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Resolution and Enantiomerization Barrier of Tetramesitylethylene

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The ^{1}H NMR spectrum of tetramesitylethylene (2) was analyzed, and the signals were assigned by means of a 2D NOESY spectrum. Attempts to observe anisochrony of the enantiotopic groups of a racemic mixture of 2 in a chiral solvent by ^{1}H NMR were unsuccessful. Molecular mechanics and MNDO calculations satisfactorily reproduce the ground-state conformation. The calculated barrier for the enantiomerization process is 21.8 (MM2) and 28.2 (MNDO) kcal mol^{-1}. 2 was chromatographically resolved on a (+)-poly(triphenylmethyl)methacrylate (PTrMA) column. Its specific rotation is $[\alpha]^{25} = -12100°$ at 365 nm and $-2300°$ at 589 nm (D line). The activation parameters for the enantiomerization of 2 in perhydrofluorene are $\Delta G^{\ddagger} = \Delta H^{\ddagger} = 39.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = 0$ cal mol^{-1} K^{-1}. The barrier for 2 is the highest determined experimentally for a correlated rotation.

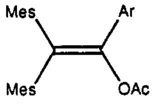
Introduction

Polyaryl-substituted compounds in which the aryl rings are attached to a central atom usually exist in a conformation where all the rings are twisted in the same sense in relation to a reference plane.[1] Such systems are dubbed "molecular propellers". If all the rings are identical and have local C_2 axes they exist in two enantiomeric forms differing in their helicity.[2] When the aryl rings are on a double bond a "vinyl propeller" results.[3–6]

Helicity reversal in molecular propellers usually involves correlated rotation of the rings. It is usually discussed in terms of "flip" mechanisms,[1,2,7] where none, some, or all the aryl rings "flip", i.e., rotate conrotatorily and pass through the plane normal to the reference plane while the nonflipping rings rotate disrotatorily and pass through the reference plane. These mechanisms are dubbed "[*n*]-ring flips", where *n* is the number of flipping rings. When all the rings are identical and have local C_2 axes any flip mechanism results in enantiomerization, and the barrier of lowest activation energy (threshold mechanism) is the enantiomerization barrier of the system.

For Ar_3X and Ar_3XY (X = C, B, N) molecular propellers where all the rings are identical and have a C_2 axis, only a single example of resolution of "helicity" enantiomers has been reported.[8] Even in the crowded trimesitylmethane the enantiomerization barrier is only 21.9 kcal mol^{-1}; i.e., the half life of racemization is ca. 2 h at 0 °C.[9] The more crowded perchlorotriphenylamine has an enantiomerization barrier of 31.4 ± 0.7 kcal mol^{-1} and has been successfully resolved.[8] The propeller-shaped 1,1,2,2-tetrakis(2,6-dimethyl-4-methoxyphenyl)- and 4-(hydroxyphenyl)ethanes were resolved by chromatography on triacetylcellulose.[10]

The reported barriers for helicity reversal for the diaryl- and triarylvinyl propellers are relatively low. For example, for the crowded trimesitylethenol[3] and trimesitylethylene[11] the threshold barriers are 18.4 and 16.8 kcal mol^{-1}, respectively. This precludes the isolation of conformationally stable helicity enantiomers at room temperature. The residual enantiomers[12] of the triarylvinyl system 1,[13] in which the resolution is possible due to the desymmetrization of the α-ring, were recently resolved. 1 exists in four stereoisomeric forms (two pairs of enantiomers), and the threshold three-ring flip route led to diastereomerization and not to enantiomerization. Even when the three-ring flip mechanism is fast at the laboratory time scale, two (residual) enantiomers can be isolated. Recently, the residual enantiomers of a Ar_3CH system (tris(2′-methylbenzimidazol-1-yl)methane) were resolved.[14]



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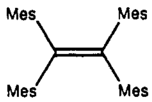
Mes = 2,4,6-$Me_3C_6H_2$
Ar = 2,4,6-Me_3-3-OMe-C_6H



