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Threshold Rotational Mechanisms and Enantiomerization Barriers of Polyarylvinyl Propellers

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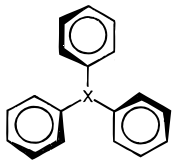
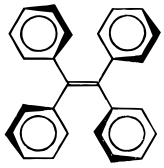
Molecular Propellers

Organic molecules may adopt conformations which resemble the three-dimensional shape of familiar objects. For example, compounds Ar_3X (**1**) resemble the propellers used in ships and airplanes. In these "molecular propellers" the aryl rings (the "blades") radiate from a central atom (the propeller "hub") and are all twisted in the same sense.[1,2] These compounds, which were extensively studied by Mislow and co-workers,[1,3,4] are chiral and exist in two enantiomeric conformations differing in the sense of twist (clockwise or counterclockwise) of the rings (the "helicity"). The rotation of the rings in unison (a correlated rotation) is energetically favored over the uncorrelated rotation.[3] In their dynamic behavior, the rings of these propellers resemble macroscopic gears and a pair of aryl rings in the molecular propellers (which may be considered as a pair of two-toothed gears) may undergo either conrotatory or disrotatory motion.[5]



1 X = CH, B, N



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Vinyl Propellers

When the aryl rings are attached to an ethylenic double bond, the resulting systems (e.g., $Ar_2C{=}CR_2$, $Ar_2C{=}CRAr$, and $Ar_2C{=}CAr_2$) can be considered as "vinyl propellers" (e.g., **2**).[6] If all rings are identical with local C_2 axes, these systems exist in two enantiomeric forms. The vinyl propellers may undergo correlated or uncorrelated ring rotations around the Ar—C= bonds.[6] By analogy to "classical" molecular propellers, the correlated rotations can be analyzed by "flip" mechanisms (Figure 1) leading to helicity reversal.[1,3,5,6] Flipping ring(s) pass through the normal to the reference double-bond plane. A "*n*-ring-flip" mechanism involves conrotatory rotation of *n* rings, while the nonflipping ring(s) (if any) rotate in the opposite direction (i.e., "nonflip") and pass through the double-bond plane. If during the helicity reversal none of the rings flips, the process is called a zero-ring flip. For rings possessing local C_2 axes, helicity reversal results in enantiomerization. The lowest activation energy mechanism (threshold mechanism) of most propellers **1** is the two-ring flip.[1,3]

Systems **2** are of interest since, in contrast to **1**, their propeller conformation results from a compromise between the opposite requirements to maximize conjugation

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(1) Reviews: Mislow, K.; Gust, D.; Finocchiaro, P.; Boettcher, R. J. *Fortschr. Chem. Forschr.* **1974**, *47*, 1. Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26. Meurer, K. P.; Vögtle, F. *Top. Curr. Chem.* **1985**, *127*, 1. Willem. R.; Gielen, M.; Hoogzand, C.; Pepermans, H. *Advances Dyn. Stereochemistry*; Gielen, M., Ed.; Academic Press: New York, 1985; Vol. 1, p 207.
(2) Recent study: Ito, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1409.
(3) Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 1535.
(4) Okamoto, Y.; Yashima, E.; Hatada, K.; Mislow, K. *J. Org. Chem.* **1984**, *49*, 557.
(5) Mislow, K. *Chemtracts: Org. Chem.* **1989**, *2*, 151.
(6) Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 477.

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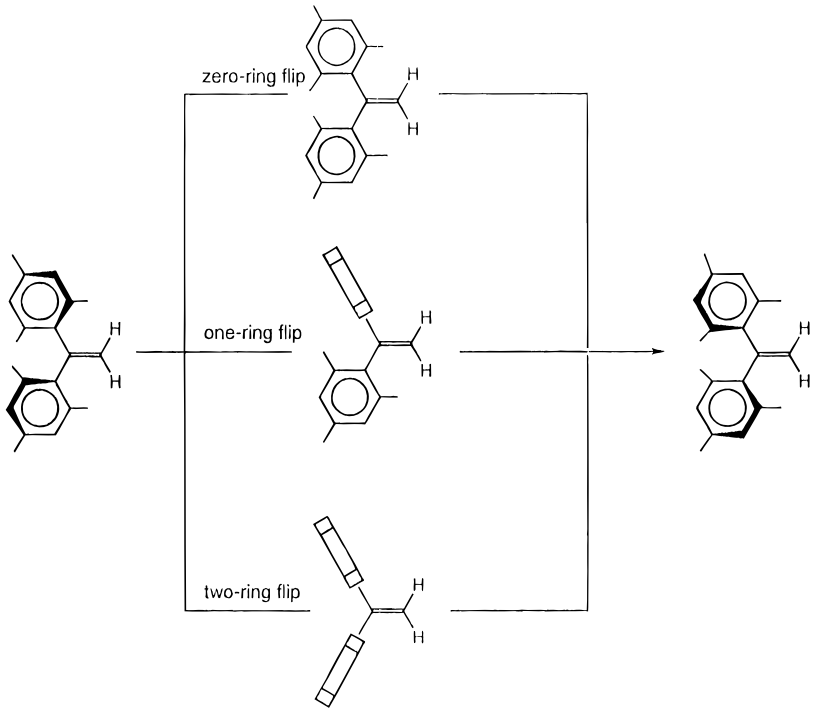


FIGURE 1. Possible flip processes for the parent 1,1-dimesitylvinyl propeller. Aryl rings perpendicular to the double-bond plane are shown side-on.

by reducing the Ar−C═C torsional angles while reducing the Ar/Ar repulsive steric interactions by increasing those angles. Since the rings and the double-bond substituent(s) (if present) are attached to the central frame in a coplanar fashion, **2** may serve as an ideal system for studying the influence of the steric bulk of the rings and substituent(s) on the barrier for the correlated rotation. The vinyl propellers have richer stereochemical options since, combined with the Ar−C rotations, additional processes such as double-bond rotation or positional rearrangement of the aryl rings (a process which may occur if a vinyl cation intermediate is formed) may be possible.

