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Intramolecular Rotations in 2,2-Dimesityl-1-(9-anthryl)- and -1-(9-triptycyl)vinyl Acetates

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2,2-Dimesityl-1-(9-anthryl)vinyl acetate (3) and 2,2-dimesityl-1-(9-triptycyl)vinyl acetate (4) were prepared. The rotation of the mesityl and 9-anthryl rings in 3 and of the mesityl rings and triptycyl substituent in 4 around their bonds to the vinylic carbon were investigated by DNMR. For each system an identical rotational barrier was measured for each substituent, indicating a correlated rotation. The rotational barriers were 16.7 ± 0.1 kcal mol^{-1} for 3 and 17.0 ± 0.1 kcal mol^{-1} for 4. The suggested rotational mechanism is a three-ring flip for 3 and a correlated (geared) rotation for the three rotors of 4. The latter process involves a two-ring flip of the two mesityl rings and a rocking process of the triptycyl moiety in which only one of its rings eclipses the C=C plane in the transition state.

The stereodynamics of di-, tri-, and tetraarylvinyl propellers[1] have been investigated by DNMR. The rotation of the aryl rings around the ArC= bonds in mesityl-substituted enols 1 and enol acetate 2 are correlated and lead to enantiomerization by various flip processes.[2] In an "*n*-ring flip" the *n*-flipping ring(s) rotate via a plane perpendicular to the C=C plane whereas the other ring(s) pass through the C=C plane.[1b] The low-energy rotational process (the threshold mechanism) is a one-ring flip for **1a**,[1c] a two-ring flip for **1b**–**1g**,[1c,g,j,l] and a three-ring flip for **1h**, **1i**, and **2**.[1b]

$Mes_2C{=}C(R)OH$

1a: R = H
b: R = Me
c: R = Et
d: R = i-Pr
e: R = t-Bu
f: R = $SiMe_3$
g: R = $Si(SiMe_3)_3$
h: R = Mes
i: R = 9-Ant (Ant)

$Mes_2C{=}C(OAc)R$

2: R = mesityl (Mes)
3: R = 9-Anthryl (9-Ant)
4: R = 9-Triptycyl (Tp)

An observed decrease of the two-ring flip barrier of **1a**–**1g** with increased bulk of R[1c,g,l] was interpreted to be partially due to increased ground state energy along the series due to increased Mes-C=C dihedral angles.[1g,i,l] It is of interest if further decrease in the barrier and increase in the dihedral angles will be observed with a bulkier R or if the rotation will then become so hindered that the barrier will increase.

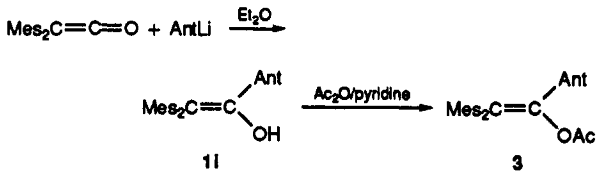
Due to its prototypical "molecular gear" properties, 9-substituted triptycyl systems have been investigated extensively by Oki,[3a,b] Mislow,[3c] Iwamura[3c] and coworkers, and concepts such as gear meshing[3c] (describing correlated Tp–X motion) and gear slippage (independent internal motion) were introduced.

However, a combination of rotors such as a three-toothed wheel (e.g., triptycyl) and two two-toothed wheels (e.g., dimesitylvinyl) has not been previously investigated.[4] We therefore decided to prepare the 2,2-dimesityl-1-(9-triptycyl)vinyl–X system in order to study the effect of the bulky triptycyl group on its internal rotation mechanism and barrier and the effect of coupling of such two molecular rotors on the rotation.

It was easier to synthesize acetate **4** from acetate **3** than to make enol **1**, R = Tp. Consequently, for evaluating the effect of the added ring bridging the 9 and 10-positions on the rotational barriers, acetates **3** and **4** were studied.

Results

Synthesis. Reaction of dimesitylketene with 9-anthryllithium in ether gives 45% of 1-(9-anthryl)-2,2-dimesitylethenol etherate (**1i**·Et_2O), thus improving the 8.7% yield obtained by using 9-anthryl-MgBr.[1b] Acetylation gave 65% of the vinyl acetate **3** displaying the UV fine structure of anthracene derivatives, ν_{CO} = 1750 cm^{-1} and $\delta(^{13}C)$ 168 ppm in $CDCl_3$ (eq 1). A major MS peak corresponds to the cation of enol **1i** due to the loss of ketene in the fragmentation.



(1)

Attempts to add triptycyllithium to dimesitylketene were unsuccessful. However, reaction of **3** with benzyne formed from *o*-benzenediazonium carboxylate hydrochlo-

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[2] Gust, D.; Mislow, K. *J. Am. Chem. Soc.* 1973, *95*, 1535.

[3] (a) Oki, M. *Top. Stereochem.* 1983, *14*, 1, especially pp 53–76. (b) Oki, M. *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH Publishers; Deerfield Beach, FL, 1985; p 302. (c) For a review, see: Iwamura, H.; Mislow, K. *Acc. Chem. Res.* 1988, *21*, 175.

[4] Combination of a three-toothed wheel and a one two-toothed wheel was previously investigated in benzyl triptycenes, e.g.: Nachbar, R. B., Jr.; Hounshell, W. D.; Naman, V. A.; Wennerström, O.; Guenzi, A.; Mislow, K. *J. Org. Chem.* 1983, *48*, 1227 and refs 12, 13, and 16.

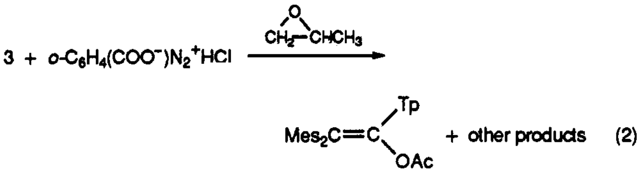
0022-3263/94/1959-1663$04.50/0

Table 1. Coalescence Data for Pairs of Diastereotopic Groups of 3 and 4

compd	solvent	δ (coalescing protons)	assignment	$\Delta\nu$, Hz	coalescence temp (T_c), K	k_c, s^{-1}	$\Delta G_c^{\ddagger}$ (kcal mol^{-1})	δ (average signal, T, K)
3[a]	$C_6D_5NO_2$	1.72, 2.28	*o*-Me-Mes	110.0	349.2	244.4	16.7	2.05 (390)
		2.02, 2.89	*o*-Me-Mes	174.7	354.8	388.1	16.7	2.50 (390)
		6.14, 6.60	*m*-H-Mes	92.8	349.4	206.2	16.8	6.42 (390)
		6.76, 7.09	*m*-H-Mes	65.9	342.6	146.5	16.7	7.00 (355)
		8.64, 8.75	1,8-H-Ant	23.9	323.9	51.1	16.5	8.79 (343)
4[b]	$C_6D_5NO_2$	2.10, 3.02	*o*-Me-Mes	364.0	375.0	80.9	17.1[c]	2.65 (415)
		1.96, 2.05	*o*-Me-Mes	16.5[a]	330.8	36.8	17.0	2.13 (435)
		8.43, 8.82	*peri*-H-Tp	153.5	356.5	341.0	16.8	8.62 (435)
	DMSO-d_6[b]	1.77, 1.91	*o*-Me-Mes	57.9	331.0[d]	128.4	16.8	1.90 (413)
		1.84, 2.91	*o*-Me-Mes	431.0	365.0[d]	957.3	16.5	2.43 (413)
		6.38, 6.79	*m*-H-Mes	162.6	360.0[d]	361.2	17.0	6.99 (413)
		6.85, 7.15	*m*-H-Tp	123.5	352.0[d]	273.6	16.8	6.99 (413)
		7.27, 7.53	*peri*-H-Tp	104.0	349.4	231.0	16.8	7.37 (413)
		8.15, 8.37	*peri*-H-Tp	87.8	348.5	195.0	16.8	8.30 (413)