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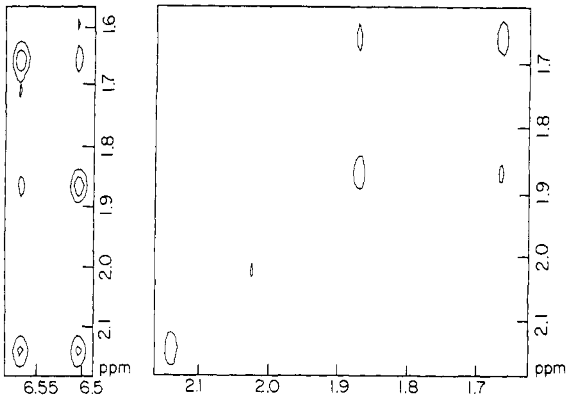

Figure 1. ^1H NOESY NMR spectrum of **2**. Right: methyl/methyl cross peaks. Left: methyl/ aromatic cross peaks.

The most crowded vinyl propeller reported to date is tetramesitylethylene (**2**), prepared in 19% and 61% yields by irradiation of dimesitylketene or dimesityldiazomethane, respectively.[15] Its X-ray diffraction first reported by Blount, Mislow, and Jacobus,[16] and independently by Griller and co-workers,[17] indicates that the molecule exists in the crystal in a chiral propeller conformation of D_2 symmetry. The high crowding present in **2** is likely to raise the enantiomerization barrier and allow separation of "helicity" enantiomers. We describe here the resolution and the determination of the enantiomerization barrier of **2**.

Results and Discussion

Preparation and Attempted Asymmetric Synthesis of 2. **2** was prepared in 15% yield by irradiation of dimesitylketene in cyclohexane with a low-pressure mercury lamp according to Zimmerman and Paskovich.[15] The other isolated photoproduct (67%) was dimesityl ketone.[15] Dimesitylacetic acid (6%), probably resulting from hydrolysis of unreacted dimesitylketene, was also formed. Irradiation with a medium-pressure mercury lamp gave a much lower yield of **2** together with dimesitylcarbinol and dimesitylmethane. When dimesitylketene was irradiated in the presence of the optically active (+)-Noe-lactol dimer, **2** (isolated in 23% yield) did not show any optical activity.

NMR Data and Signal Assignment of Tetramesitylethylene. The reported ^1H NMR spectrum of **2** in CCl_4 displays three methyl group signals and a single aromatic protons signal.[15] This fits a frozen propeller conformation of D_2 symmetry where the two *o*-methyls and the two aromatic protons of a given ring are symmetry unequivalent but the latter are accidentally isochronous. Zimmerman and Paskovich assigned the highest field signal to the *o*-methyl group forced into the face of a vicinal mesityl ring.[15] A reinvestigation in $CDCl_3$ at 400 MHz shows three Me signals (δ = 1.656, 1.862, 2.136 ppm) and two separate Ar–H signals (δ = 6.506 and 6.572); i.e., the accidental isochrony is removed. The ^{13}C NMR spectrum of **2** displays at room temperature three Me signals and seven aromatic and vinyl carbon signals, in agreement with a frozen propeller conformation of D_2 symmetry.

We assigned the different signals in the ^1H NMR spectrum of **2** with the aid of the NOESY spectrum in $CDCl_3$ at rt (Figure 1). Since saturation transfer was not detected in the normal 1D NMR spectrum (see below) even at 453 K, the cross peaks observed are ascribed to NOE effects. In the aliphatic region, cross peaks were observed only between the peaks at δ = 1.656 and 1.862 ppm. The absence of NOE effects between the *p*- and the *o*-methyl groups assigns the signal at δ = 2.136 as a *p*-Me. The NOE effects between the *o*-methyl groups are between neighboring *o*-Me groups of geminal or cis vicinal rings on the same side ("above" or "below") the C=C plane. The assignment is corroborated by the methyl-aromatic proton cross peaks. The signal at δ = 6.506 has strong and weak cross peaks with the signals at δ = 1.862 and 1.656, respectively. The aromatic signal at δ = 6.572 displays strong and weak cross peaks with the signals at δ = 1.656 and 1.862, respectively. Since both aromatic signals have a strong cross peak with the signal at δ = 2.136, this signal corresponds to a *p*-Me having two neighboring aromatic protons. The pairs of signals at δ = 1.656 and 6.572 and δ = 1.862 and 6.506 correspond therefore to vicinal *o*-methyl and aromatic protons. That the two *o*-Me groups resonate at higher field than the *p*-Me group agrees with a propeller conformation in solution since inspection of space filling (CPK) models as well as crystallographic data show that in such conformation each *o*-Me group is in the shielding region of a *cis*-vicinal or a geminal mesityl ring.