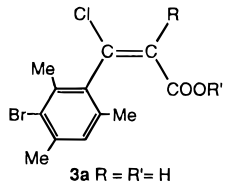
We review here our recent studies on rotational processes of vinyl propellers starting with a single ring system and continuing with systems having a larger number of vinylic aryl substituents.

Crowded Styrenes

Although there is no meaning to a "one-blade" vinyl propeller, a proper starting point is Adams' classical resolution of cinnamic acids **3a,b**[7] where atropisomerism results from steric crowding in the transition state for the rotation of the bromomesityl ring. The aryl ring is orthogonal to the C═C bond (as shown in the crystal of ester **3c**),[8] and the high barrier to transfer of bromine from "above" to "below" the C═C plane enables the resolution of **3**.

1,1-Diarylvinyl Propellers

The simplest vinyl propeller is a diarylethene. Three ring attachments are possible: geminal (1,1) and *E*- and *Z*-vicinal (1,2).



3a R = R'= H
3b R = Me, R'=H
3c R = H, R'=Me

Structural Correlation Method. The low rotational barriers of 1,1- and 1,2-diphenylethenes[9] and derivatives lacking *ortho* substituents preclude determination of their rotational barriers and preferred rotational pathway by NMR methods. 1,1-Diphenylethene has been calculated to prefer a propeller conformation with a threshold one-ring-flip enantiomerization barrier estimated as 1.2−3.9 kcal mol^{-1}.[9,10] Molecular mechanics (MM) calculate barriers of 12.9, 1.2, and 3.0 kcal mol^{-1} for the zero-, one-, and two-ring flips of 1,1-diphenylethene.[11] Interestingly, the preferred rotational pathway can be deduced by analyzing crystal structures possessing the 1,1-diarylethene subunit. The Structural Correlation Method states that "if a correlation can be found between two or more independent parameters describing the structure of a given molecular fragment in various environments, then the correlation function maps a minimum energy path in the corresponding parameter space."[12] We retrieved from the Cambridge Crystallographic Database all the X-ray determined structures possessing the Ar^1Ar^2C═C fragment and plotted the torsional angles of the two rings in a conformational map.[11] Most points concentrated near the (40°, 40°) region, suggesting a preferred propeller conformation for this fragment. Clustering of points along

(7) Adams, R.; Miller, M. W. *J. Am. Chem. Soc.* **1940**, *62*, 53. Adams, R.; Anderson, A. W.; Miller, M. W. *Ibid.* **1941**, *63*, 1589.
(8) Beit Yannai, M.; Rappoport, Z. *J. Org. Chem.*, in press.
(9) Stegemeyer, H.; Rapp, W. *Ber. Bunsen-Ges. Phys. Chem.* **1971**, *75*, 1665.
(10) Baraldi, I.; Gallinella, E.; Momicchioli, F. *J. Chim. Phys.* **1986**, *83*, 653.
(11) Kaftory, M.; Nugiel, D. A.; Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1989**, *111*, 8181.
(12) Bürgi, H.-B.; Dunitz, J. D. *Acc. Chem. Res* **1983**, *16*, 153.

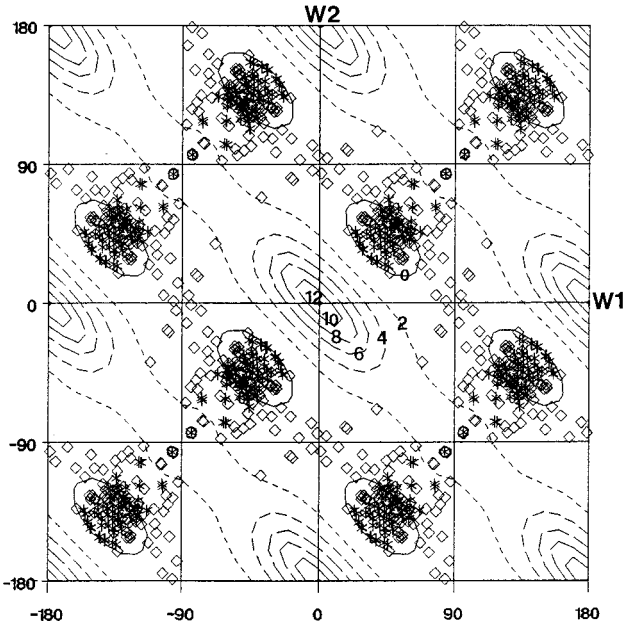
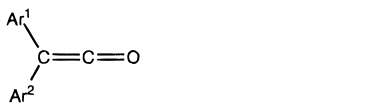


FIGURE 2. Conformational map (W1 *vs* W2) for 1,1-diarylethene compounds.[11] The contours represent the calculated MM2(85) equipotential energy regions. Each point represents the crystallographically determined torsional angles of the two rings of $Ar_2C{=}CR^1R^2$: (◇) $R^1 \neq R^2$, (*) $R^1 = R^2$. Reprinted from ref 11. Copyright American Chemical Society 1989.

the (0°, 90°); (90°, 0°) diagonal (Figure 2) suggest one-ring flip as a likely rotational mechanism for the system. Additional points (for *ortho*-substituted systems) are between the (40°, 40°) and (90°, 90°) regions, indicating that the two-ring flip is a likely rotational mechanism for bulky aryl rings. The absence of points near the (0°, 0°) region reflects the high energy of the zero-ring-flip process. Likewise, $Ar^1Ar^2C{=}O$ systems prefer propeller conformations, but the one-ring flip is strongly preferred.[13]

Nonpropeller Conformations. The compromise between conjugation and steric effects in 1,1-diarylvinyl systems is best demonstrated with the preferred conformation of diarylketenes. The absence of other double-bond substituents and the linearity of the C=C=O skeleton make the Ar−C=C torsional angles close models for their "intrinsic" values. With the symmetric diphenylketene, HF/3-21G calculations give a propeller conformation with identical Ph−C=C angles of 44.9°.[14] Solid dimesitylketene (**4a**)[15a] and ditipylketene (**4b,** tipyl = 2,4,6-triisopropylphenyl)[15b] are also propellers displaying two different Ar−C=C angles (48.8° and 56.8° for **4a**, 54.1° and 55.9° for **4b**) presumably due to crystal lattice forces. In contrast, a nonpropeller conformation is calculated for **4c** with the phenyl ring in the C=C plane and the mesityl ring perpendicular to it.[14] Since the Mes−C=C conjugation energy exceeds that of Ph−C=C by only 0.3 kcal mol^{-1},[16] whereas the planar-Ph/perpendicular Mes is much more sterically favored than the planar-Mes/perpendicular Ph arrangement, the first conformation is more stable.