[a] At 200 MHz. [b] At 400 MHz. [c] Approximate value (see text). [d] ±2° (see text).

ride in the presence of propylene oxide[5] gave 2,2-dimesityl-1-(9-triptycyl)vinyl acetate (**4**) in low yields (8–12%) (eq 2) together with two other products. One of them (8%)



$$3 + o\text{-}C_6H_4(COO^-)N_2^+HCl \xrightarrow{\text{propylene oxide}} Mes_2C{=}C(Tp)(OAc) + \text{other products} \quad (2)$$

4

is an ester (ν_{CO} 1740 cm^{-1}) which lacks the UV fine structure of anthracenes, displays in the NMR a Mes_2C moiety, and is a nontriptycyl isomer of **4**. It may be a 5,12-etheneonaphthacene derivative formed from 1,4-addition of benzyne to the terminal anthracene ring, for which a precedent is known.[6] Difficulty of separation from **3** prevented further investigation. The third compound contains, according to high-resolution MS, one chlorine (apparently from the diazonium HCl salt), and data for it appear elsewhere.[7]

Static and Dynamic Stereochemistry of 3. (a) Static Stereochemistry. Both the ^1H and the ^{13}C NMR spectra of **3** at room temperature show seven (six Ar-Me, one OAc) methyl singlets. The ^1H NMR spectrum also displays four Ar-H singlets and four anthryl group doublets (H-1, H-4, H-5, and H-8). Consequently, diastereotopic mesityl *o*-Me and *m*-H and peri anthryl-H are in a different magnetic environment, suggesting a frozen rotation around the three Ar–C bonds on the NMR time scale at room temperature.

(b) Dynamic Stereochemistry. When a sample of **3** in $C_6D_5NO_2$ is warmed, seven coalescence processes are observed. The $\Delta G_c^{\ddagger}$ values were calculated using the Gutowsky–Holm approximation[8] and the Eyring equation for the coalescence of the two pairs of *o*-Me and *m*-H signals for each ring and the pair of doublets tentatively assigned to H-1 and H-8 of the 9-anthryl ring for which the coalescence temperatures (T_c) could be measured. The singlet emerging above T_c appears at approximately the average δ of the two coalescing signals. The very similar $\Delta G_c^{\ddagger}$ values (16.5–16.8 ± 0.2 kcal mol^{-1}) are given in Table 1.

Static and Dynamic Stereochemistry of 4. Static Structure. (i) In DMSO-d_6. The 400-MHz ^1H NMR in DMSO-d_6 at room temperature (Figure 1) shows distinct signals for nearly all the aromatic hydrogens and the methyl groups, with only minor overlap indicating slow rotations around the Mes–C and the Tp–C bonds. The spectrum (Table 1) displays six mesityl-Me, one OAc, four mesityl-H, and one methine (H-10) singlets and three sets of simple entangled ABCD spin systems, one for each of the triptycyl rings with one at a higher field than the other two. Each of these displays two doublets for the "front" and "back" peri-hydrogens and two overlapping doublets of doublets for the two "central" hydrogens. $^3J_{HH}$ = 6.6–7.8 Hz, and a $^4J_{HH}$ is sometimes discernible.

Signal assignments are essential for interpreting the DNMR. Assignment of a hydrogen to a ring and its location were obtained by COSY and TOCSY, while NOE signals observed between the methine-H and the three peri doublets at 7.27, 7.28 (overlapping), and 7.53 ppm identified the latter as "back" triptycyl rings hydrogens. Me groups at δ 1.84 and 2.91 (*o*) [and 2.26 (*p*)] ppm were assigned to a mesityl ring (β') trans to the triptycyl by observing NOESY signals between *o*-Me and the two "front" peri doublets at 8.15 and 8.37 ppm. NOESY correlation between these methyls and the Ar-H at 6.76 and 7.04 ppm completed the β-ring assignments. Signals at 1.77, 1.91 (*o*), and 2.12 (*p*) ppm were analogously assigned to the β-ring. δ values are given in Figure 2.

The NOESY experiments were conducted in DMSO-d_6 at room temperature when exchange is not slow enough to avoid appearance of crosspeaks resulting from spacial proximity of both sites of a two-site exchanging system. Hence, NOESY spectra were also taken at 190 K in CD_2Cl_2, and some assignments are based on comparison of the spectra in CD_2Cl_2 and in DMSO-d_6.

(ii) In $C_6D_5NO_2$. In $C_6D_5NO_2$ seven Me signals appear in both the ^1H and ^{13}C NMR spectra at δ 1.55–3.04 and 20.47–25.95, respectively. The bridgehead H-10 singlet (δ 5.49) and two peri-H doublets (δ 8.43, 8.82)) are at lower field than in DMSO-d_6. Many signals overlap in this solvent.

(iii) In $CDCl_3$ and $Cl_2CDCDCl_2$. Solvent interference is reduced, and the δ values (*cf.* Experimental Section) differ only slightly (ca. 0.1 ppm) from δ(DMSO-d_6). A strong solvent induced shift is evident by comparing these δ values with $\delta(C_6D_5NO_2)$.

(iv) In CD_2Cl_2. At 190 K, NOESY experiments show crosspeaks due to the following correlations: (a) seven crosspeaks (two other merge into the diagonal) also

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[5] Adams, R.; Johnson, J. R.; Wilcox, C. F., Jr. *Laboratory Experiments in Organic Chemistry*, 6th ed.; McMillan: London, 1970; p 452.

[6] Klanderman, B. H. *J. Am. Chem. Soc.* **1965**, *87*, 4649.

[7] For further spectroscopic data see: Schottland, E. M.Sc. Thesis, The Hebrew University, 1992.

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

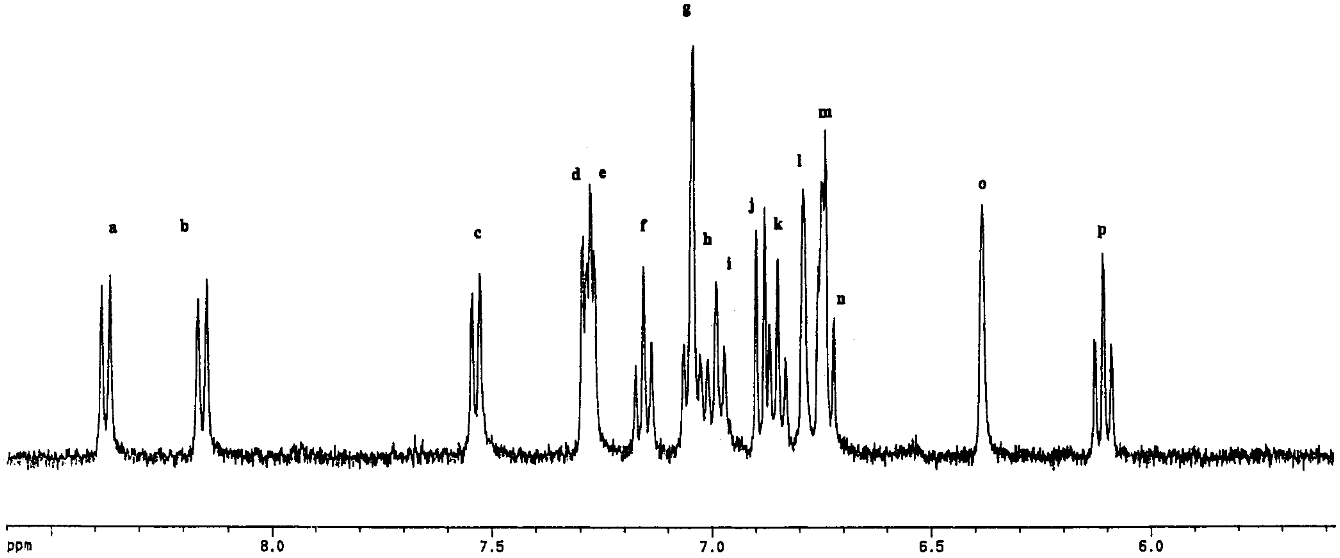


Figure 1. 400-MHz ^{1}H NMR spectrum of the aromatic region of 4 in DMSO-d_6 at 297 K. "Front" peri-H: a, b, j (doublets). "Back" peri-H: c, d, e (doublets). Other triptycyl-H: f, h; i, k; n, p (triplets). Mesityl-H: g, l, m, o (singlets). For more detailed assignment see Figure 2.