Ethylene **2** exists in a chiral conformation, and its NMR signals should be doubled in a chiral nonracemic environment if the enantiomers interconvert slowly on the NMR time scale, as is indeed the case. However, treating a solution of **2** with (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)silver (Resolve-Al AgFOD) in conjuction with the lanthanide chiral shift reagent tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium ($Eu(hfc)_3$)[18] or with Pirkle's reagent ((*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol)[19] did not double the number of signals of **2**. Since 1,2-di-*tert*-butyl-1,2-diphenylethylene undergoes complexation with silver triflate, AgOTf,[20] a THF solution of **2** was stirred with AgOTf for 1 h, but after solvent removal the residue showed no shift of the signals in the ^1H NMR spectrum. Likewise, treatment of **2** with L-silver tartrate did not result in any signal shift. Steric crowding of the molecule seems to prevent either the aryl or the ethylenic π bonds from association with the metal of the shift reagent or with the chiral solvent.

Molecular Mechanics and MNDO Calculations. (a) Ground-State Conformation. The ground-state conformation of **2** was calculated by using the MACROMODEL[21] (MM2) and MNDO[22] programs. For the MNDO calculations a D_2 symmetry was assumed. The several input tested were converged to the same final structure. The results are collected in Table I, together with the crys-

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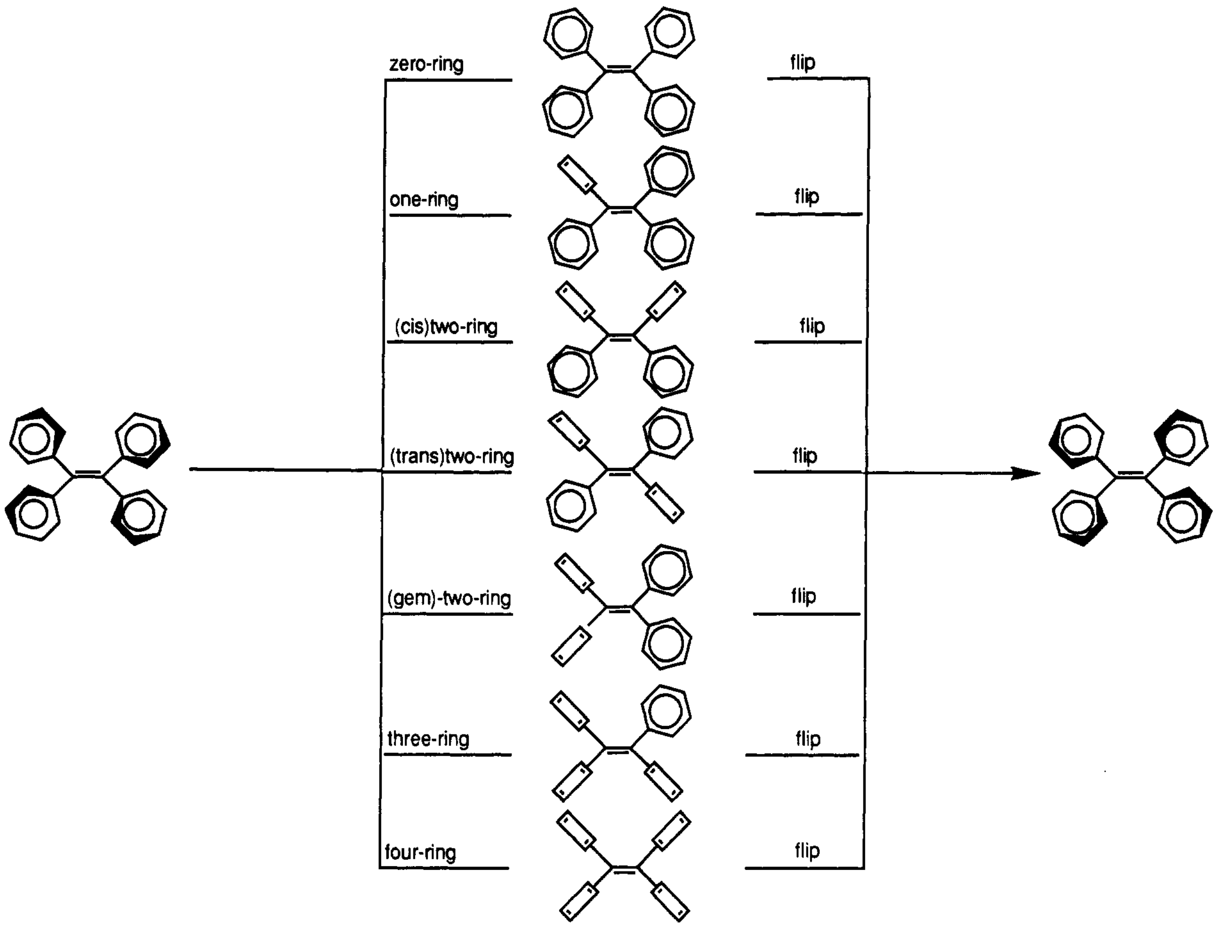
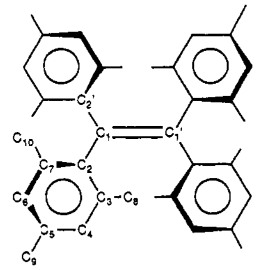


