ZnTPP), benzophenone (for **1c**), or Ph_2SO_2 (for **3a**) as the internal standard. The compound **6** was analyzed by vapor phase chromatography (20% silicone DC 550 on Celite 545, 180 °C).

MTPP-Catalyzed Decomposition of 1a and 1c in the Presence of Oxygen Acceptor. Ten moles of the oxygen acceptor (Ph_2S or Ph_2SO) relative to the cyclic diperoxide was always employed. A typical procedure is as follows. A solution containing 20 mg (0.082 mmol) of **1a**, 2 mg (0.003 mmol) of ZnTPP, and 153 mg (0.82 mmol) of Ph_2S in 1.5 mL of $CHCl_2CHCl_2$ was heated on an oil bath (90 ± 3 °C) for 10 h under bubbling nitrogen. The reaction mixture was analyzed by HPLC as described above.

Chemiluminescence Measurement. Chemiluminescence (CL) was measured by a Shimazu RF-500 fluorescence spectrometer, with the emission bandwidth setting at 40 nm. The indirect CL from 9,10-dibromoanthracene and a 1,2-dioxetane derived from 2,3-diphenyl-1,4-dioxene (92.8 °C) was used as a standard of photon emission ($\Phi^{\mathrm{T}}_{\mathrm{T}} = 0.22$,[24a] $\Phi_{\mathrm{F}}^{\mathrm{DBA}} = 0.05$,[24b] $k_{\mathrm{ET}}^{\mathrm{TS}}/(k_{\mathrm{ET}}^{\mathrm{TS}} + k_{\mathrm{ET}}^{\mathrm{TT}}) = 0.2$,[24b] intercept/slope of the $1/I_{\mathrm{CL}}$ vs. 1/[DBA] plot = 308 M^{-1} determined by us). Any corrections for the different spectral distribution of CL and the variable wavelength response of the photomultiplier tube (Hamamatsu R 446) were not made. The temperature of a sample solution (3 mL) was controlled by circulating hot water through the sample holder (±0.4 °C).

Isolation of 2-Phenoxybiphenyl. A solution of valerophenone diperoxide (**1c**) (269 mg, 0.755 mmol) in diphenyl ether (10 mL) was thermolyzed at 177 ± 5 °C for 5 h under bubbling nitrogen. The reaction mixture was separated by column chromatography on silica gel (Wakogel C-200, hexane), followed by preparative TLC (Merck Kieselgel 60 PF_{254}, hexane), to afford 59 mg (16% yield) of 2-phenoxybiphenyl as colorless oil. The product was identical with the authentic sample in every respect. Isolation of other products was not attempted in this run.

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A Two-Ring Flip as the Threshold Enantiomerization Route for a Triarylvinyl Propeller. 1D and 2D NMR and Static and Dynamic Stereochemistry of Trimesitylethylene

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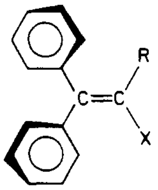
1,2,2-Trimesitylethylene (**16**) was prepared by dehydration of 1,2,2-trimesitylethanol. Its 1D ^1H and ^{13}C NMR spectra at room temperature show separate signals for pairs of groups (*o*-Me, *o*-C, *m*-C, and *m*-H) on the same ring, in agreement with a propeller conformation in solution. Assignment of the signals and derivation of the threshold rotational mechanism were aided by the use of 2D NMR techniques. Two rotational barriers were measured by dynamic NMR. The lower barrier (16.8 ± 0.1 kcal mol^{-1}) is for the threshold mechanism which is an [α,β]-two-ring flip. The higher barrier was calculated for the interchange of diastereotopic groups on the β'-ring (20.5 ± 0.1 kcal mol^{-1}). The difference in the threshold mechanisms of **16** and of trimesitylethenol (a three-ring flip) was ascribed to the presence of the small hydrogen on **16** which allows the β'-ring cis to it to undergo a nonflip process in a transition state with an energy lower than that of the three-ring flip for **16** or the two-ring flip for trimesitylethenol. The distinct rotational threshold mechanisms for $Mes_2C{=}C(X)Mes$ (X = H, and OH, (Mes = mesityl)) are clearly reflected in their different 2D exchange NMR spectra.

1,1-Diarylvinyl (**1**) and 1,2,2-triarylvinyl systems **2** exist



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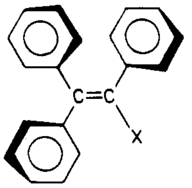

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in a "propeller" conformation in which all the rings are twisted in the same sense[1–4] and are, therefore, the vinyl analogues of molecular propellers of the type Ar_3Z (**3**) and Ar_3ZX (**4**) (Z = C, B, or N; X = H, Me, or halogen).[5] When all the rings are identical and have a local C_2 axis, these systems exist as two enantiomers differing in the helicity, i.e., in the sense of twist of the rings.

