

# Conformational Studies by Dynamic NMR. 80.<sup>1</sup> Cog-Wheel Effect in the Stereolabile Helical Enantiomers of Dimesityl Sulfoxide and Sulfone

Daniele Casarini\*

Chemistry Department, Università della Basilicata, Potenza, Italy

Stefano Grilli,<sup>2</sup> Lodovico Lunazzi, and Andrea Mazzanti\*

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

lunazzi@ms.fci.unibo.it

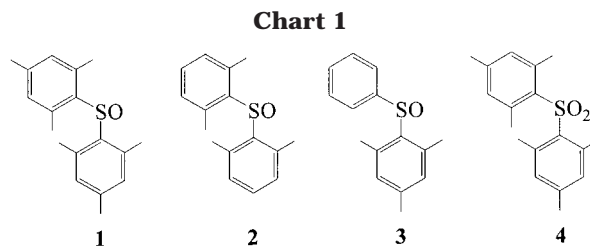
Received December 1, 2000

The <sup>1</sup>H NMR solution spectra of the title compounds display anisochronous lines for the *o*-methyl substituents below  $-170$  °C, due to the existence of two propeller-like M and P conformational enantiomers. The free energies of activation for the interconversion were determined to be 4.5 and 5.0 kcal mol<sup>-1</sup>, respectively, for dimesityl sulfoxide and dimesityl sulfone. Molecular mechanics calculations indicate that the enantiomerization process occurs via a correlated rotation (cog-wheel effect) entailing a one-ring flip (gear-meshing) pathway. <sup>13</sup>C NMR (CP-MAS) spectra and X-ray diffraction show that these helical enantiomers are stable in the crystalline state.

## Introduction

Two bladed molecular propellers comprising two mesityl rings bonded to a trigonal atom (Ar<sub>2</sub>X, with Ar = 2,4,6-trimethylphenyl, X = CO, CS, C=CH<sub>2</sub>, C=SO, C=CROH and R = H, Me, Bu<sup>t</sup>) were found to adopt conformations that entail the existence of pairs of stereolabile M and P enantiomers.<sup>1,3,4</sup> The interconversion process of these enantiomers occurs via a correlated rotation of the aromatic rings (cog-wheel effect) which can be interpreted in terms of the so-called ring-flip mechanism.<sup>5–7</sup> Similar helical enantiomers should in principle occur also in the case of two mesityl rings bonded to a tetrahedral atom, as suggested by the observations carried out on much more hindered derivatives.<sup>8,9</sup>

Dimesityl sulfoxide **1** and dimesityl sulfone **4** (see Chart 1) are simple prototypes of such a situation and were selected to check the validity of this prediction.



## Results and Discussion

Molecular Mechanics calculations (MMX force field<sup>10</sup>) indicate indeed that dimesityl sulfoxide **1** adopts an asymmetric propeller-like conformation (*C*<sub>1</sub> point group) which entails the existence of the two M and P enantiomers displayed in Scheme 1. One of the aromatic rings has its plane nearly parallel to the SO bond (the C<sub>ortho</sub>–C<sub>ipso</sub>–S–O dihedral angle being  $-9^\circ$ ) whereas the other one is nearly parallel to the direction of the lobe bearing the unpaired electrons (as a consequence the second ring is almost orthogonal to the S=O bond, having the corresponding C<sub>ortho</sub>–C<sub>ipso</sub>–S–O dihedral angle equal to  $+107^\circ$ ). As will be subsequently reported, the X-ray structure of the analogously hindered sulfoxide **2** shows indeed that one ring is nearly coplanar and the other nearly orthogonal to the S=O bond (vide infra).

Accordingly, when the mesityl–SO rotation is blocked, the four *o*-methyl groups become diastereotopic and are thus expected to display four anisochronous NMR lines in the solution spectrum. Such a situation was experimentally detected in the low temperature <sup>1</sup>H spectra of **1** reported in Figure 1. At temperatures higher than  $-140$  °C the aliphatic region displays only two lines, with the

(1) (a) Part 78. Grilli, S.; Lunazzi, L.; Mazzanti, A.; Casarini, D.; Femoni, C. *J. Org. Chem.* **2001**, *66*, 488–495. (b) Part 79. Grilli, S.; Lunazzi, L.; Mazzanti, A.; Mazzanti, G. *J. Org. Chem.* **2001**, *66*, 748–754.

(2) In partial fulfillment of the requirements for the Ph.D. in Chemical Sciences, University of Bologna.

(3) Nugiel, D. A.; Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 3357.

(4) Biali, S. E.; Nugiel, D. A.; Rappoport, Z. *J. Am. Chem. Soc.* **1989**, *111*, 846. Nugiel, D. A.; Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1989**, *111*, 8181.

(5) (a) Kurland, R. J.; Schuster, I. I.; Colter, A. K. *J. Am. Chem. Soc.* **1965**, *87*, 2279. (b) Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 1535. (c) Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26. (d) Mislow, K. *Chemtracts: Org. Chem.* **1989**, *2*, 151. (e) Glaser, R. in *Acyclic Organonitrogen Stereodynamics*; Lambert, J. B.; Takeuchi, Y., Eds.; VCH: New York, 1992; Chapter 4, p 123.