Figure 2. Diastereomeric flip mechanisms for a tetraarylvinyl propeller. ▥ indicates a ring that is perpendicular to the C═C plane.

tallographic data reported.[16] Both methods satisfactorily reproduce the broad structural features of the molecule. The long C═C bond is well reproduced by the MM calculations. The MNDO calculations which tend to overestimate C_{Ar}–C_{Ar} bond lengths[21] overestimate the length of the ethylenic and aromatic C═C bonds by 0.02–0.03 Å. Bond angles are somewhat better reproduced by MNDO. The experimental Mes—C═C torsional angles (51.2°) are well reproduced by the MM calculations (51°) and overestimated by the MNDO calculations (58.4°). The C—C═C—C torsional angles are satisfactorily reproduced by both calculations.

(b) Rotational Transition States. The seven possible flip routes for a tetraarylvinyl propeller are shown in Figure 2. When all the rings are identical and possess local C_2 axes, the one-ring and three-ring flip possess a 4-fold degeneracy while each of the cis, trans, and geminal diastereomeric two-ring flips has a 2-fold degeneracy. Calculations by Stegemeyer and Rapp[6] indicate that the four-ring flip is the favored flip mechanism for the parent tetraphenylethylene, with a barrier of 6.5 kcal mol^{-1}. A DNMR study concluded that the threshold mechanism of tetra(*o*-tolyl)ethylene is the four-ring flip.[23] The ground state of tetraphenylethylene was well reproduced by the MM2 calculations (calculated ethylenic C═C bond length 1.35 Å, experimental[24] 1.34 Å; calculated Ph—C═C torsional angle 46.6°, experimental[24] 57.1–42.9°). To calculate (by MM2) the relative energies of the flip mechanisms the eight C(ortho)—C(ipso)—C═C torsional angles were constrained to 90° or 0° (perpendicular or coplanar orientations with regard to the C═C plane, respectively) while the double bond was not constrained to planarity.

Table I. Selected Experimental[16] and Calculated Structural Parameters for 2[a]



parameter	calcd (MM2)	calcd (MNDO)	X-ray
C(1)-C(1′)	1.357	1.392	1.364
C(1)-C(2)	1.518	1.519	1.506
C(2)-C(3)	1.408	1.439	1.411
C(2)-C(7)	1.406	1.434	1.416
C(3)-C(8)	1.512	1.512	1.502
C(7)-C(10)	1.511	1.511	1.504
C(2)-C(1)-C(1′)	121.5	122.7	122.8
C(2)-C(1)-C(2′)	117	114.6	114.4
C(1)-C(2)-C(3)	120.4	121.7	122.5
C(1)-C(2)-C(7)	121.8	122.0	119.5
C(2)-C(3)-C(8)	123.4	125.8	124.5
C(2)-C(7)-C(10)	124.7	126.8	124.4
Ar-C═C	51.1	58.2	52.9
C-C(1)═C(1′)-C (cis)	2.3	2.5	4.4
C-C(1)═C(1′)-C (trans)	177.7	177.5	175.6

[a] Bond lengths in angstroms, bond and torsional angles in degrees.