4a $Ar^1 = Ar^2$ =Mes Mes = 2,4,6-$Me_3C_6H_2$
4b $Ar^1 = Ar^2$ = Tip Tip = 2,4,6-*i*-$Pr_3C_6H_2$
4c Ar^1 = Mes, Ar^2 = Ph

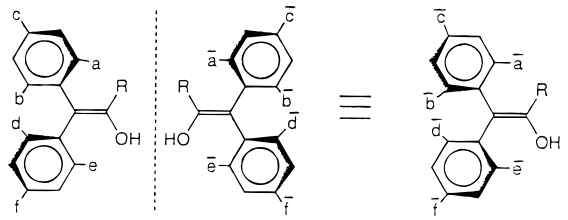
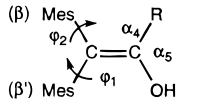


FIGURE 3. Labeling of Me groups in the two enantiomeric forms of 5. An overbar denotes an enantiotopic relationship.

Experimental Determination of the Threshold Mechanism. The threshold rotational mechanism for vinyl propellers is usually determined from the temperature-dependent NMR spectra in achiral media. This is exemplified with 1-substituted-2,2-dimesitylethenols **5**. X-ray crystallography,[11] MM calculations,[17,18] and NMR spectroscopy[17] indicate that compounds **5** adopt a propeller conformation where the *o*-Me groups on a given ring are diastereotopic. These groups are labeled by letters (e.g., a−b) and the corresponding enantiotopic sites in the enantiomer by the same letters with overbars (e.g., $\bar{a}-\bar{b}$) (Figure 3). If the β ring "flips", this exchanges the *o*-Me groups a and $\bar{b}$ (and $\bar{a}$ and b) and should result in coalescence of the signals. If a ring nonflips, enantiotopic groups are mutually exchanged (e.g., a ⇌ $\bar{a}$, b ⇌ $\bar{b}$) and no coalescence should be observed in the NMR spectrum (i.e., the process is "silent"). Consequently, for a two-ring-flip threshold mechanism, pairs of *o*-Me groups on both rings should mutually coalesce and both rings give identical barriers. For a threshold one-ring flip, only signals in the flipping ring will coalesce. The zero-ring flip cannot be followed by NMR in an achiral solvent.



5a R = H
5b R = Me
5c R = Et
5d R = *i*-Pr
5e R = *t*-Bu
5f R = $SiMe_3$
5g R = $Si(SiMe_3)_3$

Additional evidence that the rotational process followed by NMR involves an enantiomerization and that a "silent" zero-ring process is not occurring with a barrier lower than that determined experimentally from the exchange of *o*-Me groups can be obtained by attaching a chiral (e.g., an isopropyl) probe to the skeleton (as in **5d** or in the isopropyl ether of **5a**).[17] The isopropyl methyls are

(13) Rappoport, Z.; Biali, S. E.; Kaftory, M. *J. Am. Chem. Soc.* **1990**, *112*, 2, 7742.
(14) Yamataka, H.; Aleksiuk, O.; Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1996**, *118*, 12380.
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(16) Nadler, E. B.; Rappoport, Z. *J. Am. Chem. Soc.* **1987**, *109*, 2112.
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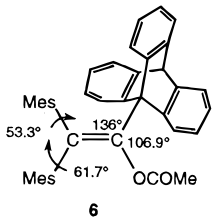
rendered diastereotopic by the helicity and "sense" the helicity reversal process since they mutually exchange only when the molecule enantiomerizes. The barriers derived for **5d** from the mutual exchange of *o*-Me or Ar-H protons at both rings or from coalescence of the *i*-Pr Me groups were identical, in agreement with a two-ring-flip process.[17] However, the enantiomerization may still involve stepwise ring rotation via a high-energy intermediate. MM calculations provide independent support that both rings rotate in unison and satisfactorily reproduce the experimental barriers of **5a**−**e**.[17,18]

Rotational Barriers. Extensive DNMR and MM studies on the threshold mechanisms and rotational barriers of systems **5** indicate that they display substituent-dependent threshold rotational mechanisms.[17−20] When R = H (**5a**), the small hydrogen enables the β-ring to adopt a coplanar Ar−C=C arrangement in the rotational transition state and the threshold mechanism is the (β')-one-ring flip (with a barrier $\Delta G_c^{\ddagger} = 10.4$ kcal mol^{-1} in CD_3COCD_3), while for the two-ring flip, $\Delta G_c^{\ddagger} = 14.2$ kcal mol^{-1}.[17] However, when R is bulkier (R = alkyl, **5b**−**e**), the passage of the rings through the C=C plane is "inhibited" by the R and OH, and the two-ring flip becomes the threshold rotational mechanism.[17]

Dynamic NMR experiments indicate that the rotational barriers of **5** decrease on increasing the bulk of the alkyl substituent ($\Delta G_c^{\ddagger} = 12.6$, 12.0, 11.7, and 10.4 kcal mol^{-1} in CD_3COCD_3 for **5b**−**e**, respectively). These barriers are linearly correlated with Taft's E_s steric parameter: the larger E_s(R), the lower the $\Delta G_c^{\ddagger}$.[17] The change of R also leads to significant geometry changes, as evident by X-ray crystallography.[11] The rotational barriers are linear with the cosine of the φ_2 torsional angle and the α_4 angle (cf. **5**). Increase in the bulk of R from H to *t*-Bu increases α_4 monotonically from 118.1° to 133.2° and decreases α_5 from 118.1° to 107.4°.[11,18,19] The Mes−C=C torsion angles increase from 56.7° (φ_1), 50.2° (φ_2) for **5a** to 66.0° (φ_1) and 63.7° (φ_2) for **5e**. The reduced Mes−C=C conjugation raises the ground-state energy, less rotation is required to achieve the 90° Ar−C=C angle in the transition state and the LFERs between $\Delta G_c^{\ddagger}$ and E_s(R) or cos φ_2[11] become self-explanatory.