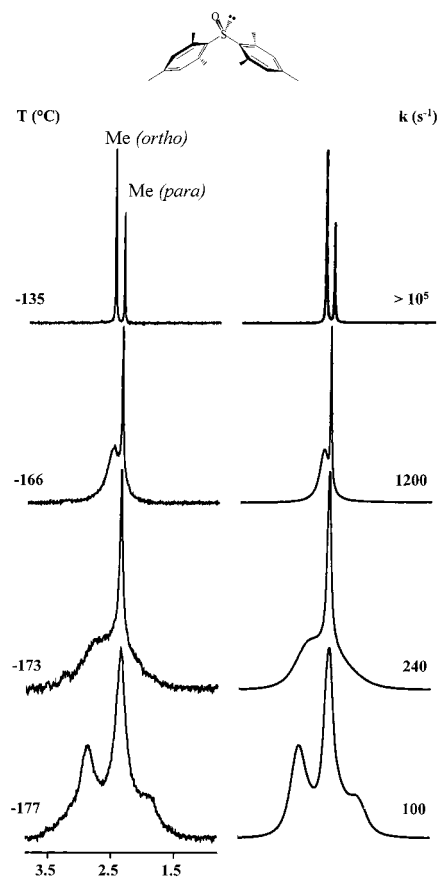
(6) Selzer, T.; Rappoport, Z. *J. Org. Chem.* **1996**, *61*, 7326.

(7) Rappoport, Z.; Biali, S. E. *Acc. Chem. Res.* **1997**, *30*, 307.

(8) (a) Akkerman, O. S.; Coops, J. *Rec. Trav. Chim. Pays Bas* **1967**, *86*, 755. (b) Akkerman, O. S. *Rec. Trav. Chim. Pays Bas* **1970**, *89*, 673.

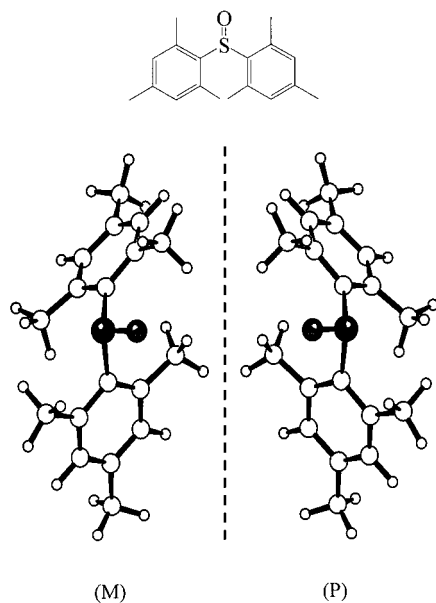
(9) Lam, W. J.; Martin, J. C. *J. Org. Chem.* **1981**, *46*, 4458.

(10) Computer package PC Model V 7.5 Serena Software, Bloomington, IN.



**Figure 1.** Experimental  $^1\text{H}$  NMR (300 MHz) signals of the methyl groups of dimesityl sulfoxide **1** in  $\text{CHF}_2\text{Cl}/\text{CHFCl}_2$  (4:1 v/v) as function of temperature (left). On the right is reported the computer simulation obtained with the rate constants reported.

**Scheme 1. Molecular Mechanics Computed Structures of the M and P Enantiomers of Dimesityl Sulfoxide, 1**



4:2 intensity ratio expected for the enantiotopic *o*- and *p*-methyl groups. On further cooling the line of the ortho broadens much more than that of the *p*-methyl groups and eventually splits, at  $-177\text{ }^\circ\text{C}$ , into three lines (2.9, 2.4, and 2.0 ppm) with a 2:1:1 relative intensity ratio,

the central of these lines (2.4 ppm) being overlapped by that of the *p*-methyl signal. The existence of this hidden line is required to make the weighted average of the shifts compatible with that (2.55 ppm) of the single ortho line observed at higher temperatures as well as to achieve a proper line shape simulation (see Figure 1). Furthermore, when the signal of the *p*-methyl substituents is eliminated, as in the case of the purposely synthesized 2,2',6,6'-tetramethyldiphenyl sulfoxide **2**, this line becomes visible, as predicted, between the other two signals (see Figure 4). The presence of only three lines for the four diastereotopic *o*-methyl substituents in the spectrum of **1** (as well as in that of **2**) is due to the high-frequency signal comprising two peaks separated by less than the line width, which accounts for its double intensity.

Even at the lowest attained temperature ( $-177\text{ }^\circ\text{C}$ ) the width of the *o*-methyl lines of **1** is broader than that of the *p*-methyl, indicating that the rotation rate is not yet wholly negligible. Accordingly, a line shape simulation provided a rate constant of  $100\text{ s}^{-1}$  at that temperature (Figure 1, bottom) from which a free energy of activation of  $4.5 \pm 0.2\text{ kcal mol}^{-1}$  was derived: this value is equal to those derived by the rate constants determined at higher temperatures (the same value was also obtained for the barrier of the analogous sulfoxide **2**). In principle, also the two *p*-methyl substituents of **1** should give two, rather than a single line, since the two mesityl rings are not enantiotopic anymore at  $-177\text{ }^\circ\text{C}$ ; however, such nonequivalence is much too small to allow the resolution of the *p*-methyl signals, given the relatively large bandwidth caused by the viscosity at such low temperatures.<sup>11</sup>