An important class of rotations in molecular propellers are correlated rotations in which all the rings rotate concomitantly. These processes are commonly analyzed in terms of "flip" mechanisms, each involving helicity reversal.[6] A "flip" of a ring is defined as its passage through a plane perpendicular to the reference plane (the double bond plane for 1 and 2[7] and the plane defined by the three

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(7) Note that for systems 1 and 2 (when R ≠ X) the molecules belong to the C_1 point group, and, therefore, the two double bond π faces reside in diastereotopic environments. For such olefins, deviation from the ideal planar arrangement should be expected. However, for simplifying the visualization of the different flip routes we will use the term "double bond plane".

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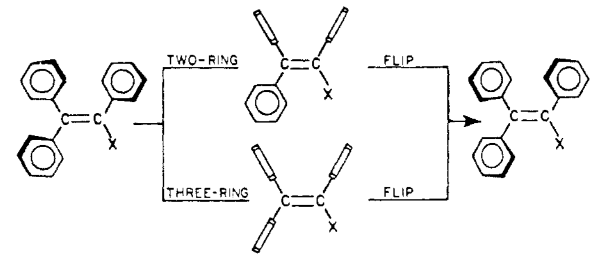
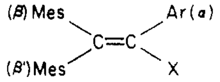
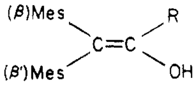


Figure 1. Examples of the idealized transition states for one of the three diastereomeric two-ring flip ([α,β]) and of the three-ring flip for a trimesitylvinyl system. The *o*- and *p*-methyl groups are omitted in order to emphasize the generality of the processes. ▭ indicates a ring that is perpendicular to the double bond plane.

aromatic ipso carbons for 3 and 4). In flip mechanism(s) some (or none) of the rings flip whereas nonflipping rings rotate concomitantly in the opposite direction and pass through the reference plane. Depending on the number of flipping rings, these mechanisms are designated zero-, one-, two-, and three-ring flip(s).[8] For systems of the type 3 and 4 dynamic NMR data[9,10] as well as molecular mechanics calculations[11] and analysis of X-rays data[12] point out that the rotational mechanism of lowest activation energy (threshold mechanism) is uniformly the two-ring flip. In contrast, for the β,β-dimesityl-α-substituted triarylvinyl propellers **5–9** (corresponding to system **2**) the threshold mechanism is the three-ring flip (Figure 1).



5, Ar = Mes; X = OH
6, Ar = Mes; X = OAc
7, Ar = Mes; X = Cl
8, Ar = 2,6-$Me_2C_6H_3$; X = OH
9, Ar = 9-anthryl; X = OH



10, R = H
11, R = Me
12, R = Et
13, R = *i*-Pr
14, R = *t*-Bu

Mes = 2,4,6-$Me_3C_6H_2$

In contrast to systems **3** and **4**, 1,1-diarylvinyl propellers show a structure-dependent threshold rotational mechanism. We have shown previously that the threshold mechanism for **10** is a one-ring flip, but it is the two-ring flip route for **11–14**.[3] This shift was interpreted in terms of steric effects. In the threshold mechanism for **10**, where R = H, the C_β-ring cis to R undergoes a nonflip rotation. This was found to be a few kcal mol^{-1} cheaper than a process involving a flip of this ring. However, increase in the bulk of R raises the activation energy of the one-ring flip by hindering the passage of this cis-β-Mes ring through the double bond plane. Simultaneously, the torsional angle of this ring in the ground state is increased with a consequent lowering of the barrier for the two-ring flip.[3,4] In order to find out whether a shift in the same direction in the threshold mechanism of the more crowded system **2** is possible on reducing the bulk of a double bond substituent, we decided to modify the structure of our extensively studied enol **5** by replacing its OH with the less bulky hydrogen atom.

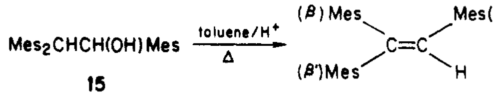
Table I. ^1H and ^{13}C Spectra of 16 at Room Temperature

	^1H NMR		
no.	assignment	δ	^{13}C NMR[a] (δ)
1	α-*o*-Me	1.71	20.40
2	β-*o*-Me	1.72	20.78
3	β'-*o*-Me	1.76	20.78
4	β-*o*-Me	1.83	21.17
5	β-*p*-Me	2.18	20.81
6	α-*p*-Me	2.22	20.91
7	α-*o*-Me	2.25	21.45
8	β'-*p*-Me	2.27	20.81
9	β'-*o*-Me	2.61	22.96
10	=C—H	6.60	
11	β-Mes-H	6.62	
12	α-Mes-H	6.66	
13	β-Mes-H	6.68	
14	β'-Mes-H	6.72	
15	α-Mes-H	6.85	
16	β'-Mes-H	6.95	

[a] Only the methyl signals were unequivocally assigned.