Since $\Delta G_c^{\ddagger}$ for the two-ring flip in **5a**−**e** provides a sensitive probe of the steric interaction across the double bond, other α-substituents were examined. The threshold two-ring-flip barrier when R = $SiMe_3$ (**5f**) is 11.1 kcal mol^{-1}, a value intermediate between those for **5d** and **5e**. Hence, the steric congestion due to α-Me_3Si is lower than that for α-*t*-Bu, although Me_3Si with the longer Si−C bonds could be regarded as being "larger" than *t*-Bu.[19] Assuming that the linear correlations for alkyl substituents between $\Delta G_c^{\ddagger}$ (two-ring flip) and E_s or cos φ_2 hold when R = Si(SiMe$_3$)$_3$ (**5g**), for which $\Delta G_c^{\ddagger} = 10.2$ kcal mol^{-1}, an E_s(Si(SiMe$_3$)$_3$) value of −1.46 ± 0.14 was estimated.[18]

Although further increasing the bulk of the substituent R is expected to further decrease the rotational barrier of the aryl rings, the 9-tripticyl derivative **6** displays a large



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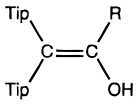


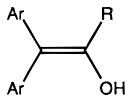
7a R=H
7b R = Me
7c R = *t*-Bu

helicity reversal barrier (17.0 kcal mol^{-1} in $C_6D_5NO_2$).[21] Acetate **6** consists of two two-toothed (mesityl) rotors and a three-toothed (tripticyl) rotor. The rotation of all rotors is coupled, with the tripticyl group rotating only partially in a "rocking" motion while the mesityl rings undergo a two-ring-flip process. Due to this coupling, the barrier of **6** is no longer correlated with the bulk of the substituent.[21]

Increasing the bulk of the aryl groups by replacing the mesityls of **5a** by tipyls (**7a**) increases the rotational barriers of both the one- and two-ring flips but the former still remains the threshold mechanism [$\Delta G_c^{\ddagger}$(**7a**) = 14.9 and 18.4 kcal mol^{-1} ($C_2D_2Cl_4$)].[22] Changing the solvent to DMSO-d_6 raises the one-ring-flip barrier to 16.5 kcal mol^{-1}, without affecting the two-ring-flip barrier. Replacing the vinylic hydrogen by a methyl renders the two-ring flip the threshold mechanism [$\Delta G_c^{\ddagger}$(**7b**) = 16.0 kcal mol^{-1} (DMSO-d_6)] but in contrast to the **5a**−**e** series, a bulkier R does not further decrease the barrier [$\Delta G_c^{\ddagger}$(**7c**) =16.5 ± 0.3 kcal mol^{-1} (DMSO-d_6)].[22] Apparently, with the limited data available, the increase in ground-state energy by twisting the aryl rings reaches a plateau for R = Me, and further increase in the bulk of R does not affect the rotational barrier.

Buttressing Effects. Buttressing effects are indirect steric effects caused when a bulky substituent is adjacent to a group located in a sterically crowded environment.[23] The buttressing group usually affects the reactivity, rotational barriers, or equilibria by hindering modes of steric relief (such as bond angles widening) of the sterically crowded group. If it affects more the transition state than the ground state, the rotational barrier is expected to increase, while if the ground state is more affected, a lower barrier is expected (an inverse buttressing effect).[24]

When all four *meta* positions of the mesityl rings of **5a** are substituted by methyl groups or by bromines, the one-ring flip remains the threshold process for **8a** and **9a**



8a Ar= Me_5C_6, R=H
8b Ar= Me_5C_6, R=Me
8c Ar= Me_5C_6, R=*t*-Bu
9a Ar= Br_2Mes, R=H
9b Ar= Br_2Mes, R=Me
9c Ar= Br_2Mes, R=*t*-Bu

(19) Nadler, E. B.; Rappoport, Z. *Tetrahedron Lett.* **1991**, *32*, 1233.
(20) Reviews on polyarylethenols: (a) Rappoport, Z.; Biali, S. E. *Acc. Chem. Res.* **1988**, *21*, 175. (b) Hart, H.; Rappoport, Z.; Biali, S. E. In *The Chemistry of Enols;* Rappoport, Z., Ed.; Wiley: Chichester, U.K., 1990; Chapter 8, p 481.
(21) Schottland, E.; Frey, J.; Rappoport, Z. *J. Org. Chem.* **1994**, *59*, 1663.
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(23) Rieger, M.; Westheimer, F. H. *J. Am. Chem. Soc.* **1950**, *72*, 19. Armstrong, R. N.; Ammon, H. L.; Darnow, J. N. *J. Am. Chem. Soc.* **1987**, *109*, 2077.
(24) Yamamoto, G.; Suzuki, M.; Oki, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 809.

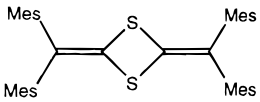
Table 1. $\Delta G_c^{\ddagger}$ Values (kcal mol^{-1}) for Ring-Flip Processes of $(X_2Mes)_2C{=}C(OH)R$ in 3:7 $CS_2{-}CD_2Cl_2$

		X		
R	ring flip	H	Me	Br
H	one-ring	9.1	11.4	12.1
	two-ring	13.6	12.3	13.0
Me	two-ring	12.0	9.9	10.8
t-Bu	two-ring	10.4[a]	<8	8.2
Mes[b]	three-ring	18.4	16.7	17.0

[a] In $C_6D_5CD_3$. [b] In $C_6D_5NO_2$.