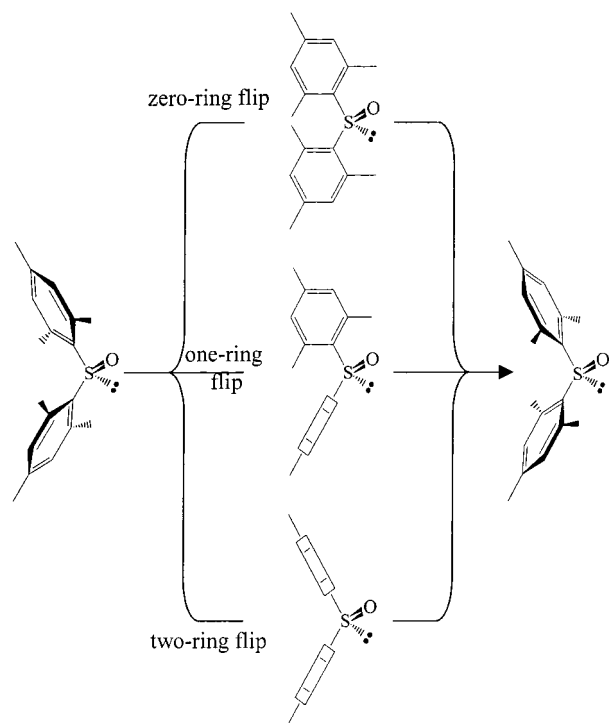
As discussed in previous works, the two mesityl rings are expected to behave as a two-toothed gear undergoing a correlated rotation (cog-wheel effect) which reverses the helicity, allowing the interconversion of the M and P conformational enantiomers of Scheme 1 to take place. This process can be analyzed in terms of the mentioned *n*-ring flip pathways, with  $n = 0, 1,$  and  $2$  (Scheme 2).<sup>5-7</sup>

The zero-ring flip mechanism corresponds to a conrotatory motion leading to a transition state whereby the two rings are both coplanar with a reference plane (corresponding to the C–S–C plane bisecting the angle defined by O, S, and the lone pair orbital) and thus coplanar with each other. In the case of substituents as large as mesityl, however, this would generate such a crowded situation as to make the corresponding energy extremely high,<sup>9</sup> leading to an interconversion barrier much larger than the experimental value of  $4.5\text{ kcal mol}^{-1}$ . For this reason such a theoretical model does not seem to be plausible.

The one-ring flip is a disrotatory motion which leads to a transition state with one ring orthogonal to and the other coplanar with the mentioned reference plane (a situation also referred to as gear-meshing<sup>9</sup>), whereas the two-ring flip is a conrotatory motion whose transition state has both rings orthogonal to the reference plane (gear-clashing<sup>9</sup>). Either of these two mechanisms might, in principle, take place so that the whole enantiomerization process was modeled by means of a Molecular Mechanics calculation in order to find out which is the most accessible transition state.<sup>10</sup> The energy of the

(11) The signal of the meta protons, which should also split at low temperature, were not observed being overlapped by the lines of the solvent ( $\text{CHF}_2\text{Cl}/\text{CHFCl}_2$ ). On the other hand the  $^{13}\text{C}$  spectra could not be obtained, due to the insufficient solubility of the compounds at such low temperatures.

**Scheme 2. Schematic Representation of the Transitions States Corresponding to Zero-, One-, and Two-Ring Flip Pathways for Dimesityl Sulfoxide, **1****

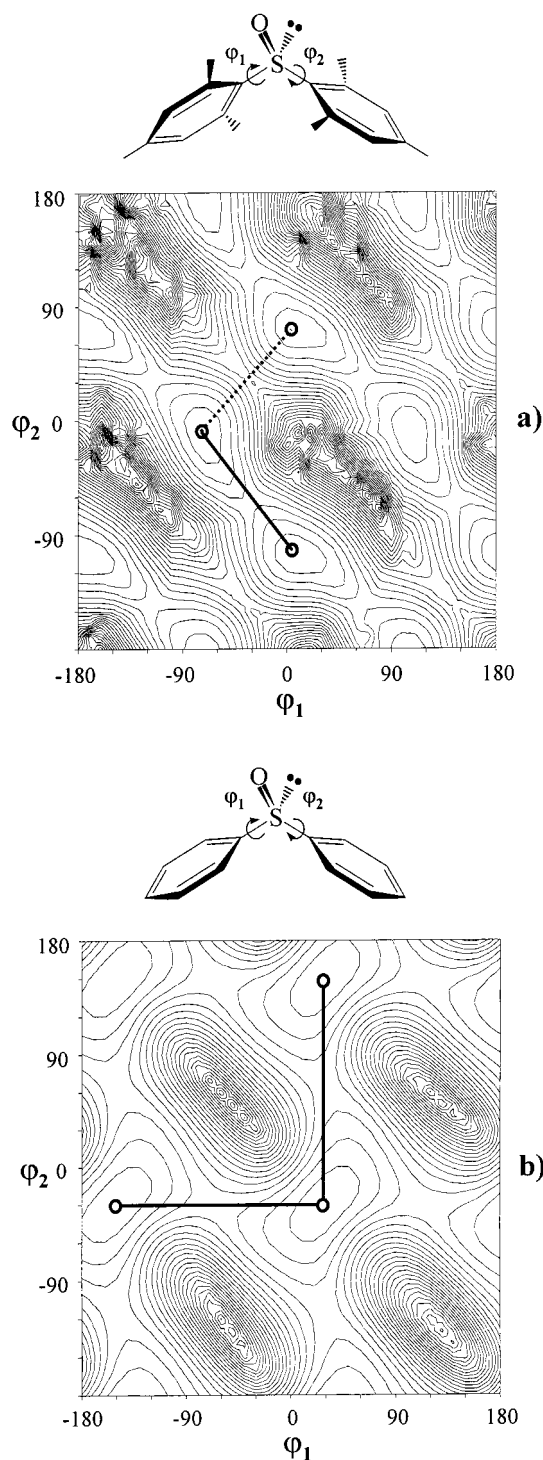


molecule was computed by driving each of the two mesityl-SO dihedral angles ( $\varphi_1$  and  $\varphi_2$ ) from  $-180^\circ$  to  $+180^\circ$ , and the three-dimensional surface obtained in this way was appropriately sliced, yielding the two-dimensional contour plot reported in Scheme 3a.