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(24) Hoekstra, A.; Vos, A. *Acta Crystallogr., Sect. B.* **1975**, *31*, 1716. Tetraphenylethylene has C_1 symmetry in the crystal and therefore the four rings have different torsional angles with the double bond.

The calculated relative energies of the four-ring, three-ring, (cis) two-ring and (trans) two-ring, (*gem*) two-ring, and one-ring flips are 5.8, 6.3, 13.8, 11.9, 30.3, and 37.7 kcal mol^{-1}, respectively. MM2 calculations for the zero-ring flip structure did not converge, probably due to its high relative steric energy. Consequently, the calculated threshold mechanism is the four-ring flip with a barrier of 5.8 kcal mol^{-1} agreeing with Stegemeyer and Rapp's calculations.[6] However, the three-ring flip lies only 0.5 kcal mol^{-1} above it. Interestingly, the energy of the (*gem*) two-ring flip pathway is appreciably higher than that of the (cis) or (trans) two-ring flips. This is probably due to the geminal relationship of the two nonflipping rings, which increases their mutual steric interactions in the transition state where both are coplanar with the double bond.

Whereas both MM2 and MNDO satisfactorily reproduce the ground-state structure of **2**, they give different barriers for the flip mechanisms. The threshold mechanism by MM2 is the three-ring flip with a barier of 21.8 kcal mol^{-1}.[25] The (cis) and (trans) two-ring flips are close in energy (23.4 and 23.6 kcal mol^{-1} above the ground state, respectively) while the (*gem*) two-ring flip, one-ring flip, and four-ring flip lie 45.0, 41.8, and 35.2 kcal mol^{-1} above the ground state. All the calculated transition states showed appreciable distortions of the mesityl rings. The calculated MNDO barriers of the flip mechanisms increase with the increasing number of nonflipping rings. They are 28.2, 35.8, 45.1, and 65.6 kcal mol^{-1} for the four-ring, three-ring, (cis) two-ring, and (trans) two-ring flip mechanisms, respectively. Inputs for the one-ring and zero-ring flip mechanisms did not converge.

Saturation Transfer Experiments. From the observed diastereotopicity of the *o*-Me groups Zimmerman and Paskovich concluded that **2** "might be capable of resolution into enantiomers".[15] Blount, Mislow and Jacobus later estimated a lower limit of 25 kcal mol^{-1} for the barrier of rotation of **2** from the lack of coalescence of these groups at high temperatures. A saturation transfer experiment,[26,27] conducted at 453 K in $C_6D_5NO_2$ by delivering a selective 180° pulse to the signal at δ 6.893 ppm, followed by a nonselective 90° pulse after increasing delays, showed no effect for the nonirradiated aromatic signal at δ 6.753. A lower limit of 28.4 kcal mol^{-1} for the barrier was estimated from this experiment.

Resolution and Specific Optical Rotation of Tetramesitylethylene. In attempts to resolve **2** three chiral HPLC columns were tested: cellulose tris(3,5-dimethylphenyl carbamate), amylose tris(3,5-dimethylphenyl carbamate), and (+)-poly(triphenylmethyl)methacrylate (PTrMA).[28] The polysaccharide-based columns showed poor chiral recognition but PTrMA completely separated the enantiomers as shown in Figure 3.