(Table 1) but the gap between it and the higher energy two-ring flip is reduced from 4.5 to 0.9 kcal mol^{-1}.[25] This results from an increase in the one-ring-flip barrier, as expected for a reduced flexibility due to buttressing of the *o*-Me groups in the nonflipping ring in the transition state. However, this is accompanied by a parallel decrease in $\Delta G_c^{\ddagger}$ (a negative buttressing effect) for the two-ring flip for the change **5a,b,e** → **8a**−**c**, **9a**−**c**. Changes in the torsional angles of **9a** and **9b** account for an appreciable part of the effect, but since these angles are lower for **8c** and **9c** than for **5e**, $\Delta G_c^{\ddagger}$ should increase. The electronic effects of the substituents on the Ar−C=C conjugation, which are more pronounced for **9** than for **8**, account for most of the observed changes.[25]

Multiple 1,1-Diarylvinyl Propellers. If a molecule contains two spatially separated 1,1-diarylethene subunits, the number of stereoisomers increases, since the helicities of the two subunits are independent.[26] For a planar central ring, the multiple vinyl propellers **10** and **11** should



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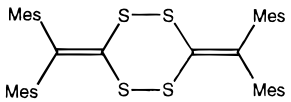
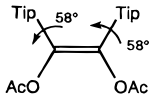


11

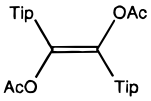
exist in three stereoisomers, a *meso* form with opposite helicities of the two subunits and an enantiomeric pair with identical helicities.[26a] In solid **10** the central ring is indeed planar and the two vinyl propeller subunits have opposite helicities. System **11** has six stereoisomers since the tetrathiane ring adopts a chiral twist-boat conformation. Static NMR spectra of **10** and **11** are consistent with this analysis and dynamic NMR gives $\Delta G_c^{\ddagger} = 12.7$ and 13.3 kcal mol^{-1}, respectively.[26a] It was suggested that in both systems the rotations of the two propellers are independent, being for **11** coupled with the inversion of the tetrathiane ring.[26a]

(*Z*)-1,2-Diarylvinyl Propellers. The *cis*-stilbene fragment was analyzed by the Structural Correlation Method. Crystal data and MM calculations indicate that it adopts a propeller conformation and that the preferred rotational mechanism is a one-ring flip.[27] However, when the double bond is in a small ring, the threshold mechanism changes. The points for 1,2-diarylcyclopropenes concentrate around the (0°, 0°) region, suggesting a nearly planar preferred conformation and a zero-ring flip as the expected threshold enantiomerization mechanism of nonplanar systems.[27]

Rotational barriers can only be measured for severely crowded stilbenes. The diacetate **12Z** exists in a propeller conformation and $\Delta G_c^{\ddagger} = 14.8$ kcal mol^{-1}. In contrast, the rotation of diastereomer **12E** could not be frozen on the NMR time scale ($\Delta G_c^{\ddagger} < 10$ kcal mol^{-1}).[28] Hence, the rotational barriers of the ditipylethenes increase in the order (*E*)-1,2-Ar_2 < (*Z*)-1,2-Ar_2 < 1,1-Ar_2.



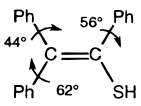
12Z



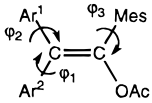
12E

1,2,2-Triarylvinyl Propellers

Threshold Rotational Mechanisms and Rotational Barriers. Triarylethenes adopt a propeller conformation but, since it has C_1 symmetry, the torsional angles of the rings should differ. This is shown for solid triphenylethenethiol (**13**).[29] Compromise between Ar−C=C conjugation and Ar/Ar interactions dictates the geometries of the acetates **14E**, **14Z,**[14] and **15**.[6,30]

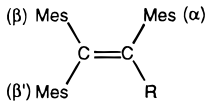


13



14E Ar^1= Mes, Ar^2 = Ph; φ_1=57°, φ_2=65°, φ_3=62°
14Z Ar^1= Ph, Ar^2 = Mes; φ_1=77°, φ_2=43°, φ_3=67°
15 Ar^1= Mes, Ar^2 = Mes; φ_1=64°, φ_2=57°, φ_3=59°

With bulky aryl groups the propeller conformation is frozen on the NMR time scale at room temperature, and for trimesitylethenol (**16a**), separate signals are observed in the ^{1}H NMR spectrum ($C_6D_5NO_2$) for the nine methyls and six aromatic protons.[6]



16a R = OH
16b R = H
16c R = OPr-*i*

The enantiomerization barriers of the crowded triarylethenes exceed those of 1,1-dimesitylethenes, but the threshold rotational mechanism still depends on the vinylic substituent. For **16b** having a vinylic hydrogen, it is an [α,*β*]-two-ring flip[31] with $\Delta G_c^{\ddagger} = 16.8$ kcal mol^{-1} and the three-ring-flip barrier is 3.7 kcal mol^{-1} higher. When the vinylic substituent is larger than hydrogen, it is a three-ring flip[6,31] with $\Delta G_c^{\ddagger} = 18.4$, 15.8, and 19.0 kcal mol^{-1} for **16a, 16c,** and **15**.

