS): $\delta = 20.7$ (CH_3), 21.1 (CH_3), 129.8 (CH), 136.6 (q), 138.4 (q), 140.0 (q), 202.5 (CO). The DSC trace of **1** was obtained with a scanning rate of 5°/min, heating the sample from -70 to $+160$ °C; the only observed phase transition corresponded to the melting point.

1,1-Dimesitylethylene, 2. Prepared as reported in the literature.[34]

Dimesitylthioketone, 3.[35] To a mixture of mesitylene (25 mL) and $AlCl_3$ (4.3 g, 33 mmol) cooled to -20 °C, thiophosgene (1 mL, 13 mmol, neat) was added dropwise and after 20 min the mixture was slowly heated to 80−90 °C, monitoring the formation of the thioketone by TLC. After 30 min the deep red mixture was cooled to ambient temperature and then poured onto 200 g of crusched ice. The product was extracted with Et_2O, and the organic layers were washed twice with aqueous KOH and then dried over Na_2SO_4. The solvents were removed at reduced pressure followed by distillation of the residual mesitylene. The crude was purified on silica gel in two steps, first on a column eluted with 10:1 v/v petroleum ether/Et_2O and then on preparative TLC (eluent: 10:1 v/v pentane/toluene) to yield 0.40 g (11%) of pure dimesitylthioketone. Blue solid, Mp 92−93 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 22 °C, TMS): $\delta = 2.18$ (s, 12H, Me), 2.34 (s, 6H, CH_3), 6.90 (s, 4H, CH). ^{13}C NMR (50.3 MHz, $CDCl_3$, 22 °C, TMS): $\delta = 21.0$ (CH_3), 21.9 (CH_3), 130.1 (CH), 135.3 (q), 138.6 (q), 147.6 (q), 244.8 (CS).

Crystal Data of Dimesitylketone, 1. $C_{19}H_{22}O$ (266.37), monoclinic, space group $P2_1/n$, $Z = 4$, $a = 10.3430(7)$ Å, $b = 12.5006(8)$ Å, $c = 12.0976(8)$ Å, $\beta = 95.572(2)°$, $V = 1556.75(18)$ Å^3, $D_c = 1.136$ g cm^{-3}, $F(000) = 576$, $\mu_{Mo} = 0.068$ cm^{-1}, $T = 293$ K. Data were collected using a graphite monochromated Mo Kα X-radiation ($\lambda = 0.710\,73$ Å) range of $2.48° < \theta < 25.00°$. Of 13 722 reflections measured, 2730 were found to be independent ($R_{int} = 0.0432$), 2075 of which were considered as observed [$I > 2\sigma(I)$], and were used in the refinement of 181 parameters leading to a final R_1 of 0.0792 and an R_{all} of 0.0924. The structure was solved by direct method and refined by full-matrix least squares on F^2, using SHELXTL 97 program packages. In refinements, weights were used according to the scheme $w = [\sigma^2(F_o{}^2) + (0.1891P)^2 + 0.0000P]^{-1}$, where $P = (F_o{}^2 + 2F_c{}^2)/3$. The hydrogen atoms, including the OH hydrogen, were located by geometrical calculations and refined using a "riding" method. wR_2 was equal to 0.2833. The goodness of fit parameter S was 1.238. The largest difference peak and hole were 0.484 and -0.437 e Å^{-3}. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center, CCDC-145898.

NMR Measurements. The samples for the low-temperature measurements were prepared by connecting to a vacuum line the NMR tubes containing the desired compounds dissolved in some C_6D_6 or CD_2Cl_2 for locking purpose and condensing therein the gaseous solvents by means of liquid nitrogen. The tubes were subsequently sealed in vacuo and introduced into the precooled probe of the 300 MHz spectrometer operating at 75.45 MHz for ^{13}C or the 400 MHz spectrometer operating at 100.6 MHz for ^{13}C. The assignment of the ^{13}C signals was obtained by means of DEPT sequences. The temperatures were calibrated by substituting the sample with a precision Cu/Ni thermocouple before the measurements. Total line shape simulations were achieved by using a PC version of the DNMR-6 program.[36] Since at the low temperatures required to observe the exchange process the intrinsic line width was significantly temperature dependent, the values measured for the line of the para methyl group (which does not experience exchange broadening) were assumed to be equal to that of the two ortho signals. We also checked that errors as large as 50% on this value affected the activation energy by less than 0.05 kcal mol^{-1} in the temperature range investigated.[1a] The high-resolution ^{13}C NMR solid state CP-MAS (cross polarization magic angle spinning) spectra were obtained at 75.45 MHz. The compounds were introduced into a tightly sealed 7 mm zirconia rotor, spun at the magic angle with a speed of 3.0−3.5 kHz. The line assignment was obtained by the "nonquaternary suppression" pulse sequence. The cooling was achieved by means of a flow of dry nitrogen, precooled in a heat exchanger immersed in liquid nitrogen.

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The temperatures within the solid-state probe were calibrated by using the shift dependence of the ^{13}C NMR lines of 2-chlorobutane absorbed upon solid dicalite, assuming a dependence equal to that observed in neat liquid,[37] which had been previously calibrated by the same Cu/Ni thermocouple. The chemical shifts were measured, by replacement, with respect to the lower frequency signal of the adamantane (29.4 ppm).

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