Results and Discussion

Synthesis and Static NMR of Trimesitylethylene. Trimesitylethylene (**16**) was prepared by acid-catalyzed dehydration of 1,2,2-trimesitylethanol (**15**)[13] (eq 1). Single-crystal X-ray diffraction shows that **16** exists in a propeller conformation in which the torsional angles of the mesityl rings (defined by the $C_{(ortho)}C_{(ipso)}C{=}C$ atoms) are 54.4° (α), 52.9° (β), and 59.3° (β'), similar to those of the two crystallographic forms of **5** [52.7° and 55° (α), 52.5° and 51.4 (β), and 54.6° and 58° (β')].[1] Consequently, the modification OH → H does not result in an appreciable change in the conformation of the molecule in the solid state.



15 **16** (1)

The NMR data of **16** at room temperature resembles the corresponding NMR for **5**. The ^1H 200-MHz NMR spectrum of **16** in $CDCl_3$ shows 16 signals: nine aliphatic methyl singlets at δ 1.71–2.61 and six broad and one sharp singlets at δ 6.60–7.00 (Table I). Similarly the broad band proton noise decoupled 50.33-MHz ^{13}C NMR of **16** in $CDCl_3$ displayed a total of 26 signals: seven of which corresponding to the methyl groups are at δ 20.40–22.96 (see Table I and Experimental Section). The diastereotopicity of pairs of ortho methyls, ortho carbons, meta carbons, and mesityl hydrogens signals on the same ring is in agreement with a propeller conformation for **16** in solution.

The signals in the ^1H NMR spectrum as well as the ^{13}C methyl signals were assigned by comparing the spectra of **16** with that of the analogous **5** (for which a complete assignment of the signals was made)[2,14] in $CDCl_3$ and by the saturation transfer method[15] by which pairs of signals (ortho methyls and meta hydrogens) on the same ring can be identified. The link between the methyl signals in the ^1H and ^{13}C spectra was made by the 2D ^{13}C, ^1H correlated spectra[16,17] (Figure 2).

The sharp signal in the ^1H NMR at δ 6.60 is assigned to the vinylic proton since long range couplings ($^4J_{meta}$ and

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[8] Ideal transition states for the zero-, one-, two-, and three-ring flips are shown in Figure 3 of ref 2.

[9] Hummel, J. P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 2168.

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[16] For a review on 2D NMR techniques, see: Benn, R.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 350.

[17] The program used was HCCORR as implemented by Bruker.

Table II. Magnetization Transfer Matrices of the Different Flip Mechanisms of 16

zero-ring flip

	1	2	3	4	5	6	7	8	9
1	·	·	·	·	·	·	·	·	·
2	·	·	·	·	·	·	·	·	·
3	·	·	·	·	·	·	·	·	·
4	·	·	·	·	·	·	·	·	·
5	·	·	·	·	·	·	·	·	·
6	·	·	·	·	·	·	·	·	·
7	·	·	·	·	·	·	·	·	·
8	·	·	·	·	·	·	·	·	·
9	·	·	·	·	·	·	·	·	·

[α]-one ring flip

	1	2	3	4	5	6	7	8	9
1	·	·	·	·	·	·	1	·	·
2	·	·	·	·	·	·	·	·	·
3	·	·	·	·	·	·	·	·	·
4	·	·	·	·	·	·	·	·	·
5	·	·	·	·	·	·	·	·	·
6	·	·	·	·	·	·	·	·	·
7	1	·	·	·	·	·	·	·	·
8	·	·	·	·	·	·	·	·	·
9	·	·	·	·	·	·	·	·	·

[β]-one ring flip

	1	2	3	4	5	6	7	8	9
1	·	·	·	·	·	·	·	·	·
2	·	·	·	1	·	·	·	·	·
3	·	·	·	·	·	·	·	·	·
4	·	1	·	·	·	·	·	·	·
5	·	·	·	·	·	·	·	·	·
6	·	·	·	·	·	·	·	·	·
7	·	·	·	·	·	·	·	·	·
8	·	·	·	·	·	·	·	·	·
9	·	·	·	·	·	·	·	·	·

[β']-one ring flip

	1	2	3	4	5	6	7	8	9
1	·	·	·	·	·	·	·	·	·
2	·	·	·	·	·	·	·	·	·
3	·	·	·	·	·	·	·	·	1
4	·	·	·	·	·	·	·	·	·
5	·	·	·	·	·	·	·	·	·
6	·	·	·	·	·	·	·	·	·
7	·	·	·	·	·	·	·	·	·
8	·	·	·	·	·	·	·	·	·
9	·	·	1	·	·	·	·	·	·