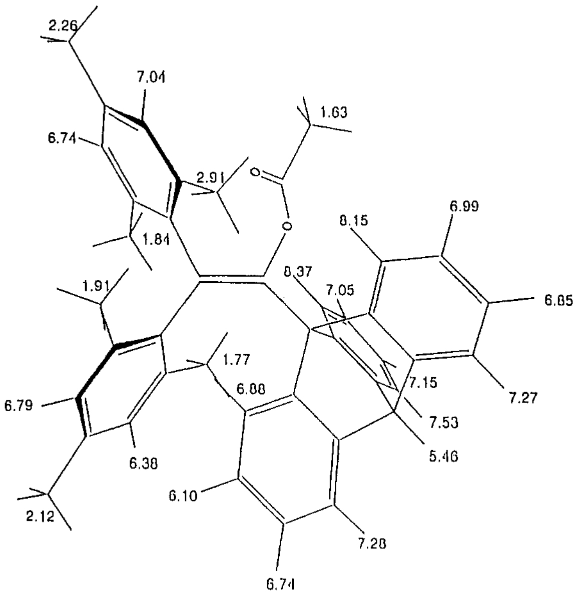


Figure 2. Assignment of all the signals in the ^{1}H NMR spectrum of 4, δ values in DMSO-d_6 at 297 K.

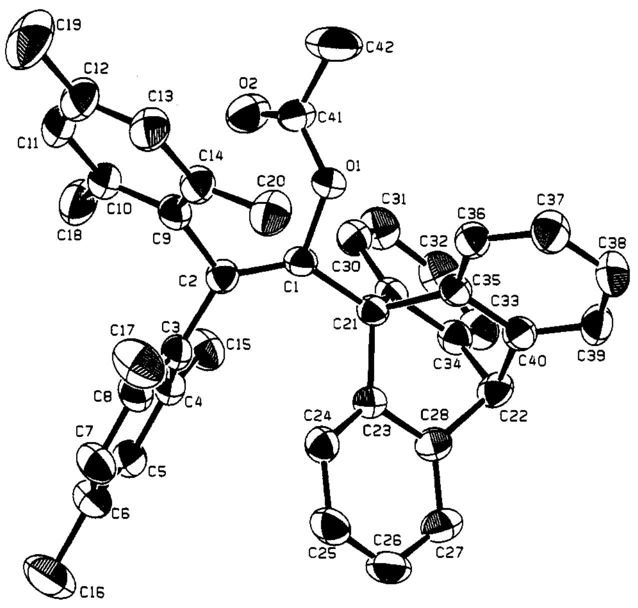


Figure 3. ORTEP drawing of 4.

observed in COSY spectra, due to neighboring triptycyl hydrogens; (b) eight crosspeaks for neighboring Me/*m*-H pairs on the mesityl rings; and (c) eight crosspeaks corresponding to spacial proximity between hydrogens on different rings or moieties, resulting in the following assignments. (i) OAc (δ 1.59)/"front"-peri-H (δ 8.07); (ii) OAc (δ 1.57)/β′-*o*-Me (δ 2.78); (iii) β-*o*-Me (δ 1.79)/β′-*o*-Me (δ 2.78) on different rings; (iv) β-*o*-Me (δ 1.64)/"front"-peri-H (δ 8.28); (v) β′-*o*-Me (δ 2.78)/"front"-peri-H (δ 8.07); and (vi–viii) methine-CH (δ ca. 5.2)/"back"-peri-H (δ 6.92; 7.18 (2H)). By assuming that the solid-state distances (Figure 3) also apply in CD$_2$Cl$_2$ solution at 190 K these assignments are corroborated by calculating the following nonbonded distances of sufficiently close hydrogens to give a NOESY correlation: (i) 3.22 Å; (ii) 2.82 Å; (iii) 2.31 Å; (iv) 2.11 Å; (v) 2.42 Å.

X-ray Structure. The solid-state structure of 4 was determined by X-ray diffraction. The ORTEP drawing is in Figure 3, and interesting bond lengths and angles are in Table 2. The stereoview of 4 is given in the supplementary material, and a complete list of bond lengths, angles, structure, and positional and thermal parameters for 4 has been deposited with the Cambridge Crystallographic Data Centre.[22] The following features are of interest: (a) the triptycyl-C= bond C1–C21 is 1.538(3) Å, longer than a regular sp^3–sp^2 bond; (b) the C1–C2 bond of 1.359(3) Å is longer than other C=C bonds; (c) the four mesityl C$_{ipso}$–C$_o$ bonds of 1.410(3)–1.433(3) Å are appreciably longer than the average ring bond length of 1.385 ± 0.006 Å; (d) the three triptycyl C21–Ar bonds are longer (1.556(3)–1.577(3) Å) than a "normal" C–C bond; the three C22–Ar bonds have normal sp^3–sp^2 bond lengths (1.504(3)–1.519(3) Å), and the longest bonds in the triptycyl aryl rings are those shared by the [2.2.2]bicyclooctane skeleton; (e) the C2–C1–C21 bond angle is opened extensively to 136°, whereas the O1–C1–C21 angle of 106.9° is unusually small for an sp^2-hybridized carbon; other angles are ∠Mes–C–Mes = 114.7° and ∠C1–C2–C3 = 127.2°; (f) within the mesityl rings, the C$_o$–C$_m$–C$_p$ angles are 4°