There, the circles represent the ground state of the enantiomers, and the connecting lines indicate the possible interconversion pathways. The dotted line describes the two-ring flip mechanism, which has a computed barrier of  $7.9 \text{ kcal mol}^{-1}$  and the full line the one-ring flip pathway, whose barrier is  $3.2 \text{ kcal mol}^{-1}$ . Not only the latter corresponds to the lower value, but is also the one showing the best agreement with the experimental measurement (the line for the zero-ring flip pathway was not displayed since computations predict an unrealistic high barrier of  $21 \text{ kcal mol}^{-1}$  for the interconversion). It seems thus conceivable that the one-ring flip is the pathway followed by dimesityl sulfoxide **1** to achieve the enantiomerization of the M and P antipodes.

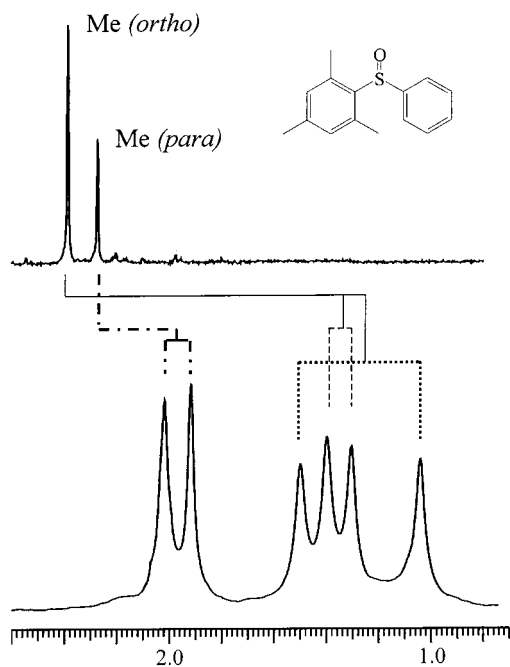
It should be also observed that the lines connecting the enantiomers of Scheme 3a have a diagonal trend with respect to the axes where the variation of the two Mes-SO dihedral angles  $\varphi_1$  and  $\varphi_2$  are reported. This shows that the theoretical description of the process requires the two rotations to be correlated since the torsion of one ring drives a concomitant torsion of the second one. Had the rotation of one mesityl ring been independent of the other, the connecting lines would have had a trend either parallel or perpendicular to the axes.<sup>1b</sup> To clarify this point the interconversion process was modeled also for diphenyl sulfoxide ( $\text{Ph}_2\text{S}=\text{O}$ ) which, being less sterically hindered, is not expected to display cog-wheel effects. The calculations indicate that, contrary to **1**, diphenyl sulfoxide adopts a symmetric (butterfly-like) ground state conformation ( $C_s$  point group), with both rings having the same  $28^\circ$  dihedral angle with respect to the SO bond (see

**Scheme 3. (a) Two-Dimensional Contour Plot of the Energy Surface of **1** Computed as Function of the Ar-SO Dihedral Angles  $\varphi_1$ ,  $\varphi_2$ . (b) Corresponding Plot for Diphenyl Sulfoxide**



Scheme 3b), and also that the Ph-SO rotation barrier is too low (about  $1.6 \text{ kcal mol}^{-1}$ ) to be detectable by NMR experiments in solution. As shown in Scheme 3b, the corresponding rotation pathways turn out to be represented, in this case, by lines parallel or perpendicular to the axes.

In addition to this theoretical indication, an experimental support for the existence of a correlated motion in **1** can be found in the very low barrier measured for the rotation process of **1** compared with those of other

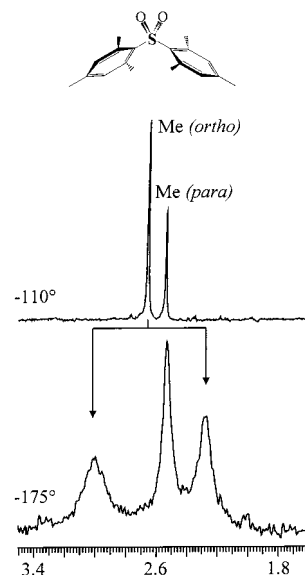


**Figure 2.** The  $^1\text{H}$  NMR spectrum (300 MHz) for the *o*- and *p*-methyl groups of mesityl phenyl sulfoxide **3** yields two lines (intensity ratio 2:1) at ambient temperature in  $\text{CD}_2\text{Cl}_2$  (upper trace). Six lines, with the same integrated intensity, are detected when the spectrum is taken at  $-100\text{ }^\circ\text{C}$  in a chiral environment (lower trace). In these conditions two lines correspond to the *p*- and four to the *o*-methyl substituents (see text).

aryl sulfoxides:<sup>12–14</sup> a correlated motion renders in fact more facile the interconversion processes.<sup>5b,7</sup> To further strengthen this interpretation, we investigated the NMR spectrum of mesitylphenyl sulfoxide, **3** which is the less hindered analogue of **1**.

On lowering the temperature, the  $^1\text{H}$  and  $^{13}\text{C}$  lines of the *o*-methyl substituents of **3** split, at about  $-100\text{ }^\circ\text{C}$ , into a pair of equally intense lines since the restriction of the mesityl–SO rotation has placed one of the *o*-methyls closer than the other to the oxygen atom.<sup>15</sup> Despite the lower steric requirements, the rotation barrier of **3** turns out to be much higher (the measured value is  $9.0\text{ kcal mol}^{-1}$ ) than that of **1** and **2**. This is because the mesityl rotation is now independent of that of the phenyl and cannot take advantage of the cog-wheel effect for lowering the corresponding barrier. A further contribution to the increasing of the barrier in **3** might also arise from the stabilization of the corresponding ground state conformation where the steric hindrance is lower than in that of **2** or **1**.