[α,β]-two ring flip

	1	2	3	4	5	6	7	8	9
1	·	·	·	·	·	·	1	·	·
2	·	·	·	1	·	·	·	·	·
3	·	·	·	·	·	·	·	·	·
4	·	1	·	·	·	·	·	·	·
5	·	·	·	·	·	·	·	·	·
6	·	·	·	·	·	·	·	·	·
7	1	·	·	·	·	·	·	·	·
8	·	·	·	·	·	·	·	·	·
9	·	·	·	·	·	·	·	·	·

[α,β']-two ring flip

	1	2	3	4	5	6	7	8	9
1	·	·	·	·	·	·	1	·	·
2	·	·	·	·	·	·	·	·	·
3	·	·	·	·	·	·	·	·	1
4	·	·	·	·	·	·	·	·	·
5	·	·	·	·	·	·	·	·	·
6	·	·	·	·	·	·	·	·	·
7	1	·	·	·	·	·	·	·	·
8	·	·	·	·	·	·	·	·	·
9	·	·	1	·	·	·	·	·	·

[β,β']-two ring flip

	1	2	3	4	5	6	7	8	9
1	·	·	·	·	·	·	·	·	·
2	·	·	·	1	·	·	·	·	·
3	·	·	·	·	·	·	·	·	1
4	·	1	·	·	·	·	·	·	·
5	·	·	·	·	·	·	·	·	·
6	·	·	·	·	·	·	·	·	·
7	·	·	·	·	·	·	·	·	·
8	·	·	·	·	·	·	·	·	·
9	·	·	1	·	·	·	·	·	·

[α,β,β']-three ring flip

	1	2	3	4	5	6	7	8	9
1	·	·	·	·	·	·	1	·	·
2	·	·	·	1	·	·	·	·	·
3	·	·	·	·	·	·	·	·	1
4	·	1	·	·	·	·	·	·	·
5	·	·	·	·	·	·	·	·	·
6	·	·	·	·	·	·	·	·	·
7	1	·	·	·	·	·	·	·	·
8	·	·	·	·	·	·	·	·	·
9	·	·	1	·	·	·	·	·	·

$^4J_{\text{H-Me}}$) are expected to broaden the aromatic signals.[18] The more deshielded methyl signal in both the ^{1}H and ^{13}C NMR spectra is due to the same methyl group (Figure 2).[20] It is assigned to one β'-*o*-methyl group since an analogous signal in **5** is the most downfield shifted of all methyl signals.[2,14] Similarly, the most downfield shifted aromatic proton signal at δ 6.95 is assigned to one β'-mesityl ring proton. Inspection of space-filling models shows that in the propeller conformation, one β'-*o*-methyl is at the intersection of the planes of the α- and β-rings and is, therefore, subjected to their combined deshielding effect.[2] By similar arguments, the second most downfield shifted ortho methyl signal in the ^{1}H NMR is assigned to an α-*o*-methyl group. We conclude that the NMR spectra are consistent with a frozen propeller conformation in solution.

Dynamic Stereochemistry of 16. In a previous analysis of the different flip routes for vinyl propeller **2**, we showed that a flip of a given ring will exchange pairs of signals (*o*-Me, *m*-H) on the same ring at different magnetic sites.[2] This leads to coalescence of this pair of signals in the NMR spectrum. In a nonflip process such exchange does not take place since the initial and final sites of a given *o*-Me or a *m*-H are enantiotopic. We presented the different flip routes in a tabular form showing the relationship between the exchanged sites.[2] In the present paper we analyze these routes in an equivalent way, but more useful when using 2D exchange spectroscopy. In Table II the magnetic site exchanges of the different flip mechanisms are presented in the form of Kubo–Sack matrices of magnetic site exchange.[21–23] Since in the 2D-exchange NMR spectrum the normal 1D spectrum appears

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(18) $^4J_{\text{meta}}$ coupling was resolved in the spectrum of related **5** by deuterating the methyl groups[14] ($^4J_{\text{meta}}$ 1.90–2.08 Hz). $^4J_{\text{H-Me}}$ coupling was measured for **5** with the aid of high field (500 MHz) and resolution enhancement via the Lorentz-to-Gauss lineshape transformation.[14,19]

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(20) We have also carried out the 2D ^{13}C, ^{1}H correlated NMR spectra of the methyl region of **5** in CDCl$_3$ and found it to be in full agreement with our previous assignment.[2] This technique enables us to assign the signals in the ^{13}C spectra at δ 20.64, 21.40,and 21.62, which were previously assigned to the methyls of the β ring without specification, to the β-*p*-Me, β-*o*-Me, and β-*o*-Me groups, respectively.