The specific rotation of the (−)-enantiomer (obtained as the second fraction in the chromatographic resolution) was determined in chloroform, and the concentration was estimated from UV data. The specific rotation $[\alpha]^{25}$ was −12100° at 365 nm and −2300° at 589 nm (D line). The high absolute value of the specific rotation is reminiscent of the high values observed for the [*n*]helicenes (e.g., $[\alpha]_D$ = −3640° for [6]helicene).[29]

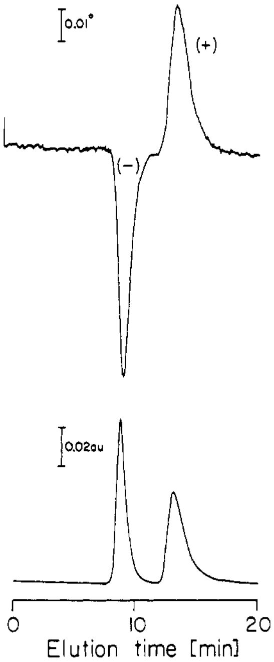

Figure 3. Chromatographic separation of **2**. Top: optical rotation of the eluted fractions. Bottom: chromatographic trace.

Enantiomerization Barrier of Tetramesitylethylene. Racemization of one of the resolved enantiomers was not achieved when it was heated for 8 h in hexane at 373 K or for 3 days in decalin at 423 K. Racemization was observed when **2** was heated at 473, 483, and 493 K (200, 210, and 220 °C, respectively) in perhydrofluorene. Five samples were analyzed during a 3-day period, and the enantiomeric excess of each was determined by chiral chromatography. Excellent first-order kinetics were displayed by the data points, from which rate constants of 5.0×10^{-6} (473 K), 1.2×10^{-5} (483 K), and 2.9×10^{-5} (493 K) s^{-1} were calculated for the enantiomerization process, considering that the racemization rate is twice the enantiomerization rate. This gives $\Delta G^\ddagger$ values of 39.6 kcal mol^{-1} for the enantiomerization (helicity reversal) process at each temperature.

The $\Delta S^\ddagger$ for the enantiomerization of **2** is of interest since Lii and Allinger have recently pointed out that systems in which methyl groups become sterically crowded in the transition state are expected to display substantial contributions to the $\Delta S^\ddagger$ [30] due to restriction in the torsional motion of the methyl groups in the transition state. Hence, we expected that the enantiomerization of **2** should display a large $\Delta S^\ddagger$ since four pairs of *o*-methyl groups mutually interact in the transition state. From the Arrhenius plot, E_a = 40.5 kcal mol^{-1}, hence $\Delta H^\ddagger$ = 39.6 kcal mol^{-1} and $\Delta S^\ddagger$ = 0 cal mol^{-1} K^{-1}. Consequently, the entropy due to *o*-Me–*o*-Me interactions is almost identical in the ground and in the transition state. This is surprising in view of the high barrier and Lii and Allinger's analysis, but at present we have no explanation for the entirely enthalpic barrier.

Both the MM2 and MNDO calculations grossly underestimate the enantiomerization barrier. Although part of the discrepancy between the calculations and the experimental result arises from our inability to properly locate the saddle point, it seems to us that at least the MM2 calculations overestimate the flexibility of the mesityl rings.

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(25) Interestingly, MM calculations predict a lower enantiomerization barrier for tetrakis(3,5-dibromo-2,4,6-trimethylphenyl)ethylene than for **2**. The compound was synthesized by electrophilic bromination of **2** and is currently under investigation.

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Attempted Enantiomeric Enrichment of 2 by Asymmetric Induction. Whereas the enantiomers are conformationally stable at room temperature, fast enantiomerization at the laboratory time scale may be accomplished at high temperatures. This will be detected even at low enantiomeric enrichments of **2** due to the high specific rotation. We therefore attempted the enantiomeric enrichment by refluxing racemic solutions of **2** for 8 h in optically pure (*R*)-(+)-2-phenylethanol or for 5 days in (1*R*,2*S*,5*R*)-(−)-menthol. Polarimetric analysis did not give any optical rotation, i.e., no enantiomeric enrichment took place.

Conclusions

The crowded tetramesitylethylene (**2**) can be resolved into helicity enantiomers. The enantiomerization barrier is appreciable (39.6 kcal mol^{-1}), but despite the large number of methyl groups which presumably interact in the transition state, this barrier has no entropic contribution. Empirical and semiempirical calculations reproduce correctly the ground state of **2**, but grossly underestimate the enantiomerization barrier and differ in their prediction of the favored flip mechanism. The barrier for **2** is the highest determined experimentally for a correlated rotation.