Since the sulfur atom in **3** corresponds to a chiral center, the compound is actually constituted by a pair of configurational enantiomers, each of which should yield distinct NMR spectra when the environment is made chiral. As shown in Figure 2, both enantiomers display restricted rotation about the mesityl–SO bond in that the *o*-methyl groups exhibit, at  $-100\text{ }^\circ\text{C}$ , four lines (two



**Figure 3.**  $^1\text{H}$  NMR signals (300 MHz) of the methyl groups of dimesityl sulfone **4** in  $\text{CHF}_2\text{Cl}/\text{CHFCl}_2$  (4:1 v/v) at temperatures above and below the coalescence point.

for each enantiomer) in the presence of a chiral solvating agent (CSA).<sup>16</sup> Line shape simulation at various temperatures yielded two rotation barriers that have essentially the same value ( $9.2\text{ kcal mol}^{-1}$ ) as that previously measured for the racemate in a nonchiral solvent.

Dimesityl sulfone **4** is expected to have a chiral helical conformation with a  $C_2$  rather than a  $C_1$  symmetry, thus entailing two pairs of diastereotopic *o*-methyl substituents, with the *p*-methyl groups remaining homotopic. Accordingly, the  $^1\text{H}$  NMR single line for the *o*-methyls splits into two lines with equal integrated intensity at  $-175\text{ }^\circ\text{C}$  (Figure 3). Line shape simulation yielded a free energy of activation of  $5.0\text{ kcal mol}^{-1}$ , and the slightly higher value with respect to that ( $4.5\text{ kcal mol}^{-1}$ ) determined for sulfoxides **1** and **2** probably reflects the increased hindrance due to the presence of a second oxygen atom substituting the lone pair electrons.

It is also worth noticing that in the  $-175\text{ }^\circ\text{C}$  spectrum of Figure 3 the *o*-methyl signal at higher frequency (3.0 ppm) has a width (52 Hz) much broader than that (32 Hz) of its lower frequency companion (at 2.25 ppm). Because of its higher frequency position, this line is likely to correspond to the pair of methyls closer to either of the oxygen atoms,<sup>17</sup> thus experiencing a greater steric hindrance than the other pair. The rotation rate about these two Me–aryl bonds is accordingly expected to be slower and, although the temperature corresponding to the decoalescence into three separate lines could not be attained, the occurrence of a restricted Me–Ar rotation seems the most plausible explanation for the quite large differential line broadening observed here, as reported in a number of other cases.<sup>18</sup>

(16) An excess (molar ratio 3:1) of *R*-1-(9-anthryl)-2,2,2-trifluoroethanol was employed. See: Pirkle, W. H. *J. Am. Chem. Soc.* **1966**, *88*, 1837.

(17) Proton signals close to the oxygen atoms of  $\text{SO}_2$  moiety are known to be significantly shifted to higher frequencies. According to MMX calculations,<sup>10</sup> the average distance from the nearest oxygen atom in sulfone **4** are  $2.79\text{ \AA}$  for one pair of methyls and  $3.25\text{ \AA}$  for the other pair. These values are close to those found in the crystalline state<sup>20</sup> ( $2.78$  and  $3.10\text{ \AA}$ ).

(18) Anderson, J. E. *J. Chem. Soc., Chem. Commun.* **1996**, 93 and references quoted therein.

(12) Buchanan, G. W. *J. Org. Chem.* **1975**, *40*, 2537.

(13) Casarini, D.; Foresti, E.; Gasparrini, F.; Lunazzi, L.; Macciantelli, D.; Misiti, D.; Villani, C. *J. Org. Chem.* **1993**, *58*, 5674.

(14) Jennings, W. B.; Kochanewycz, M. J.; Lunazzi, L. *J. Chem. Soc. Perkin Trans. 2* **1997**, 2271.

(15) The MMX calculations<sup>10</sup> predict the distances between the oxygen and the carbon atoms of the *o*-methyl substituents to be  $3.18$  and  $4.12\text{ \AA}$ , respectively.



**Table 1.**  $^{13}\text{C}$  NMR Shifts of **1**, **2**, **4** in the Solid State

	dimesityl sulfoxide ( <b>1</b> )	2,2',6,6'-tetramethyldiphenyl sulfoxide ( <b>2</b> )	dimesityl sulfone ( <b>4</b> )
C(quat)	142.6, 139.4 [4], 138.0, 134.4 [2]	141.9, 140.5 [2], 139.1, 138.6, 136.2	143.0, 142.0, 139.8, 139.5, 138.2 [3], 137.5
CH	132.5 [3], 128.3	133.1, 131.3 [2], 130.5, 129.1, 128.6	132.4 [4]
Me	22.5, 21.6 [2], 20.8, 20.2, 18.4	22.7, 20.3, 19.8 [0.5], 19.0 [0.5], 17.3	23.9, 22.2, 21.6, 21.0, 19.8 [2]