Whereas the two-ring-flip barriers of **5** decrease on increasing the bulk of the aliphatic substituent R, the three-ring-flip barriers of **17** decrease with the decreased bulk of the α-aryl in the order Mes (18.4) > 9-anthryl (16.0)

(25) Eventova, I.; Nadler, E. B.; Rochlin, E.; Frey, J.; Rappoport, Z. *J. Am. Chem. Soc.* **1993**, *115*, 1290.
(26) (a) Selzer, T.; Rappoport, Z. *J. Org. Chem.* **1996**, *61*, 7326. (b) Several multiple propellers derived from **1** (e.g., $RC(CH_2PPh_2)_3$) have been studied as ligands. See, for example: Janssen, B. C.; Sernau, V.; Huttner, G.; Asam, A.; Walter, O.; Büchner, M.; Zsolnai, L. *Chem. Ber.* **1995**, *128*, 63.
(27) (a) Gur, E.; Biali, S. E.; Rappoport, Z.; Kaftory, M. 56th Annual Meeting of the Israel Chemical Society, Jerusalem, February 11−12, 1991. Abstract 98. (b) Gur, E. M.Sc. Thesis, The Hebrew University, 1991.
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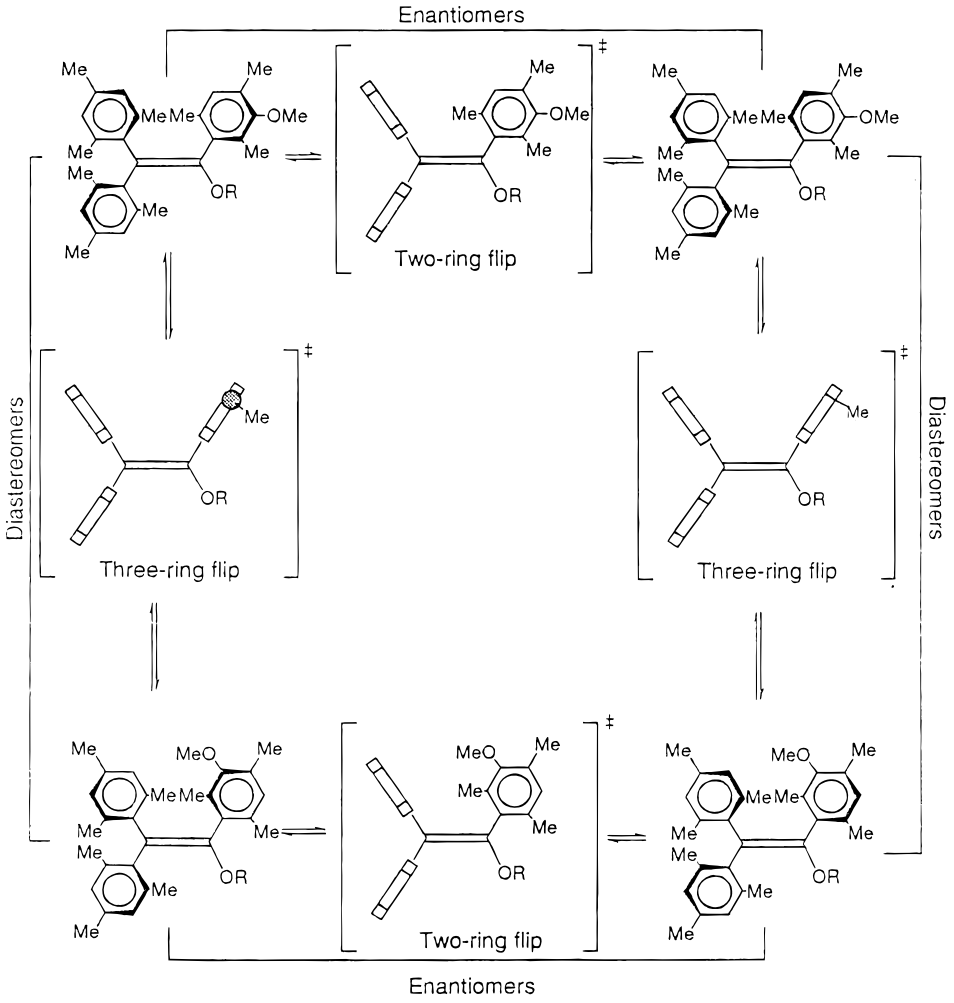


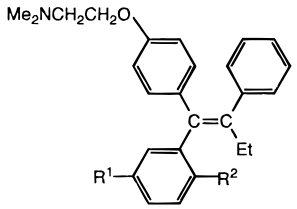
FIGURE 4. Four stereoisomers of a triarylvinyl propeller with one ring tagged by a *meta* substituent. Two diastereomeric [β,β']-two-ring flips and two enantiomeric [α,β,β']-three-ring flips are shown. The ●—Me represents an MeO group "above" the double-bond plane.

> Ph (13.7 kcal mol^{-1}).[6,32] Buttressing by four methyls or bromines in the β-rings of **16a** also reduces the barrier (Table 1).[25]

$Mes_2C{=}C(OH)Ar$

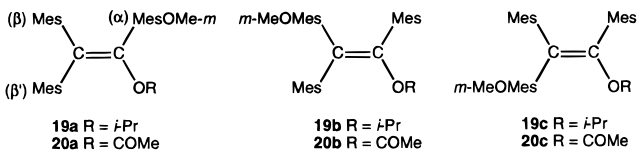
17

Residual Stereoisomerism. An initial claim that the rotational barriers of derivatives of the drug tamoxifen (**18a,b**) are sufficiently high to enable separation of their stereoisomers was proven to be incorrect.[33]



18a R^1 = H, R^2 =OH
18b R^1 = OH, R^2 =H

The barrier height of the threshold rotational mechanism of even the most crowded triarylethenes studied (e.g., **15**) does not allow their resolution at room temperature. Breaking the C_2 symmetry of a ring by introducing a single *meta* "tag" in the trimesitylvinyl skeleton increases the number of stereoisomers to four (disregarding *E*/*Z* isomerism) due to the two possible helicities of the propeller blades ("clockwise" and "counterclockwise") and the two possible locations ("above" and "below" the reference plane) of the tag substituent (Figure 4). Enantiomerization requires both helicity reversal and passage of the tagged ring through the reference plane (a nonflip process). If the threshold mechanism does not involve a nonflip of the tagged ring, under conditions of a fast three-ring flip, the system should still exist in two (residual)[34] enantiomers. If the threshold barrier involving a nonflip of a tagged ring is appreciable, the two enantiomers (each being a rapidly interconverting diastereomeric pair) should be resolvable. Indeed, residual enantiomers of ether **19a** and acetates **20a**—**c** were partially or completely resolved on an optically active triacetylcellulose column.[35,37]