Experimental Section

NMR spectra were recorded on a Bruker AMX-400 pulsed FT spectrometer. Shift reagents and chiral materials were purchased from Aldrich. The solvents for the irradiation were dried and distilled prior to use. Dimesitylketene was prepared according to Fuson.[3,31] The chromatographic resolution of **2** was accomplished on a (+)-poly(triphenylmethyl)methacrylate (PTrMA) column (column size 25 × 0.46 (i.d.) cm) using a JASCO-BIP-I chromatograph equipped with a JASCO-875 (UV) and JASCO-DIP-181C (optical rotation) detectors. The separation was carried out at room temperature, using hexane as eluent (flow rate: 0.5 mL/min).

Tetramesitylethylene (2). The compound (mp 299 °C, lit.[15] mp 299–300 °C) was prepared by a 1-week irradiation of dimesitylketene with a low-pressure mercury lamp.[15] ^{1}H NMR spectrum ($C_6D_5NO_2$, 453 K) δ: 2.054, 2.306, 2.322 (3 Me), 6.753, 6.893 (Mes-H). ^{13}C NMR ($CDCl_3$, rt) δ: 20.7, 22.1, 22.3 (3 Me), 128.6, 130.0, 135.4, 138.0, 138.6, 139.1, 141.8 ppm (6 C_{Ar} + C=C).

Irradiation of Dimesitylketene with a Medium-Pressure Mercury Vapor Lamp. Dimesitylketene (5.84 g) in cyclohexane (850 mL) was irradiated in a water-cooled glass irradiation vessel with a medium-pressure mercury vapor lamp for 7 days. Water was added to the mixture, the organic phase was evaporated, and the residue was chromatographed. The isolated products were **2** (2.6 mg, 0.05%), dimesitylmethane (1.44 g, 27.7%), mp 133 °C (lit.[32] mp 134.4–135.4 °C), dimesitylcarbinol (0.59 g, 10.5%), mp 147 °C (lit.[15] mp 149–150 °C), and small amounts of dimesityl ketone and dimesitylacetic acid.

Irradiation of Dimesitylketene in the Presence of (+)-Noe-Lactol Dimer. Into a 80-mL quartz vessel were introduced 1 g of dimesitylketene, 850 mg (+)-Noe-lactol dimer, and 80 mL of dry degassed cyclohexane. After irradiation with a low-pressure mercury lamp for 6 days the tetramesitylethylene formed (in 23% yield) showed no optical activity.

Attempts To Complex 2 with Silver Salts. (a) 1 mL of a saturated solution of **2** in THF was treated with 1 mL of a saturated solution of either AgOTf or L-silver tartrate in THF.

(b) 13 mg (0.026 mmol) of **2** and 20 mg (0.078 mmol) of AgOTf were dissolved in THF (4 mL), and the mixture was stirred overnight.

The two mixtures were protected from light. The solvent was evaporated at the end of the reaction, and the residue was analyzed by ^{1}H NMR and by melting point. These were identical with those of pure **2**; i.e., no complexation took place.

Attempts To Induce Anisochrony into a Racemic Mixture of 2. (a) To a 0.5-mL solution of **2** in $CDCl_3$ (2 mM) were added 1.6–3.0 equiv of Pirkle's reagent.[19] The most shifted signal (by 35 ppb) was that of one of the *o*-methyl groups, but no doubling of the signals was observed.

(b) 50 mg of **2**, 20 mg of (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)silver (Resolve-Al AgFOD), and 210 mg of tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium (Eu(hfc)$_3$) were dissolved in 0.5 mL of $CDCl_3$. The ^{1}H NMR spectrum after 30 min was identical with that of **2** in the absence of the shift reagent and the silver salt.

Attempted Enantiomeric Enrichment of 2 by Asymmetric Induction. (a) A solution of racemic **2** (25 mg) in (1*R*,2*S*,5*R*)-(−)-menthol (3.9 g) was refluxed for 5 days at 485 K.

(b) **2** (10 mg) was dissolved in (*R*)-(+)-2-phenylethanol (1.5 mL), and the solution was refluxed for 8 h at 481 K. After evaporation of the solvent both residues were purified by chromatography (eluent: petroleum ether) and analyzed polarimetrically but no optical rotation was observed.

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