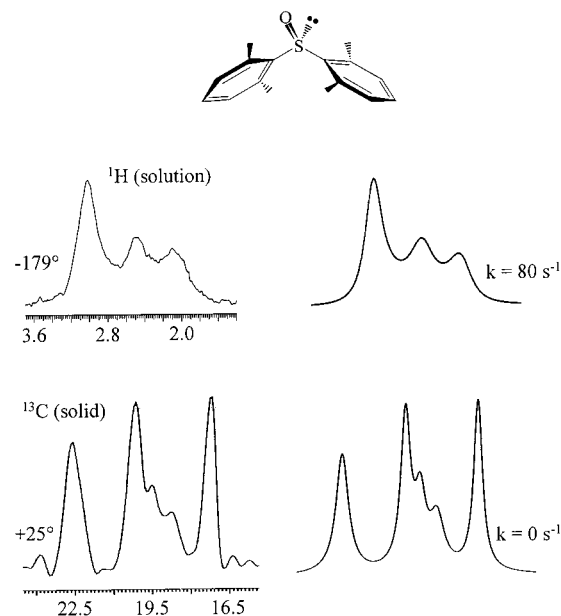
Whereas the enantiomers of **1**, **2**, **4** interconvert very rapidly at ambient temperature in solution, they are quite long living in the solid state. This can be demonstrated by means of the  $^{13}\text{C}$  NMR CP-MAS spectrum of crystalline **1** which displays at ambient temperature five lines (Table 1) for the six methyl carbons, the shifts of two such lines being accidentally coincident. To have the *o*-methyl groups diastereotopic, the P and M enantiomers must be stable with respect to the NMR time scale. Five lines are likewise observed (again two shifts are accidentally coincident) for the six methyl groups in the CP-MAS spectrum of dimesityl sulfone **4** at ambient temperature (Table 1). As previously mentioned, the helical enantiomers of dimesityl sulfone **4** comprise a  $C_2$  symmetry axis and should therefore display, when the interconversion of the enantiomers is blocked, only three lines (two for the *o*- and one for the *p*-methyl substituents), as observed in solution at low temperature. The greater multiplicity detected in the solid-state NMR spectrum is a consequence of the molecular symmetry not being coincident with the site symmetry of the crystal, a feature which makes the two mesityl rings diastereotopic.<sup>19</sup> The space group *Pbca* of crystalline **4**, in fact, has 2-fold symmetry axes not coincident with the  $C_2$  axis of the molecule.<sup>20</sup> This also accounts for the six lines spectrum (one of these peaks has a triple intensity due to the accidental coincidence of three signals) exhibited by the eight quaternary ring carbons (Table 1): four equally intense lines would have been observed had molecular and site symmetry been coincident.

A different kind of CP-MAS spectrum was observed for the solid 2,2',6,6'-tetramethyldiphenyl sulfoxide, **2**, in that the four *o*-methyl groups exhibit five  $^{13}\text{C}$  lines (Figure 4). Two such lines have a lower intensity, but their sum corresponds to the intensity of each of the remaining three. As reported in Table 1, such pairs of weaker lines were not observed for any of the aromatic carbon signals, their number and relative intensity corresponding to the expected 12 aromatic carbon atoms. In principle the five methyl lines might be explained by the presence of two solid phases, each exhibiting a spectrum with chemical shifts different from those of the other, although it seems unlikely that solely in the case of a single methyl group such a difference had become detectable, at variance with the numerous reported examples<sup>21</sup> where the great majority of lines does split in the presence of two solid phases. Actually a differential scanning calorimetry (DSC) determination (see Experi-

(19) Casarini, D.; Lunazzi, L.; Macciantelli, D. *J. Org. Chem.* **1988**, *53*, 182 and references quoted therein.

(20) Chawdhury, S. A.; Hargreaves, A. *Acta Crystallogr. Sect. B* **1971**, *26*, 548. See also: Cambridge Structural Data Base by Cambridge Crystallographic Data Center Ver. 2.3.8 1999.

(21) Olivieri, A.; Paul, I. C.; Curtin, D. Y. *Magn. Reson. Chem.* **1990**, *28*, 119. 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.



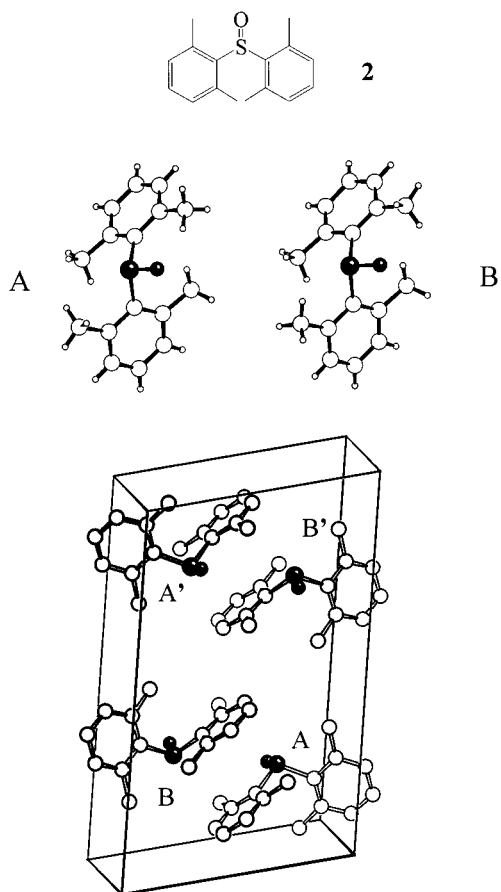
**Figure 4.** NMR Spectra of the aliphatic region of 2,2',6,6'-tetramethyldiphenyl sulfoxide **2**, taken in conditions where the diastereotopicity of the methyl substituents becomes detectable. Top: Experimental  $^1\text{H}$  spectrum (300 MHz) in solution ( $\text{CHF}_2\text{-Cl}/\text{CHFC}_2\text{Cl}$  4:1 v/v) at  $-179^\circ\text{C}$ , displaying three resolved lines (left) and computer simulation (right) obtained with the rate constant indicated. Bottom: Experimental  $^{13}\text{C}$  solid state CP-MAS spectrum (75.45 MHz) at ambient temperature, displaying five resolved lines (left) and computer simulation (right) obtained assuming six appropriately spaced lines<sup>22</sup> with a 1:1:2:1:1:2 relative intensity and a negligible rate constant.

mental Section) showed that only a single phase is present in crystalline **2**, the only phase change occurring at the melting point ( $+146.5^\circ\text{C}$ ).