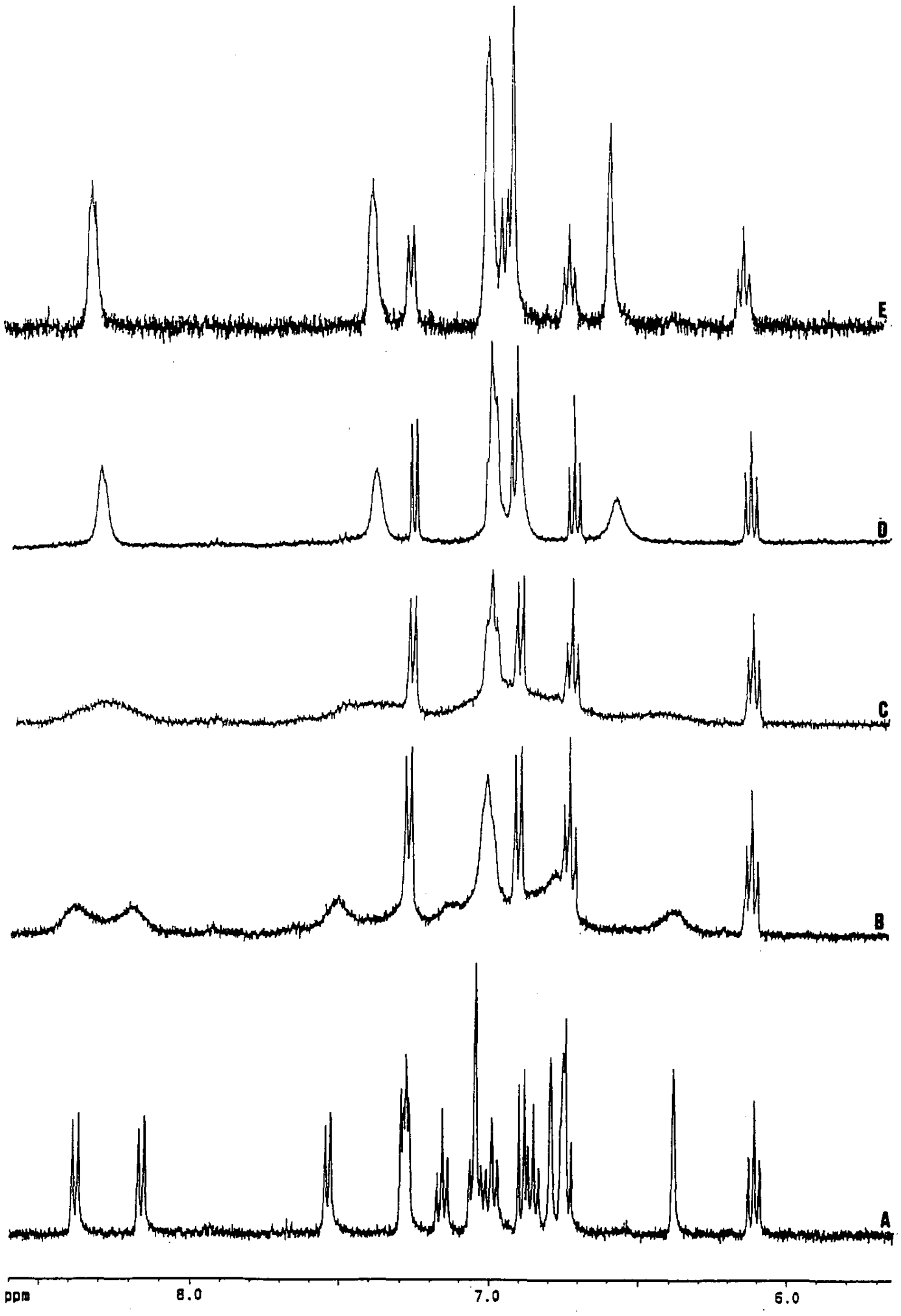
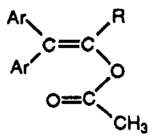


Figure 4. Spectral changes of 4 with the temperature in a DNMR experiment in DMSO-d_6: A, at 297 K (slow exchange); B, at 345 K (signal broadening); C at 349 K (T_c of "back"-peri-H); D, at 398 K (buildup of average peaks after coalescence of pairs of Mes-H and triptycyl hydrogens); and E, at 413 K (fast exchange).

larger than the other inter-ring angles, and the C_{ipso}–C_o–C_{Me} angles are the larger angles involving the methyl group; (g) in the triptycyl moiety the C_o–C_{ipso}–C_o angles where C_{ipso} is attached to C21 are the smallest; (h) the Mes–C=C dihedral angles are 53.3° and 61.7° for the mesityl cis and trans, respectively, to the triptycyl; (i) the C=C torsional angle is 8.8°, appreciably lower than in 1e;[1i] (j) the conformation of the acetate group is *syn-anti* 5 rather than *anti-anti* 6; (k) there is a short distance (2.260 Å) between the triptycyl peri-hydrogen H36 and the vinylic oxygen O1; the C36–H36–O1 angle is 112.5° (this may indicate an O1···C36 hydrogen bond; (l) the deviation of all five aromatic rings from planarity is small (mean values are 0.0047–0.0250 Å); and (m) the dihedral angles of the three triptycyl rings containing C23, C35, and C29 with the C2–C1–C21 plane are 21°, 139°, and 255°, respectively.



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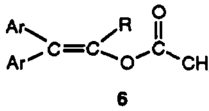

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Dynamic Behavior of 4. (a) In $C_6D_5NO_2$. On warming a sample of 4 in $C_6D_5NO_2$ several coalescence processes take place, but signal overlap enabled determination of T_c only for three of them. For one pair of *o*-Me groups (δ 1.96, 2.05 ppm) T_c = 330.8 K was accurately

Table 2. Selected Bond Lengths and Angles for 4

bond	length, Å	angle	deg
C1–O1	1.417(3)	O1–C1–C21	106.9(2)
C1–C2	1.359(3)	O1–C1–C2	116.8(2)
C1–C21	1.538(3)	C2–C1–C21	136.1(2)
C2–C3	1.511(3)	C1–C2–C3	127.2(2)
C2–C9	1.506(3)	C1–C2–C9	118.1(2)
O1–C41	1.364(3)	C3–C2–C9	114.7(2)
O2–C41	1.188(3)	C1–O1–C41	124.4(2)
C41–C42	1.500(4)	six C_o–C_m–C_p and C_o–C_{ipso}–C_o(Mes)	117.1(1)–120.0(2)
eight Mes–C_o–C_m and C_m–C_p	1.372(4)–1.395(3)		avg 119.0 ± 0.7
	avg 1.385 ± 0.006	four C_o–C_m–C_p(Mes)	122.6(2)–123.6(2)
C3–C4	1.413(3)		avg 123.1 ± 0.4
C3–C8	1.433(3)	two C_m–C_p–C_m(Mes)	116.1(2); 117.4(2)
C9–C10	1.411(3)	four C2–C_{ipso}–C_o(Mes)	avg 121.1 ± 0.8
C9–C14	1.410(3)	four C_{ipso}–C_o–C_{Me}(Mes)	avg 123.4 ± 0.5
six C(Mes)–C(Me)	1.493(4)–1.508(4)	15 C=C–C (Tp)	119.0–121.7
	avg 1.501 ± 0.003[a]		avg 120.3 ± 0.8
C21–C23	1.556(3)	C24–C23–C28	117.6(2)
C21–C29	1.558(3)	C36–C35–C40	118.2(2)
C21–C35	1.577(3)	C30–C29–C34	118.3(2)
three C22–C(Tp)	1.504(3)–1.519(3)	C1–C21–C23	117.4(2)
15 C–C (Tp)	1.375(3)–1.394(3)	C1–C21–C29	111.1(2)
	avg 1.381 ± 0.004	C1–C21–C35	115.8(2)
C23–C28	1.401(3)	C21–C–C (out of ring)[b]	116.7(2)–129.7(2)
C29–C34	1.391(3)		
C35–C40	1.408(3)	C21–C–C (central ring)[c]	112.1(2)–114.9(2)
H36···O[f]	2.26	C23–C21–C29	108.9(2)
		C28–C22–C34	108.7(2)
		C23–C21–C35	100.3(2)
		C29–C21–C35	101.8(2)
		C28–C22–C40	104.5(2)
		C34–C22–C40	105.2(2)
		C22–C–C (central ring)[d]	112.2(9)–114.5(2)
		C22–C–C (out of ring)[e]	121.7(2)–124.7(2)

[a] Longer bond: C8–C17. [b] C–C = C23–C24; C29–C30; C35–C36. [c] C–C = C23–C28; C29–C34; C35–C40. [d] C–C = C28–C23; C34–C29; C40–C35. [e] C–C = C34–C33; C28–C27; C40–C39. [f] Nonbonded distance.

measured, giving $\Delta G_c^{\ddagger}$ of 17.0 ± 0.1 kcal mol^{-1}. The average signal growing at δ 2.13 nearly overlaps the *o*-Me signal at δ 2.10 (which coalesces with the *o*-Me at δ 3.02) causing the T_c (375 K) and $\Delta G_c^{\ddagger}$ (17.1 kcal mol^{-1}) for this process to be less accurate. The third coalescence involves the two low-field triptycyl peri-H doublets at δ 8.43 and 8.82. The third doublet, which overlaps other signals, does not coalesce as deduced by integration of the new 2H signal emerging $>T_c$ at δ 8.62. The $\Delta G_c^{\ddagger}$ of 16.8 kcal mol^{-1} resembles those obtained from the mesityl signals (Table 1).