19a R = *i*-Pr
20a R = COMe

19b R = *i*-Pr
20b R = COMe

19c R = *i*-Pr
20c R = COMe

The residual enantiomers of the α-9-anthryl systems **21**—**23** were resolved by chiral chromatography. Partially

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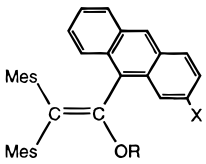


21 X = OMe, R= H
22 X = F, R= H
23 X = F, R = Ac

resolved **21** and resolved enol **22** rapidly enantiomerized at 0 °C with $\Delta G^{\ddagger}$(**22**) of 21.9 kcal mol^{-1}.[37] This process most likely involves reaction at the OH, is catalyzed by base, and may be connected with rotation around the formal double bond in the derived enolate ion. In contrast, acetate **23** enantiomerized slowly and its barrier which was ascribed to a [β,β']-two-ring flip is 26.3 kcal mol^{-1}.

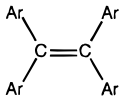
Mapping of the Enantiomerization Routes. If the tag is small with minor electronic effect (e.g., *m*-MeO), its influence on the various rotational barriers is expected to be small and the three-ring flip should remain the threshold mechanism. A *meta* substituent renders the two edges of the substituted ring symmetry nonequivalent, and two diastereomeric transition states exist for each rotational process involving a nonflip of the tagged ring, since the tag may be syn or anti oriented to the double bond. The calculated energy differences between the two transition states for [β,β']-two-ring flips (Figure 4) are 0.1−2.1 kcal mol^{-1}.[38]

Introduction of a *m*-MeO group in each of the three aryl rings of **16c** (i.e., **19a**−**c**) enabled the determination of barrier heights of the three diastereomeric two-ring flips of the system.[38] From the coalescence of the two *o*-Me signals a three-ring-flip barrier of 15.8−16.1 kcal mol^{-1} was measured for **16c** and **19a**−**c**. The [β,β']-, [α,β]-, and [α,β']-two-ring-flips barriers were determined from the coalescence of the isopropyl methyls as 25.2, 23.1, and 21.1 kcal mol^{-1}. Hence, in the transition state of the highest two-ring-flip process, the α-ring becomes coplanar with the C=C plane.[38] These barriers can be reasonably reproduced by MM when ring planarity and nearly planar ring−C(*o*-Me) constraints are imposed.

From combination of DNMR and racemization of partially or completely resolved acetates **20a**−**c**, the order of the observed barriers for the *n*-ring flips (in kcal mol^{-1}) [α,β] (27.3) > [α,β'] (23.4) > [β,β'] (22.0) > [α,β,β'] (19.0)[35,38] differs from that obtained for **19a**−**c**.[38] This is ascribed to a strong dependence of the barrier on the conformation of the *i*-PrO or AcO substituent.

Tetraarylvinyl Propellers

Rotational Barriers. Resolutions of the residual enantiomers of triarylvinyl propellers becomes possible by hindering passage of the tagged ring through the C=C plane. Since on the separation time scale the aryl ring(s) are on an average perpendicular to the C=C plane, the resolutions are not exclusively due to the different helicities. It could be expected that tetraarylvinyl propellers will possess larger barriers for helicity reversal. Early calculations on tetraphenylethene indicated a four-ring-flip threshold mechanism with a barrier of 6.5 kcal mol^{-1}.[9] Dynamic NMR indicated that the helicity reversal barrier of tetrakis(*o*-tolyl)ethene (**24**) is 12−16 kcal mol^{-1} and that the threshold mechanism is a four-ring flip.[39] Introducing bulkier rings increases the barrier, thus enabling the resolution of configurationally stable vinyl propellers.



24 Ar = 2-MeC$_6$H$_4$
25 Ar = 2,4,6-Me$_3$C$_6$H$_2$
26 Ar = 2,3,4,5,6-Me$_5$C$_6$

Tetramesitylethene. One of the most crowded tetraarylethenes known is tetramesitylethene (**25**).[40] Its NMR spectrum is consistent with a "frozen" propeller conformation, and from the observed room-temperature diastereotopicity of the *o*-Me groups, it was suggested that it "might be capable of resolution into enantiomers".[40] Blount, Mislow, and Jacobus estimated the rotational barrier of **25** as ≥25 kcal mol^{-1}.[41a] Two X-ray structures indicated that it exists in a chiral propeller conformation of approximate D_2 symmetry.[41]

25 was resolved by chiral chromatography and, as expected for an helical structure, the specific rotation is high: $[\alpha]_{365} = -12\,100°$, $[\alpha]_D = -2300$ nm.[42] Racemization of **25** was followed at 473−493 K, and the enantiomerization barrier was exclusively due to enthalpy ($\Delta G^{\ddagger} = 39.6$ kcal mol^{-1}, $\Delta H^{\ddagger} = 39.6$ kcal mol^{-1}, $\Delta S^{\ddagger} = 0$ cal mol^{-1} K^{-1}).[42]

Buttressing Effects. The rotational barrier of tetrakis(pentamethylphenyl)ethene (**26**) was of interest due to a possible large buttressing effect.[43] X-ray crystallography showed a propeller conformation of crystallographic C_2 symmetry. MM3 calculations indicated that one mode of steric relief present in **25** (opening the Me−C$_{ortho}$−C$_{ipso}$ angle) is disallowed in **26** by the buttressing groups, and therefore, the Ar-C=C bonds and the central C=C bond are elongated. The predicted barriers are 40.3 and 43.4 kcal mol^{-1} for the four-ring flips of **25** and **26**. Resolution of **26** enabled determination of the enantiomerization barrier in the 513−538 K range ($\Delta G^{\ddagger} = 43.1 \pm 0.1$ kcal mol^{-1}, $\Delta H^{\ddagger} = 39.6 \pm 4.2$ kcal mol^{-1}, and $\Delta S^{\ddagger}$(523 K) = −6.7 ± 7.9 cal mol^{-1} K^{-1}).[43] The buttressing effects of the eight cooperatively acting *m*-Me groups only moderately increase the rotational barrier. Notwithstanding the errors due to the narrow temperature range, the different barriers of **25** and **26** can be ascribed to entropy differences, which may suggest that methyl group rotations are more restricted in the transition state than in the ground state.