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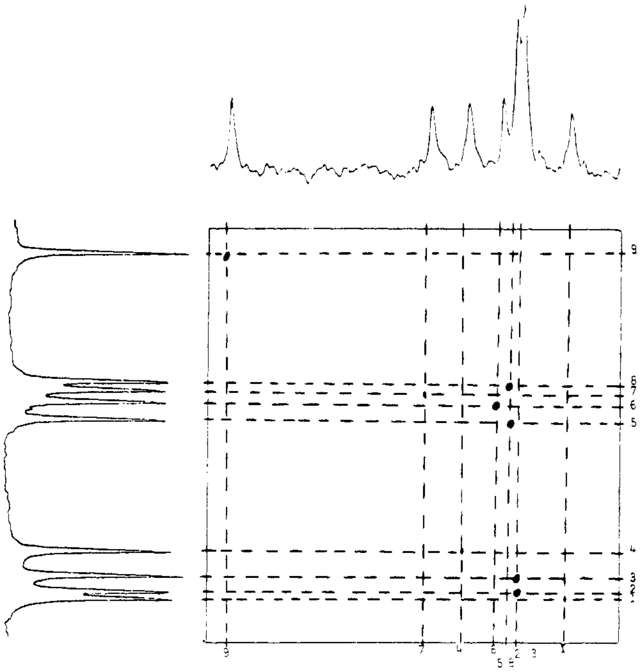

Figure 2. 2D ^{13}C, ^{1}H NMR correlation diagram of the methyl region of **16** in $CDCl_3$ at 293 K. The abscissa (the F_2 dimension) shows the ^{1}H decoupled 1D ^{13}C NMR spectrum, and the ordinate (the F_1 dimension) shows the 1D ^{1}H NMR spectrum. The numbering of the signals is according to their assignment as given in Table I.

along the diagonal, in order to facilitate the comparison with the 2D NMR all the diagonal elements from (1,1) to (9,9) were arbitrarily set equal to zero. A complete transfer of magnetization between magnetic sites is represented by the number 1, and the absence of magnetization transfer is represented by a dot. The advantage of this representation is that the slow-exchange 2D spectrum is a representation of the matrix of exchange of magnetic sites of the mechanisms responsible for the exchange, with the normal spectrum appearing as contours along the diagonal and with "cross peaks" (out of the main diagonal) at coordinates (yz) and (zy) indicating a reciprocal magnetization transfer between the sites y and z. The 2D slow-exchange spectrum[24] of the methyl region of **16** in $CDCl_3$ at 290 K is shown in Figure 3[25] on which we have superimposed a lattice of rows and columns representing the different magnetic sites of **16**. The figure shows that cross peaks having similar intensities appear at the coordinates (1,7), (7,1) and (2,4), (4,2) qualitatively indicating magnetization transfer between signals 1 and 7 and between signals 2 and 4 having similar (or even identical) rates. A similar picture was obtained when the slow-exchange 2D NMR of **16** was carried out at the aromatic proton region. Only two pairs of aromatic signals (11,13) and (12, 15) showed cross peaks. The 2D spectra of Figure 3 is a clear representation of the Kubo–Sack matrix of the [α,β]-two-ring flip in Table II. We conclude that the slow-exchange 2D NMR spectrum supports the [α,β]-two-ring flip as the threshold rotational mechanism, in clear contrast to the behavior of **5**.

Table III. ^{1}H **Coalescence Data for 16 in** $C_6D_5NO_2$

signal	$\Delta\nu$, Hz	T_c, K	$\Delta G_c^{\ddagger}$, kcal mol^{-1}
α-Mes-H	88.0[a]	347[a]	16.8
α-o-Me	128.7[a]	353[a]	16.8
β-Mes-H	59.9[a]	347[a]	17.0
β-o-Me	21.9[a]	329[a]	16.7
β'-Mes-H	55.9[b]	414[b]	20.5
β'-o-Me	51.9[c]	415[c]	20.6

[a] At 300 MHz. [b] At 200 MHz. [c] At 60 MHz.

The difference in the threshold rotational route for **16** and **5** is clearly manifested in their different 2D spectrum. The slow-exchange 2D NMR of the methyl region of **5** in $C_6D_5NO_2$ (where each methyl group appears as a separate signal) at 330 K[26] is also shown in Figure 3, with a signal numbering parallel to that of **16**. It can readily be seen that *three* pairs of cross peaks having similar intensities at coordinates (1, 7) (7, 1); (2, 4), (4, 2); and (3, 9), (9, 3) exist for **5**, indicating a similar rate of magnetization transfer simultaneously at the three rings. This behavior strongly supports a three-ring flip as the threshold rotational mechanism.[27] Figure 3 shows clearly the different rotational behavior of **16** and **5**.