As an alternative hypothesis, the crystal cell might contain two independent molecules that would thus experience two different spatial environments yielding, as a consequence, two distinct NMR spectra (again it should be admitted that only in the case of a single methyl signal<sup>22</sup> is the difference large enough to be experimentally visible). Actually a X-ray diffraction determination (see Experimental Section) shows that in the crystal cell of **2** (*P*-1 point group) there are four molecules, two with a P and two with an M structure (heterochiral crystals), but that there are only two independent molecules (with the same chirality), in that the two corresponding enantiomers are related by a reflection through the center of symmetry of the crystal. This result explains the splitting observed in the NMR spectrum because, in addition to occupying distinct sites, the two independent molecules also have slightly dissimilar propeller-like structures, with a few geometrical parameters exhibiting differences that exceed the experimental errors.

In Figure 5 (top) the two structures of **2** (A and B) have been represented from the same perspective point of view of the computed structure for **1** in Scheme 1. All these

(22) It should be outlined that the methyl line at highest frequency (Figure 4, bottom left) is definitely broader than the other four and could be simulated (Figure 4, bottom right) only assuming that it is constituted by two equally intense peaks with a separation (18 Hz) smaller than the line width (32 Hz). This suggests that this line is actually a nonresolved doublet, so that there is also a second methyl substituent which experiences the effect of two different sites.



**Figure 5.** X-ray diffraction structures (A and B) for the two independent molecules of **2** (top). Underneath is shown the elementary cell containing four molecules of **2** (i.e., the two pairs of enantiomers A, A' and B, B').

propeller-like structures are extremely similar, having one ring nearly parallel and the other nearly orthogonal to the S=O bond. The experimental dihedral angles for the nearly parallel ring are  $-9.1^\circ$  and  $-9.6^\circ$ , respectively, for the structures A and B of **2**, both values being quite close to that ( $-9^\circ$ ) computed for **1**. The dihedral angles for the ring *quasi* orthogonal to the S=O bond are  $+113.2$  and  $+112.8$  for the structures A and B, respectively: also these values are in reasonable agreement with that ( $+107^\circ$ ) computed for **1**. In Figure 5 (bottom) is also reported the crystal cell of **2** displaying the two independent molecules A and B, as well as their enantiomeric forms A' and B'.

### Experimental Section

**Material.** Dimesityl sulfoxide (**1**),<sup>23</sup> 2,2',6,6'-tetramethyldiphenyl sulfoxide (**2**),<sup>23</sup> and mesityl phenyl sulfoxide (**3**)<sup>24</sup> were prepared according to known procedures. Dimesityl sulfone (**4**) was prepared by stirring (4 h) at ambient temperature a mixture of mesityl sulfonyl chloride (10 mmol), mesitylene (10 mL), and  $\text{AlCl}_3$  (25 mmol, 3.32 g). After addition of aqueous  $\text{NH}_4\text{Cl}$  and extraction with  $\text{Et}_2\text{O}$ , the organic layers were dried ( $\text{Na}_2\text{SO}_4$ ), and the solvent was removed at reduced pressure. The crude was purified by crystallization (pentane/ $\text{Et}_2\text{O}$ , yield 90%).

**Dimesityl sulfoxide (1):** white solid mp  $153.5\text{--}154^\circ\text{C}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz,  $25^\circ\text{C}$ )  $\delta$  2.20 (6H, s, *p*-Me), 2.40 (12H, s, *o*-Me), 6.80 (4H, s, CH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50.3 MHz,  $25^\circ\text{C}$ ),  $\delta$  19.4 (4 *o*-Me), 20.8 (2 *p*-Me), 131.0 (CH), 136.4 (2 quat), 138.3 (4 quat), 140.4 (2 quat).

**2,2',6,6'-Tetramethyldiphenyl sulfoxide (2):** white solid, mp  $146.5^\circ\text{C}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $25^\circ\text{C}$ )  $\delta$  2.45 (12H, s, Me), 7.01 (4H, d,  $J = 7.6$  Hz, *m*-CH), 7.20 (2H, t,  $J = 7.6$  Hz, *p*-CH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz,  $25^\circ\text{C}$ ),  $\delta$  19.5 (4 Me), 130.4 (4 *m*-CH), 130.5 (2 *p*-CH), 138.5 (4 quat), 139.4 (2 quat). Anal. Calcd for  $\text{C}_{16}\text{H}_{18}\text{OS}$ : C, 74.38; H, 7.02; S, 12.41. Found: C, 74.43; H, 6.94; S, 12.37.

**Mesityl phenyl sulfoxide (3):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz,  $25^\circ\text{C}$ )  $\delta$  2.29 (3H, s, *p*- $\text{CH}_3$ ), 2.42 (6H, s, *o*- $\text{CH}_3$ ), 6.88 (2H, s, CH, Mes), 7.42 (5H, m, CH, Ph);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50.3 MHz,  $25^\circ\text{C}$ ),  $\delta$  19.3 (*o*- $\text{CH}_3$ ), 21.2 (*p*- $\text{CH}_3$ ), 124.5 (CH), 128.8 (CH), 129.5 (CH) 130.7 (CH), 132.1 (quat), 139.9 (2 quat), 142.2 (quat), 144.0 (quat).