(b) In DMSO-d_6. This was the best solvent for the DNMR study. On raising the temperature, many signals of **4**, but not all, coalesced. These included the 4 *o*-Me-Mes and 4 *m*-H-Mes and all ABCD signals of two of the triptycyl ring systems. The remaining four multiplets of the third ring started to broaden only at 413 K. Pairs of coalescing groups were assigned by saturation transfer and NOESY experiments. Six rotation barriers were calculated: two for *o*-Me groups, one for *m*-Mes-H, two for two pairs of triptycyl-peri-H, and one for a pair of *m*-triptycl-H. Due to the simultaneous appearance of coalescence signals and partial overlap, several T_c values are accurate to ±2 °C. The DNMR data are given in Table 1.

Signals at 413 K ($>T_c$) appear only at an approximately average δ value and display a complex pattern (see, e.g., the low-field signal at 413 K). This may result from temperature-induced shifts which are unequal for the average signals appearing after coalescence.

Broadening of the pairs of signals at δ 6.74 and 7.04 (*m*-Mes-H) and 6.99 and 7.05 (*m*-Tp-H), which at 413 K gave two signals at δ 6.90 and 6.99, respectively, was also observed. However, T_c could not be determined.

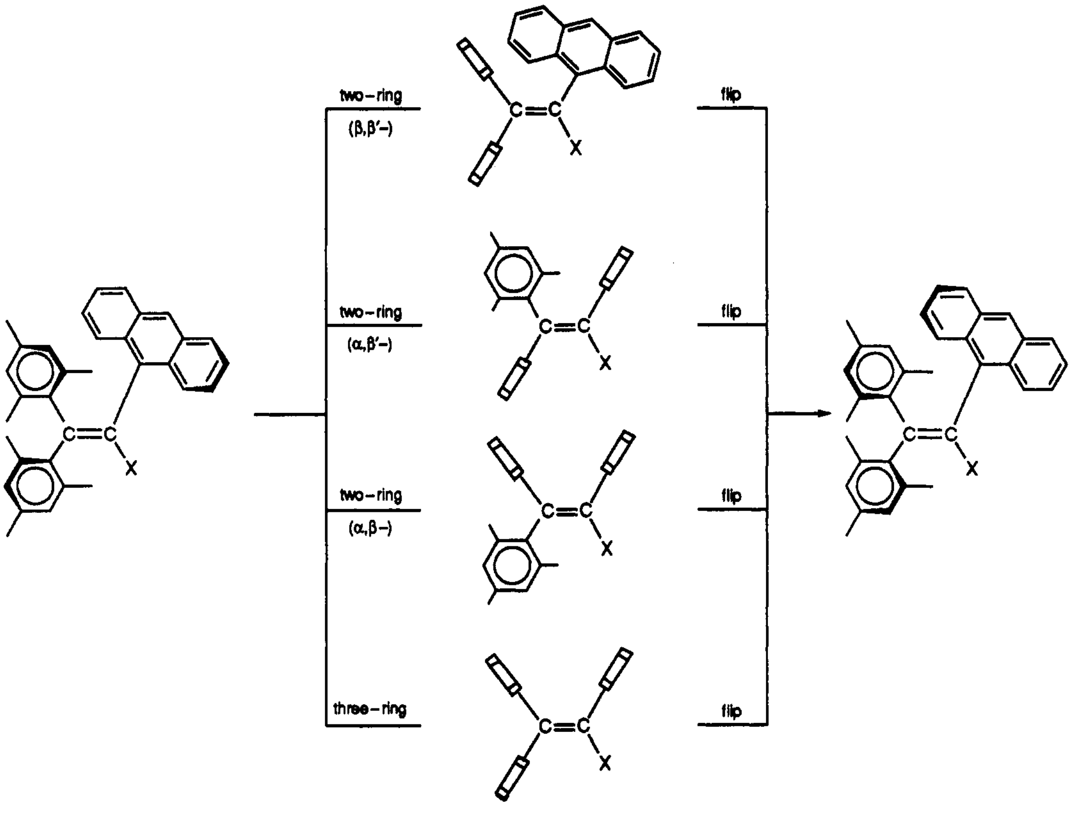
In all the coalescence processes involving triptycyl rings, only two sets of signals from two different rings coalesce while the other four multiplets of the third ring remained sharp. On raising the temperature to 413 K the signals broadened slightly but did not coalesce with the average postcoalescence signals of the other rings. Lower limits of the barriers for coalescence involving the three rings were calculated from the $\Delta\nu$ values. The values obtained (18.6, 20.6, 19.9, and 19.0 kcal mol^{-1} for the δ 6.93, 8.3; 7.25, 7.37; 6.71, 6.98; 6.13, 6.98 pairs, respectively) should be much lower than the actual values since from the shape of the slightly broadened signals, $T_c \gg 413$ K.

Discussion

The Rotational Mechanism for 3. The five rotational barriers measured for **3** (Table 1) include coalescence of diastereotopic *o*-Me and *m*-H signals of the mesityl rings and of the 9-anthryl ring (peri-H). They are within the combined experimental error, i.e., the rotational barrier around the Ar–C= bond of each ring is the same. A similar behavior was previously ascribed to a correlated rotation in which all rings rotate concommitantly.[1a–g,j,l] Of the eight processes possible for **3** (a zero-ring flip, three one- or two-ring flips, and a three-ring flip) four are demonstrated in Scheme 1 with "ideal" transition states, where the flipping ring is perpendicular to the C=C bond. Since diastereotopic groups on non-flipping rings do not show coalescence in the DNMR experiment, and in analogy with the behavior of related compounds, including enol **1i**,[1b] it is suggested that the threshold mechanism leading to enantiomerization is a 3-ring flip with transition state **7**.

The average rotational barrier of 16.7 ± 0.1 kcal mol^{-1} for **3** is 0.5 kcal mol^{-1} higher than the barrier for enol **1i**.[1b]

Scheme 1. "Ideal" Transition States for the Three Isomeric Two-Ring Flips and the One Three-Ring Flip Mechanism for 4[a]



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[a] ▭ indicates a ring which is perpendicular to the C=C bond.

A similar difference exists between the three-ring flip barriers of trimesitylethenol **1h** and its acetate **2**.[1b] This difference may be due to an electronic effect or to different ground-state Ar–C=C dihedral angles in **3** and **1i**.

The Rotational Mechanism for 4. Comparison of acetate **4** and enols **1** should take account of possible difference due to the OAc and the OH groups. Comparison of crystallographic data for **1h** and **2**,[8] or for (*Z*)-1,2-dimesityl-2-phenylethenol with its acetate,[9] showed that the configuration of the acetate group is *anti-anti* **6**. This increases the O–C1–R angle and decreases the R–C=C angle compared with the enol. Also, the Ar–C2–Ar angle is smaller and the β-Ar–C=C and β'-Ar–C=C dihedral angles are larger in the acetates than in the enols.

In contrast, the conformation of the acetate in **4** is *syn-anti* **5** rather than *anti-anti* **6**. Apparently, the part of the triptycyl group remote from the C=C bond is bulky enough to cause severe steric interaction with the acetate group, favoring conformation **5**. Steric hindrance is also reflected in the short internuclear distance (2.260 Å) between H36 and the vinylic oxygen. Hydrogen bonding [O···H···C(36)] may slightly stabilize conformation **5**.