Rotational Barriers of 16. The rotational barrier for the threshold mechanism of **16** was calculated by means of conventional 1D NMR. By raising the temperature of a sample of **16** in $C_6D_5NO_2$ at 300 MHz, two pairs of singals in the methyl region and two pairs in the aromatic region broadened and coalesced. Exchange rates at the coalescence temperature were calculated by using the Gutowsky–Holm approximation[28] and the Eyring equation assuming a transmission coefficient of unity. The coalescence data for **16** is summarized in Table III. At temperatures near 350 K at 300 MHz in which the α and β signals show a coalescence process, the β' signals do not coalesce, i.e., they show residual diastereotopism.[29] In order to follow the coalescence process of these signals, a higher temperature was required. This was achieved in NMR instruments operating at lower frequencies (200 and 60 MHz) (Table III). From the data a barrier of 16.8 ± 0.1 kcal mol^{-1} was calculated for the exchange of groups on the α and β rings and a barrier of 20.5 ± 0.1 kcal mol^{-1} for the exchange of groups on the β' ring.

Discussion

Rotational Mechanisms for 16. The dynamic NMR data for **16** can apriori be interpreted in terms of "flip" and "nonflip" mechanisms.[6] We have previously showed that rotation of the rings for the structurally related **5** leads to enantiomerization, i.e., the rotation involves a flip mechanism and is not a rotation of the rings by 180° which results in coalescence but retains the helicity. The identity of the barriers for two rings is consistent with a similar behavior of **16**. Consequently, we will discuss the rotational processes for **16** only in terms of flip mechanisms, each of which involving enantiomerization.

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[24] The program used was NOESY.AU (Nuclear Overhauser Enhancement Correlated Spectroscopy) as implemented by Bruker, in which shift correlations are due to chemical exchange of NOE. That the appearance of the cross peaks is indeed a consequence of chemical exchange was corroborated by saturation transfer experiments.

[25] Note that in order to facilitate the comparison with the different Kubo–Sack matrices, in Figure 3 the F_1 dimension is plotted along the x axis and the F_2 dimension along the y axis in contrast with the common representation of 2D spectra.

[26] The higher barrier of the threshold mechanism for **5** compared with that for **16** (see text) necessitates a higher temperature in order to observe the magnetization transfer.

[27] The numbering of the signals of **16** in Table I is according to their δ values. Since the numbering of the signals for **5** follows the assignment of the signals for **16** but the relative δ values of the different signals of **5** and **16** are not identical, the 2D spectrum of **5** is a representation of the [α,β,β'] matrix of Table II in which the 1 and 3 as well as the 7 and 8 columns and rows are permuted.

[28] Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.

[29] (a) Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 3205. (b) Finocchiaro, P.; Hounshell, W. D.; Mislow, K. *Ibid.* **1976**, *98*, 4952.

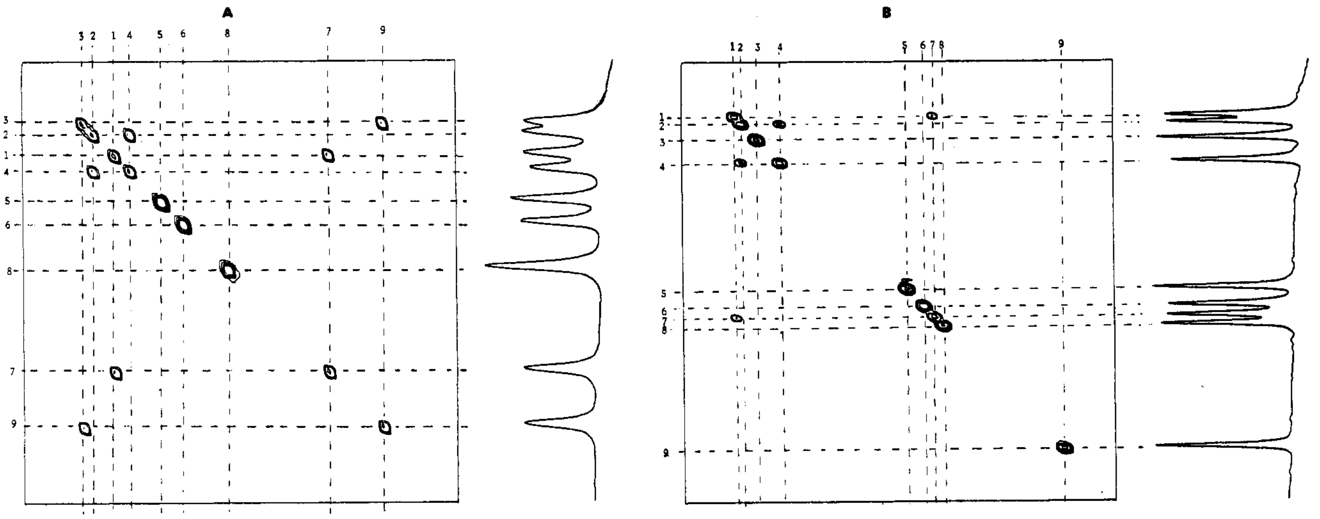

Figure 3. 200-MHz ^{1}H 2D exchange NMR spectra of the methyl region of **16** in $CDCl_3$ at 293 K (B) and of **5** in $C_6D_5NO_2$ at 330 K (A). The numbering of the signals is according to their assignment as given for **16** in Table I.