**Dimesityl sulfone (4):** white solid, mp  $204\text{--}205^\circ\text{C}$ ;<sup>24</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $25^\circ\text{C}$ )  $\delta$  2.28 (6H, s, *p*- $\text{CH}_3$ ), 2.42 (12H, s, *o*- $\text{CH}_3$ ), 6.87 (4H, s, CH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz,  $25^\circ\text{C}$ ),  $\delta$  20.9 (*p*- $\text{CH}_3$ ), 21.6 (*o*- $\text{CH}_3$ ), 131.9 (CH), 137.9 (2 quat, C-S), 138.4 (4 quat), 142.2 (2 quat).

**NMR Measurements.** The assignment of the  $^{13}\text{C}$  NMR signals was carried out by DEPT sequence. 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  $\text{C}_6\text{D}_6$  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  $^{13}\text{C}$ . The assignment of the  $^{13}\text{C}$  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.<sup>26</sup> Since at the low temperatures required to observe the exchange process the intrinsic line width of **1** was significantly temperature dependent, the widths measured for the line of the *p*-methyl group (which does not display a noticeable exchange broadening) was assumed to remain equal to that of the two ortho signals also in the exchange region. In the case of **2**, where there is not a line for the *p*-methyl groups, the ratio between the line width of the compound and that of the solvent was determined in the range  $-90^\circ$  to  $-150^\circ\text{C}$  where the width was only dependent upon the viscosity of the solution. The values of this ratio were extrapolated below  $-150^\circ\text{C}$  (they were found, however, to remain almost constant) where the exchange process start to take place and the line width of the solvent determined in the appropriate range ( $-169^\circ$  to  $-179^\circ\text{C}$ ). By multiplying the solvent line width by this ratio, a reasonable value was obtained for the intrinsic line width of the ortho signal of **2** in the temperature range of interest.<sup>27</sup> We also checked that errors as large as 50% on the intrinsic line width affected the activation energy by less than 0.05 kcal  $\text{mol}^{-1}$  in the range investigated. The high resolution  $^{13}\text{C}$  NMR solid-state CP-MAS 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 about 3.5 kHz. The line assignment was obtained by the "nonquaternary suppression" pulse sequence. The chemical shifts were measured, by replacement, with respect to the lower frequency signal of the adamantane (29.4 ppm).

**DSC Measurements.** This determination was obtained with a scanning rate of  $5^\circ/\text{min}$ , heating a sample of **2** from  $-50^\circ$  to  $+150^\circ\text{C}$ .

**X-ray Diffraction.** Crystal data of 2,2',6,6'-Tetramethyldiphenyl sulfoxide:  $\text{C}_{16}\text{H}_{18}\text{OS}$  (258.36), triclinic, space group

(25) Maclean, M. E.; Adams, R. *J. Am. Chem. Soc.* **1933**, *55*, 4683.

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

(27) Grilli, S.; Lunazzi, L.; Mazzanti, A. *J. Org. Chem.* **2000**, *65*, 3563. Casarini, D.; Lunazzi, L.; Mazzanti, A. *J. Org. Chem.* **1998**, *63*, 9125. Casarini, D.; Lunazzi, L.; Mazzanti, A. *J. Org. Chem.* **1997**, *62*, 7592.

(23) Bast, S.; Andersen, K. *J. Org. Chem.* **1968**, *33*, 846

(24) Czarnik, A. W. *J. Org. Chem.* **1984**, *49*, 924 and Lupatelli, P.; Ruzziconi, R.; Scafato, P.; Degl'Innocenti, A.; Paolobelli, A. P. *Synth. Commun.* **1997**, *27*, 441.

$P-1$ ,  $Z = 4$ ,  $a = 8.0112(10)$ ,  $b = 10.8828(14)$ ,  $c = 17.6700(22)$  Å,  $\alpha = 74.747(3)$ ,  $\beta = 88.235(3)$ ,  $\gamma = 68.888(3)$ ,  $V = 1382.5(3)$  Å<sup>3</sup>,  $D_c = 1.241$  g cm<sup>-3</sup>,  $F(000) = 552$ ,  $\mu_{M_0} = 0.220$  cm<sup>-1</sup>,  $T = 293$  K; the unit cell contains two independent molecules, both of the same chirality. Data were collected using a graphite monochromated Mo-K $\alpha$  X-radiation ( $\lambda = 0.71073$  Å) range  $1.20^\circ < \theta < 30.00^\circ$ . Of 18615 reflections measured, 8030 were found to be independent ( $R_{\text{int}} = 0.0670$ ), 2154 of which were considered as observed [ $I > 2\sigma(I)$ ], and were used in the refinement of 333 parameters leading to a final  $R_1$  of 0.0521 and a  $R_{\text{all}}$  of 0.2140. The structure was solved by direct method and refined by full-matrix least squares on  $F^2$ , using SHELXTL 97 program packages. In refinements were used weights according to the scheme  $w = [\sigma^2(F_o^2) + (0.0639P)^2 + 0.0000P]^{-1}$  where  $P = (F_o^2) + 2F_c^2/3$ . The hydrogen atoms were located by geometrical calculations and refined using a "riding" method.  $wR_2$  was equal to 0.1183. The goodness of fit parameters  $S$  was 0.712. Largest difference between peak and hole

was 0.211 and  $-0.351$  eÅ<sup>-3</sup>. Crystallographic data (excluding structure factors and including selected torsion angles) have been deposited with the Cambridge Crystallographic Data Center, CCDC 159925.

**Acknowledgment.** Thanks are due to Drs. E. Di-martino and P. Svensson (University of Bologna) for helping with the X-ray data collection, to I.Co.C.E.A. CNR, Bologna, for access to the solid-state NMR facilities, and to Professor R. K. Harris, University of Durham, UK, for helpful comments. Financial support was received from MURST (national project Stereoselection in Organic Synthesis) and from the University of Bologna (Funds for selected research topics 2000–2002).

JO001689T