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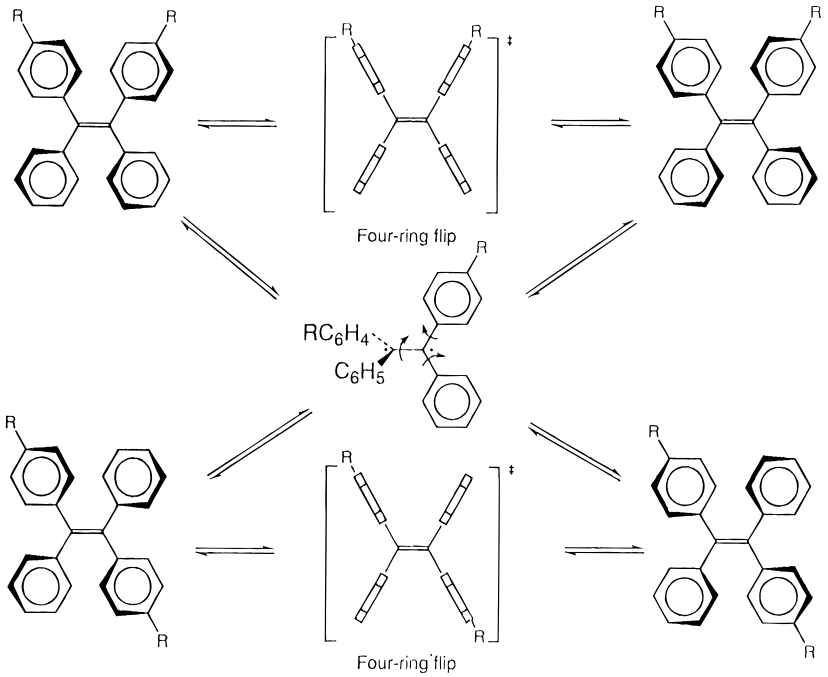
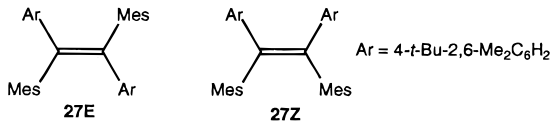


FIGURE 5. Possible enantiomerization and (*E*/*Z*) diastereomerization pathways of a tetraarylethene disubstituted at the *para* positions of two vicinal rings.

Ring *vs* Double-Bond Rotation. Enantiomerization of **25** must involve ring rotations around the four aryl-C═ bonds. For noncrowded ethenes, the rotation barrier around a double bond which involves deconjugation of the two p orbitals to the biradical (62−65 kcal mol^{-1})[44] is usually substantially higher than the rotation barrier around single bonds, although steric crowding and conjugation decrease it.[44,45] The experimental enantiomerization barriers for **25** and **26** are within the range of the barriers of double-bond rotations of structurally related polyarylethenes.[44] Consequently, enantiomerization of these crowded systems by double-bond rotation with a lower barrier than the single-bond rotation barriers cannot be unequivocally excluded. For monitoring both helicity reversal and double-bond rotation processes, the tetraarylvinyl propeller 1,2-bis(4′-*tert*-butyl-2′,6′-dimethylphenyl)-1,2-dimesitylethene (**27**) was synthesized.[46] It exists in two diastereomers (**27Z** and **27E**) each having two enantiomeric forms (+**27Z**/−**27Z**, +**27E**/−**27E**) (Figure 5).



27E and **27Z** were resolved by chiral chromatography. For the enantiomerization which was followed by studying the +**27Z**/−**27Z** (or +**27E**/−**27E**) interconversions at 528−543 K, $\Delta G^{\ddagger} = 44.8 \pm 0.7$ kcal mol^{-1}, $\Delta H^{\ddagger} = 44.2 \pm 0.3$ kcal mol^{-1}, and $\Delta S^{\ddagger}(500\ \mathrm{K}) = -1.2 \pm 0.7$ e.u.[46] Notably, a **27Z** ⇌ **27E** interconversion was not observed under the enantiomerization conditions and hence the threshold enantiomerization process of **27** does not involve a double-bond rotation, which requires ≥48.7 kcal mol^{-1}. The larger double-bond rotation barrier observed for **27** compared with less crowded tetraarylethenes[44] is most likely due to a combination of steric and electronic effects on the diradical transition state.[46]

Epilogue

Helicity reversal in vinyl propellers proceeds by correlated rotation of the rings. The barriers increase with the number of identical aryl rings in the order 1,2-Ar$_2$ (trans) < 1,2-Ar$_2$ (cis) < 1,1-Ar$_2$ < 1,1,2-Ar$_3$ < 1,1,2,2-Ar$_4$, and with the bulk of the aryl rings. For *n* rings, the threshold mechanisms are (*n* − 1)- and (*n*)-ring flips when the substituent is a vinylic hydrogen or larger, respectively. The Ar—C═C torsional angles increase and the rotational barrier decrease on increasing the bulk of the vinylic substituent. The barriers are still lower than the C═C bond rotation barriers in these systems. By breaking the symmetry of the rings, several high-energy rotational routes were monitored in addition to the threshold mechanism. Resolution of residual enantiomers of several vinyl propellers was achieved. Future prospects in this field include development of probes for mapping completely the many ring-flip barriers for tri- and tetraarylvinyl propellers, studying the helicity change in aryl rearrangements in triarylvinyl cations, and the use of resolved stable tetraarylvinyl propellers as rigid building blocks.

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AR960216Z

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