Comparison of the crystallographic data for enols **1b**, **1d**, and **1e** with those for **4** shows that (i) the C1–C2, C1–R, and C1–O bonds in **4** are longer than those found in **1e**, the most hindered reference compound, (ii) the R–C=C bond angle of 136.1(2)° and the β-Mes–C=C bond angle in **4** are the largest known for crowded enols and enol esters, but (iii) the bond angles between geminal double bond substituents are smaller in **4**. The dihedral Mes–C=C angles are ϕ_1 (**1a**) < ϕ_1 (**4**) < ϕ_1 (**1b**) and ϕ_2 (**1d**) < ϕ_2 (**4**) < ϕ_2 (**1e**). The C=C bond twist angle is smaller than for **1e**.[1i]

The rotational barriers measured for **4** are the same within the experimental errors. In $C_6D_5NO_2$, the barriers for the two mesityl rings (from *o*-Me coalescence) are 17.0 and 17.1 kcal mol^{-1} and for the triptycyl ring (from H-1/H-8 coalescence) $\Delta G_c^{\ddagger}$ = 16.8 kcal mol^{-1}. In DMSO-d_6, the six barriers for the two mesityl rings and the triptycyl group are 16.8 kcal mol^{-1}.

The similar $\Delta G_c^{\ddagger}$ values for the two mesityl rings of the Mes$_2$C=C moiety suggests a correlated rotation either via two consecutive one-ring flips with equal $\Delta G_c^{\ddagger}$ or via a two-ring flip. Since for enols **1** two-ring flips are the threshold routes for enols with R's bulkier than H[1c,g] and since different barriers for the different 1-ring flips are expected,[10] the most likely rotation mechanism of the dimesitylvinyl moiety is a two-ring flip.

The two-ring flip barriers decrease from 14.2 kcal mol^{-1} for **1a** to 10.4 kcal mol^{-1} for **1e**.[1c,g] Extrapolating to bulkier R's, and considering the slightly higher barrier expected for **4** than for **1**, R = Tp, the expected barrier for **4** is <10 kcal mol^{-1}. The observed barrier is much larger than that predicted.

Since the sum of the dihedral Mes–C=C angles ϕ_1 and ϕ_2 is closer to that found in **1a** than in **1e**, the correlation

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(9) Kaftory, M.; Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* 1985, *107*, 1701.

(10) Based on the observation that the three barriers for the non-threshold two-ring flips for methoxy-substituted trimesitylvinyl isopropyl ethers are different: Rochlin, E.; Rappoport, Z.; Frey, J.; Schottland, E. The 52nd Meeting of the Israel Chemical Society, Ramat Gan, 17–18 Feb 1993, Abs P41.

with positive slope between these angles and the $\Delta G_c^{\ddagger}$ values[1f,g] is qualitatively consistent with the inequality $\Delta G_c^{\ddagger}$ (4) > $\Delta G_c^{\ddagger}$ (1e). Since $\Delta G_c^{\ddagger}$ (1a) = 14.2 kcal mol^{-1}, $\Delta G_c^{\ddagger}$ (4) is still 2–2.5 kcal mol^{-1} higher than that expected from the correlation. However, a larger difference of 6 kcal mol^{-1} is obtained from a plot of $\Delta G_c^{\ddagger}$ vs the steric parameter Es[1f] if the unknown Es(Tp) resembles Es(t-Bu).

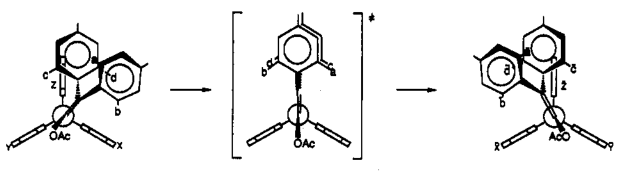
Consequently, part of the barrier should be connected with the coupled rotations of the mesityls with the triptycyl, a phenomenon absent in **1a**–**1e**. Although the similarity of the measured $\Delta G_c^{\ddagger}$ for the three rotors is not *unequivocal* evidence for their correlated rotation, it is highly likely that a single rotation is indeed being measured.

Compound **4** represents a new three-rotor system where two two-toothed and one three-toothed wheels are in a close proximity. Such systems can show either a correlated rotation (geared motion) when the torsional motions of the rotors are strongly coupled[3,11] or a noncorrelated rotation (gear slippage). For singly peri-substituted 9-(3,5-dimethylphenoxy)triptycene the rotation is correlated for a small peri-substituent[12] and noncorrelated when it is large.[13] In benzyltriptycene a gear slippage is the lowest energy process.[12] Iwamura and Mislow found much lower barriers to geared than for the gear slippage processes for Tp_2X.[3c]

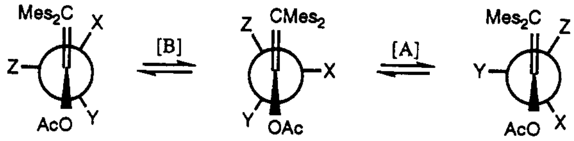
Few rotations in a Tp–C=C moiety were investigated. *trans*-1,2-Bis(9-triptycyl)ethylene or a tetramethyl derivative showed a temperature-independent DNMR, suggesting a low barrier.[14] The intramolecular rotation in *cis*-1,2-bis(2′-methyl-9′-triptycyl)ethylene was recently investigated and gave $\Delta H^{\ddagger}$ = 30.0 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −3.7 en (Kawada, Y.; Sakai, H.; Oguri, M.; Kaga, G. *Tetrahedron Lett.* **1994**, *35*, 139). For rotation around the C9–C=C bond of 9-(buten-2-yl)triptycenes, the *Z*-olefins gave higher barriers than *E*-olefins, and di-peri-Me-substituted compounds gave higher barriers than unsubstituted systems.[15] MM calculations suggest a transition state for the enantiomerization process in which the double bond passes over the substituted ring. A "roundabout" process was proposed in which the rotation is 360 − 2θ rather than 2θ where θ is the dihedral angle between these two groups.

The rotational mechanism of **4** should account for both the correlated rotation of the three rotors and the coalescence of only the protons of *two* triptycyl rings. Two processes in which the triptycyl group rotates only partially during this enantiomerization, i.e., all the mesityl *m*-H and *o*-Me groups undergo exchange but only the hydrogens of two triptycyl rings are exchanged, should be considered. In both routes the dimesitylvinyl group is located in the ground state in a notch between two of the triptycyl rings and undergoes the two-ring flip process discussed above. They differ in the movement of the $Mes_2C=$ and the acetate groups in relation to the triptycene rings. In mechanism A (Scheme 2) the dimesitylvinyl group moves from one notch to another, via a transition state in which it eclipses the triptycyl ring common to both notches. Viewed differently, the triptycyl ring undergoes a rocking process in relation to the double bond (eq 3, A, where XYZ represent the three triptycyl rings). Using the labeling a–d for the *o*-Me groups, X–Z for the triptycyl rings, and bars for the same groups in the enantiomer, the groups and rings exchanged are $(a\bar{b})(b\bar{a})(c\bar{d})(d\bar{c})$; $(X\bar{Y})(Y\bar{X})(Z\bar{Z})$. The process converts a–d and X, Y to their enantiotopic groups. However, although the Z ring undergoes the largest steric interaction in the transition state, the change involved in it, i.e., $(Z\bar{Z})$ is not recorded in the DNMR experiment.

Scheme 2. Mechanism A for the Enantiomerization of 4[a]



[a] The $Mes_2C=$ moiety eclipses a triptycyl ring (*Z*) in the transition state.



(3)

In mechanism B (Scheme 3) the dimesitylvinyl group rocks within the same notch, and in the transition state the acetate group eclipses a triptycyl ring, which is different from the one rocking in mechanism A (cf. eq 3, B). The groups exchanged are $(a\bar{b})(b\bar{a})(c\bar{d})(d\bar{c})$;$(X\bar{Z})(Y\bar{Y})(Z\bar{X})$, and since the Y and Z rings of **4** are undistinguishable by labeling, again only exchange of signals in two triptycyl rings will be observed.