Identity of the barriers for interchange of the *o*-Me and Mes-H groups at both the α and β rings can be due to two reasons: (a) accidental identity of the barriers for the two diastereomeric $[\alpha]$- and $[\beta]$-one-ring flips and (b) single rotational $[\alpha,\beta]$-two-ring flip mechanism. The α and β rings reside in appreciably different steric environments, and since steric crowding strongly influences the rotational barriers,[30] we should expect different barriers for the $[\alpha]$- and $[\beta]$-one-ring flips, thus excluding possibility a. Possibility b where the barriers observed for the α and β rings are measures of a single rotational process involving changes of diastereotopic groups at the two rings seems more likely, especially since an extensive structural variation in the series of vinyl propellers **5–9** gave uniformly identical barriers for the three rings. This was taken as strong evidence against accidental identity of the one-ring flip barriers.[2]

From the previous discussion it can be concluded that the threshold mechanism for **16** is an $[\alpha,\beta]$-two-ring flip, with a barrier of 16.8 ± 0.2 kcal mol^{-1}. The higher barrier (20.5 ± 0.1 kcal mol^{-1}) found for the interchange of groups at the β'-mesityl ring is due to another rotational process. Since an interchange of diastereotopic magnetic sites at a certain ring in a correlated rotation is a consequence of a flip of that ring, this higher energy process should involve flip of the β'-ring, i.e., it may be a $[\beta']$-one-ring flip, an $[\alpha,\beta']$- or a $[\beta,\beta']$-two-ring flip, or a $[\alpha,\beta,\beta']$-three-ring flip. Since the nonflip of either the α or the β ring would lead to severe steric interactions in the transition state, and since the threshold mechanism for **5** is the three-ring flip, the most plausible higher barrier process for **16** is a three-ring flip.

Consequently, the rotational mechanism for the trimesitylvinyl propellers is not uniform but depends on the bulk of the fourth double bond substituent X. For all the substituents previously studied (X = Cl, OH, OAc, *i*-OPr)[2] which are bulkier than hydrogen, a severe steric crowding is generated when the β'-ring passes through the double bond plane and comes to a close contact with X in the course of its nonflip process. This interaction raises the energy of the transition state of the $[\alpha,\beta]$-two-ring flip above that of the three-ring flip, and the latter becomes the threshold mechanism for all these systems. When the bulk of X is reduced (and **16**, X = H is the extreme case), the steric hindrance and the energy of the transition state of the $[\alpha,\beta]$-two-ring flip are lowered. Since for the same steric reason the ground-state energy is also reduced more with the smaller X groups, it is not obvious that the rotational activation energy will be lower for the system with the smaller X. However, the steric interactions are at a maximum in the transition state where the β'-ring is enforced to a close contact with X, whereas in the ground state these interactions are efficiently reduced by torsion of the ring or by a change in bond angles. The steric effect on the transition state should be, therefore, much more important with a consequent lowering of the energy of the process where the β'-ring passes via the double-bond plane for systems with smaller X. This explains why the threshold barrier is larger for **5** than for **16**. On the other hand, the higher barrier for the three-ring flip of **16** (the lower limit is 20.5 kcal mol^{-1}) than that for **5** (18.4 kcal mol^{-1}) is likely to be due, at least in part, to relative lowering of the ground-state energy of **16**. That this is not reflected in an appreciable decrease in the torsional angle of the β'-ring in the solid state[1] is not surprising since this angle is mainly affected by the presence of the geminal mesityl group. The torsional angles of the β and β'-mesityl rings in dimesitylketene, 1,1-dimesitylethylene, and tetramesitylethylene, where the α-substituents are absent, small, or bulky, respectively, are 47.8°, 56.7°,[1] 50.0°, 57.7°,[4] and 54.6°.[31] The effect is more pronounced on the C=C—X bond angle which is 115° for **16** and 119° and 122° for the two crystallographic forms of **5**,[1]—a difference which reflects the effect of steric interaction between X and the β'-ring on the ground-state structure of the system.

From the previous and present data a picture of the dynamic behavior of vinyl propellers substituted by geminal bulky rings on one carbon begins to emerge. If the other two double bond substituents are relatively bulky (Cl, OH, OR, OAc, Ar, or alkyl) the threshold mechanism involves flip of all the aryl rings. Examples are the two-ring flip for **11–14**, the three-ring flip for **5–9**, and the four-ring flip for tetra-*o*-tolylethylene.[32] If one substituent is a hydrogen, the steric interaction with the ring cis to it in the transition state is significantly lowered and in some cases it leads to a flip process where the number of the flipping rings is one less than the maximum possible and the ring cis to the hydrogen is the nonflipping ring. Ex-

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amples are the one-ring flip for **10** and the two-ring flip for **16**.

An interesting related question is whether a shift to a threshold mechanism with a lower number of flipping rings would be observed by modifying system **2** not by changing X, but by diminishing the size of one of the rotors; e.g., the modification Mes → Ph in **5** will reduce the energy of the transition state for the nonflip process of the phenyl ring. Preliminary results showed, however, that such a change can lead to a different type of rotational mechanism. In a 2,2-dimesityl-1-(3′,5′-disubstituted-aryl)ethenol the result is a noncorrelated rotation of the less bulky α-aryl ring.[33]

Comparison of the Threshold Mechanisms of 16 and Trimesitylmethane. It is interesting to compare the rotational barriers for trimesitylmethane (**17**)[34] and its vinyl analogue **16**. The threshold mechanism for both compounds is the two-ring flip but the barrier for **17** (21.9 kcal mol^{-1} at 167 °C)[34] is 5.1 kcal mol^{-1} higher. We attribute the lower barrier of **16** to the different geometries. In the vinyl propeller the three rings are attached to a multiatomic frame and this should reduce the steric interaction between the flipping α and β rings in the [α,β]-two-ring flip compared with that in **17**, where both rings are connected to a single carbon. Another difference is that due to the C_3 point group symmetry of **17** the three two-ring flips involving each of the three mesityl rings are degenerate, while for **16** the three mechanisms are nondegenerate since the three mesityl rings are chemically distinct. Therefore, there is no need to multiply the rate constant derived from the coalescence of the signals of **16** by three, as in the case of **17**.[34]

Experimental Section

The 2D spectra were recorded on a Bruker WP 200 SY pulsed FT spectrometer equipped with an aspect 2000 computer. For the 2D exchange experiments and for the ^{13}C, ^{1}H correlation 64 FID's and 128 FID's (each consisting of 16 scans of 512 data points) were accumulated, respectively. In the case of the 2D exchange experiment the FID was zero filled to 256 W in the F_1 dimension. Typical aquisition parameters were the following: SW_2 170 Hz, SW_1 ±85 Hz (for the 2D exchange) and SW_3 113 Hz, SW_1 ±120 Hz (for the ^{13}C, ^{1}H correlation) a sine bell window function was used.

Trimesitylethylene (16). To a solution of 1,1,2-trimesitylethanol (**15**)[13] (100 mg, 0.25 mmol) in toluene (10 mL) was added *p*-toluenesulfonic acid (5 mg), and the mixture was refluxed overnight. The solvent was evaporated, and the residue was dissolved in ether. The ethereal solution was washed with aqueous solution of 5% K_2CO_3 (20 mL) and dried ($MgSO_4$), and the solvent was evaporated, giving a residue which after recrystallization from ethanol gave trimesitylethylene (**16**) (70 mg, 73%): mp 136 °C; ^{13}C NMR ($CDCl_3$, room temperature) δ (sp^2 region) 128.50, 129.17, 129.25, 129.60, 129.98, 134.19, 135.22, 135.54, 135.80, 136.06, 136.19, 136.33, 136.83, 136.92, 137.06, 137.14, 137.49, 138.69, 140.71. For the Me region see Table I.[35] Anal. Calcd for $C_{29}H_{34}$: C, 91.04; H, 8.96. Found: C, 91.20; H, 8.82.

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Registry No. **15**, 94203-60-8; **16**, 94800-90-5.

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Localized Molecular Orbitals of Acyclic Polyenes as a Basis for a New Approach to Resonance Energies

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π-Localized molecular orbitals have been obtained for a large set of acyclic conjugated polyenes in the HMO approximation. On the basis of these results, a convenient classification of π-bond types of conjugated hydrocarbons is proposed. This bond type classification is subsequently used to obtain a set of π-bond energy reference parameters for the calculation of resonance energies of conjugated hydrocarbons. The parameters resulting from the present method have a direct physical significance, contrary to those obtained by using previously reported methods.

One important concern of theoretical organic chemistry has always been the quantification and interpretation of aromaticity in cyclic conjugated systems, leading to several definitions of the resonance energy (RE) of a molecule.[1] These can be grouped in the following general expression:

$$\mathrm{RE} = E_\pi(\text{conjugated molecule}) - E_\pi(\text{reference structure})$$

The simplest choice for the reference structure of a conjugated system with $n_{C=C}$ double bonds consists in taking $n_{C=C}$ isolated carbon–carbon double bonds. Making this choice and using the Hückel method to calculate the π-energies, we obtain the classical Hückel resonance energy[2] (HRE):

$$\mathrm{HRE} = E_\pi(\text{conjugated molecule}) - n_{C=C}(2\alpha + 2\beta)$$

In what follows we will take β as the energy unit and $\alpha = 0$ as the energy origin, so that

$$\mathrm{HRE} = E_\pi(\text{conjugated molecule}) - 2n_{C=C}$$

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