In both mechanisms two protons of one ring, which either eclipses in the transition state the $Mes_2C=$ moiety (mechanism A) or the OAc group (mechanism B), do not coalesce. Following the NOESY assignment of the protons to each ring, we favor mechanism A. From the DNMR experiment the two "front" coalescing peri-protons at δ 8.16 and 8.28 show NOESY crosspeaks with the OAc and the *o*-Me protons. Consequently, the third ring with peri-H at δ 6.88 is the one eclipsing the double bond in the transition state, and indeed, its protons do not coalesce. The X-ray data show that this ring has the smallest dihedral angle (21°) with the C2–C1–C21 plane, whereas the other two rings are at angles of 139° and 255° to it. This mechanism differs from that for the butenyltriptycenes.[15]

In the correlated rotation of 2,4,6-trimethylbenzyltriptycene[16] the aryl ring is nearly periplanar with the C9–CH_2 bond and is in a notch in the triptycyl ring. In contrast, the X-ray structure of **4** shows that the β'-mesityl ring and the triptycyl group are sufficiently remote, and the main interaction is with the β-ring cis to the triptycyl. This ring is more remote than in 2,4,6-trimethylbenzyltriptycene, and the gear meshing is not tight in spite of severe steric interference. This may contribute to the relatively high barrier compared with systems where gear meshing is tight.

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[11] Hounshell, W. D.; Iroff, L. D.; Iverson, D. J.; Wroczynski, R. J.; Mislow, K. *Isr. J. Chem.* **1980**, *20*, 65 and references cited therein. Hounshell, W. D.; Iroff, L. D.; Wroczynski, R. J.; Mislow, K. *J. Am. Chem. Soc.* **1978**, *100*, 5212 and references cited therein.

[12] Yamamoto, G. *Tetrahedron* **1990**, *46*, 2761.

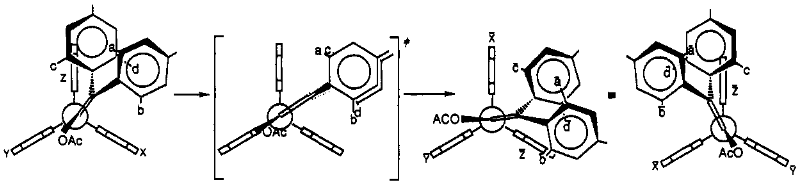
[13] Yamamoto, G.; Oki, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3597.

[14] Mew, P. K. T.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1975**, *18*, 159.

[15] Oki, M.; Taguchi, T.; Toyota, S. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2616.

[16] Yamamoto, G.; Oki, M. *J. Org. Chem.* **1983**, *48*, 1233.

Scheme 3. Mechanism B for the enantiomerization of 4[a]



[a] The OAc group eclipses a triptycyl ring (Y) in the transition state.

The rotations of 3 and 4 in $C_6D_5NO_2$ could be compared. The triptycene unit can be *formally* regarded as a twisted anthryl ring substituted by a 9,10 benzo bridge. In mechanism A the rocking benzene ring passes via the C=C plane while the twisted anthracene moiety flips, giving a modified three-ring flip process. The 0.3 kcal mol^{-1} difference in the rotational barriers for 3 and 4 indicates then that the benzo bridge has only a small effect on $\Delta G_c^{\ddagger}$.

Experimental Section

General. Melting points were measured with Mel-Temp II instrument and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 spectrometer operating at 400.13 and 100.61 MHz, respectively, or on a Bruker WP 200 S4 spectrometer at 200.13 and 50.30 MHz, respectively. Temperature measurements were based on the chemical shift separation of the protons of either methanol or ethylene glycol samples and the use of known temperature–shift correlations.[17] The sample was thermally equilibrated at the reaction temperature for 15 min before measurement. IR spectra were measured with a Perkin-Elmer 458-G instrument and UV spectra with Uvikon 860 or 930 instruments. Mass spectra were recorded with MAT-311 and Finnigan TSQ-70B instruments.

Solvents and Materials. Ether distilled from $LiAlH_4$ was immediately used. *n*-BuLi solution in hexane (2.4 M) and 9-bromoanthracene were purchased from Aldrich. Dimesitylketene was prepared from dimesitylacetic acid.[1b] 9-Bromotriptycene was prepared from 9-bromoanthracene and benzyne.[18]

1-(9-Anthryl)-2,2-dimesitylethenol (1i). To a solution of 9-bromoanthracene (1.87 g, 7.3 mmol) in ether (40 mL) at 0 °C was added *n*-BuLi in hexane (3.2 mL of 2.5 M solution, 8 mmol). The solution turned yellow. After 10 min a solution of dimesitylketene (2 g, 7.2 mmol) in ether (30 mL) was added dropwise and the solution remained for 10 h at rt. HCl (5%, 40 mL) was added, the phases were separated, and the organic phase was washed with saturated aqueous Na_2CO_3 solution (50 mL), dried ($MgSO_4$), and evaporated. Chromatography on silica using petroleum ether 40–60 °C as eluent gave anthracene (350 mg) and a fraction which after crystallization from ether gave 1-(9-anthryl)-2,2-dimesitylethenol etherate (1i·Et$_2$O) as a yellow solid, mp 237 °C (lit.[1b] mp 236–7 °C) (1.64 g, 45%). Acidification of the aqueous phase gave dimesitylacetic acid.

1-(9-Anthryl)-2,2-dimesitylvinyl Acetate (3). A solution of 1-(9-anthryl)-2,2-dimesitylethenol etherate (1i·Et$_2$O) (0.69 g, 2.3 mmol) in acetic anhydride (6 mL)–pyridine (2 mL) was refluxed for 4 h and then poured into ice–water (10 mL) and extracted with methylene chloride (4 mL). The organic phase was dried ($MgSO_4$), and evaporated, leaving an oil that on crystallization from 2-propanol gave 1-(9-anthryl)-2,2-dimesitylvinyl acetate (3) as a yellow solid, mp 246 °C (0.45 g, 65%).

^{1}H NMR ($C_6D_5NO_2$, 200 MHz, 300 K) δ: 1.73, 1.81, 1.87, 2.02, 2.28, 2.33, 2.90 (21H, 7s, Me + OAc), 6.14, 6.60, 6.76, 7.09 (4H, 4s, Mes-H), 7.17, 7.34 (2 × 2H, 2m, H-2, 3, 6, 7), 7.58, 7.74 (2 × 1H, 2d, H4, 5), 8.40 (1H, s, H-10), 8.66 (1H, d, *J* = 8 Hz), 8.77 (1H, d, *J* = 9 Hz) H-1,8). ^{13}C NMR ($CDCl_3$, 300 K) δ: 20.43, 20.84, 21.10, 21.38, 22.47, 23.51, 29.69 (Me), 124.55, 124.79, 125.02, 125.95, 126.54, 128.26, 128.43, 128.53, 129.11, 129.28, 129.96, 130.00, 130.08, 130.34, 131.36, 133.40, 135.71, 136.27, 137.33, 138.86, 144.32 (Ar-C), 168.19 (COO). UV (CH_2Cl_2) λ_{max}: 283 nm (ϵ = 75 000), 360 (50 000), 402 (70 000). IR (Nujol) ν_{max} = 1750 (s, C=O), 1600 (C=C) cm^{-1}. Mass spectrum (70 eV, 130 °C) *m/z* (relative abundance, assignment): 498 (49, M), 456 (86, M − CH_2=C=O), 236 (16, Mes$_2$ − 2 H or AntOAc), 221 (10, AntC(OH)Me), 205 (9, AntCO), 179 (13, AntH$_2$), 178 (9, Ant), 119 (12, Mes), 18 (B, H_2O). Anal. Calcd for $C_{36}H_{34}O_2$: C, 86.71; H, 6.87. Found: C, 86.43; H, 6.66.

Attempted Preparation of 1-(9-Triptycyl)-2,2-dimesitylethenol. (a) To a solution of 9-bromotriptycene (0.3 g, 0.9 mmol) in ether (10 mL) was added n-BuLi (1.2 mL of 1.6 M, 1.8 mmol) in hexane dropwise, and the mixture was stirred for 2 h at room temperature. The ^{1}H NMR spectrum showed a complete conversion to the Li reagent. To this solution was added a solution of dimesitylketene (0.83 g, 3 mmol) in ether (23 mL) dropwise. After the solution was allowed to stand for 2 days at rt, 5% aqueous HCl (30 mL) was added, the phases were separated, and the organic phase was washed with aqueous Na_2CO_3 solution (4 mL). Acidification of the aqueous phase with concd HCl gave dimesitylacetic acid. ^{1}H NMR ($CDCl_3$) of the organic phase after evaporation of the solvent showed only the signals of triptycene.

(b) To Li (small pieces, 0.14 g, 0.02 mol) which was stirred for 30 min at rt in THF (10 mL) was added dropwise a solution of 9-bromotriptycene (0.133 g, 1 mmol) and dimesitylketene (0.39 g, 1.3 mmol) in THF (20 mL). Stirring for 1 day at rt and workup as above gave only 9-bromotriptycene in the organic phase.

1-(9-Triptycyl)-2,2-dimesitylvinyl Acetate (4). To a solution of 1-(9-anthryl)-2,2-dimesitylvinyl acetate (3) (0.48 g, 0.96 mmol) was added in three identical portions benzenediazonium 2-carboxylate hydrochloride (3 g, 16 mmol) and propylene oxide (2 mL, 27 mmol). After the addition of each portion the mixture was refluxed for 1 h. The NMR then showed that all the precursor had reacted, and the solvent was evaporated, leaving an oil which on chromatography on silica (1:20–1:10 petroleum ether/ether eluent) gave three fractions:

Fraction 1. After crystallization from EtOH it gave 1-(9-triptycyl)-2,2-dimesitylvinyl acetate (4) as a yellow solid, mp 280 °C dec (60 mg, 12%). UV (CH_2Cl_2) λ_{max}: 281 nm (ϵ 67 000) 393 (430), 414 (430). IR (Nujol) ν_{max}: 1750 (s, C=O), 1660 (ArC=C) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.66, 1.85 (2 × 3H, 2s, Me), 1.97 (6H, br s, 2Me), 2.12, 2.28, 2.95 (3 × 3H, 3s, Me), 5.17 (1H, s, Tp-H-10), 6.15 (1H, m Tp-H), 6.35 (1H, s, Mes-H), 6.79 (4H, m, Tp-H), 6.92 (2H, m, Ar-H), 6.97 (1H, s, Mes-H), 7.12, 7.18 (2 × 2H, 2m, Tp-H), 7.43, 8.18, 8.46 (3 × 1H, 3d, Tp-peri-H). ^{1}H NMR ($C_6D_5NO_2$, 200 MHz, 300 K) δ: 1.52, 1.96, 2.05, 2.10, 2.17, 2.28, 3.02 (21H, 7s, Me + Ac), 5.51 (1H, s, H-10), 6.26, 6.76, 7.04, 7.19 (4 × 2H, 4m) 7.37 (3H, m), 8.43, 8.82 (2H, 2d, *J* = 7.7 Hz). Few hydrogens are hidden under the solvent signals. ^{13}C NMR ($C_6D_5NO_2$, 300 K) δ: 20.47, 20.75, 21.18, 21.65, 22.18, 24.03, 25.95 (Me), 55.71, 65.26 (Tp-C-9,C-10), 122.32, 122.39, 122.81, 123.21, 123.89, 124.20, 124.56, 125.22, 125.92, 127.69, 128.61, 130.63, 132.84, 136.27, 136.95, 138.48, 139.97, 141.23, 144.96, 146.24 (Ar), 166.64 (CO). Mass spectrum (CI, isobutane) *m/z* (relative abundance, assignment): 575 (19, MH$^+$), 557 (6, MH − H_2O), 515 (B, Mes$_2$C=CTp), 439 (s, Mes$_2$C=C-Ant), 397 (14, Mes$_2$C=C-Tp − MesH); (EI, high resolution) *m/z* 574.2916 (M), 532.2777 (M − CH_2=C=O). Anal. Calcd for $C_{42}H_{38}O_2$: C, 87.77; H, 6.66; Found: C, 87.51; H, 6.72.

Fraction 2. After crystallization from EtOH a mixture of 15% of 4 and 85% of a yellow compound, mp 300 °C dec (60 mg, 12%) was formed. UV(CH_2Cl_2) λ_{max}: 312 nm (ϵ = 12 000), 382 (9800), 401 (9500). IR (nujol) ν_{max} = 1740 (s, C=O), 1590 (Ar) cm^{-1}. ^{1}H

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NMR ($CDCl_3$, 200 MHz, 300 K) δ: 1.73, 1.91, 2.14, 2.17, 2.31, 2.82 (18H, 6s, Me), 5.04 (1H, d, J = 5.4 Hz), 5.52 (2H, m), 6.65 (1H, s), 6.82 (1H, t, J = 7.2 Hz), 6.78 (1H, s), 6.82 (1H, s), 7.03 (4H, m), 7.31 (4H, m), 7.55 (1H, s), 7.62 (1H, m), 8.10 (1H, m). Mass spectrum (CI, isobutane) m/z (relative abundance, assignment): 575 (18, MH^+), 515 (100, M − OAc), 498 (10), 439 (41, $Mes_2C{=}CAnt$), 371 (24).

Fraction 3. Unidentified compound, giving one spot in the TLC. Crystallization from ether gave a yellow solid, mp 240 °C (30 mg). High-resolution mass spectra m/z (relative abundance, suggested structure): 696.2656 (5, $C_{45}H_{41}ClO_5$), 654.2573 (3.2, $C_{43}H_{39}ClO_4$), 558.2392 (76, $C_{38}H_{35}ClO_2$), 516.2283 (100, $C_{36}H_{33}ClO$), 498.2090 (76, $C_{36}H_{31}Cl$), 480.2454 (20.0, $C_{36}H_{32}O$). Anal. Found: C, 71.11; H, 5.65; Cl, ca. 6; N, 0.[7]

Crystallographic parameters for 4: $C_{42}H_{38}O_2$; space group $P\bar{1}$, a = 11.270(2) Å, b = 18.188(2) Å, c = 8.200(2) Å, α = 91.01(2)°, β = 105.63(2)°, γ = 78.75(1)°, V = 1586.5(6) Å^3, Z = 2, ρ_{calcd} = 1.20 g cm^{-3}, μ(Cu Kα) = 5.23 cm^{-1}, no. of unique reflections = 4715, no. of reflections with $I \geqslant 3\sigma$) = 4178, R = 0.059, R_w = 0.097.

X-ray Crystal Structure Analysis. Data were measured on an Enraf-Nonius CAD-4 automatic diffractometer. Cu Kα (λ = 1.4178 Å) radiation with a graphite crystal monochromator in the incident beam was used. The standard CAD-4 centering, indexing, and data collection programs were used. The unit cell dimensions were obtained by a least-squares fit of 24 centered reflections in the range of $2 \leqslant \theta \leqslant 28°$. The method and the calculations[19,20] (using the SHELXS-86 analysis) are identical to those described previously.[21,22]

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Supplementary Material Available: Stereoscopic view of 4 (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[19] Sheldrick, G. M. Crystallographic Computing 3, Oxford University Press: Oxford, 1985; pp 175–189.

[20] All crystallographic computing was done on a VAX computer at the Hebrew University of Jerusalem, using the TEXSAN structure Analysis Software.

[21] Nadler, E. B.; Rappoport, Z. *J. Am. Chem. Soc.* 1987, *105*, 2212.

[22] The author has deposited atomic coordinates for 4 with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.