Electronic effects in polyarylvinyl propellers. Solid state structures and dynamic behaviour in solution of several crowded enol derivatives

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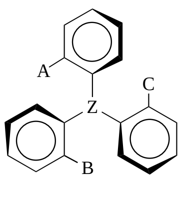
By means of dynamic NMR (DNMR) investigations the dynamic behaviour of several crowded enol derivatives 5–11 and of the enols 12 and 13 has been studied. The NMR data are in agreement with the presence of vinyl propeller structures in solution, which fits the results of X-ray structural analysis. As deduced from a comparison with electrochemical data for the compounds investigated a severe electronic influence of the residue R attached at the enol ether oxygen atom on the rotation barriers can be ruled out. For $Mes_2C{=}C(Ph)OR$ systems, two different kinds of dynamic processes have been deduced on the basis of the DNMR data: first, an isolated rotation of the phenyl ring with a low activation barrier and, secondly, a correlated rotation of the two β-mesityl rings with a substantially higher barrier.

Introduction

Topology and dynamics of molecules have been of great interest to chemists in recent years.[1] A sub-topic of this field is concerned with molecular polyaryl propellers,[2] the helical conformation of which is due to steric repulsion between aryl groups. Such systems of the general formula $Ar^1Ar^2Ar^3Z$ (Z = CX, B, N) (**1**) have been studied in depth by Mislow and co-workers[2] and the study was partially extended by Rappoport and co-workers to vinyl propellers **2** where Z = C=CX (**2**).[3,4]



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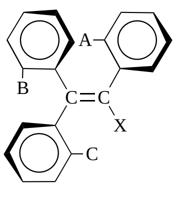

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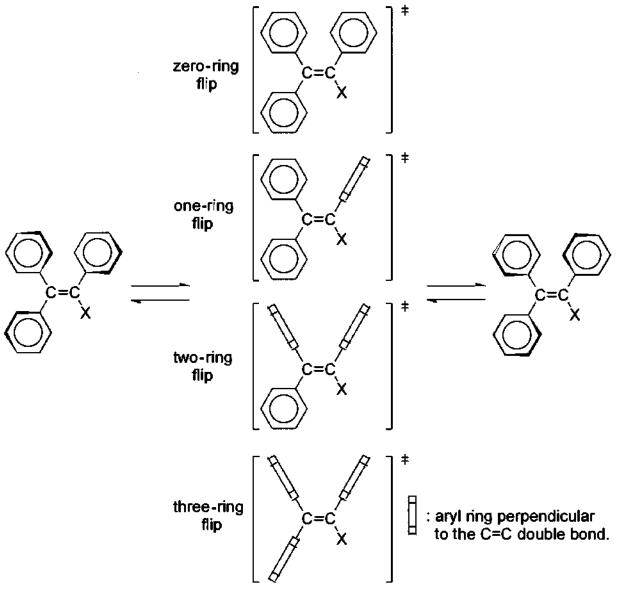
In vinyl propellers **2** two elements leading to isomerism can be envisaged, disregarding *E*–*Z* isomerism: (*i*) chirality plane if aryl groups without a local C_2 axis are present, and (*ii*) helicity (chirality axis) which is due to the same sense of twisting of the aryl groups. Since in the following we investigated only systems with a local C_2 axis at each aryl group, helicity is the only structural feature giving rise to stereoisomerism.

Trimesitylethenol [$Mes_2C{=}C(OH)Mes$] **3** is a typical crowded triarylvinyl system which exists in a propeller conformation in the solid state.[3a] Due to its C_1 symmetry the conformation is chiral and therefore the enol exists in two enantiomeric forms which can interconvert through helicity reversal. Biali and Rappoport[3a] have shown that the dynamic processes involved are rotations of the aryl groups. The rotational barriers probed at the different rings through dynamic NMR investigations were shown to be identical, in agreement with a correlated rotation of the rings, *i.e.* rotation takes place simultaneously in a geared motion. Such helicity reversal in polyarylvinyl compounds can occur by 'flip mechanism' a term first introduced by Kurland *et al.*[5] and extended by Mislow and co-workers.[2] In our systems the ring(s) that flip pass through a plane perpendicular to the double bond plane, whereas the non-flipping rings pass simultaneously through the double-bond plane. Depending on the number of flipping rings in $Ar^1(Ar^2)C{=}C(Ar^3)X$ these mechanisms are called zero-, one-, two- or three-ring flip (Scheme 1). (In Scheme 1 only one of the three possible one-ring flips and one of the three possible two-ring flips is displayed.)



It was found for **3** that the rotational mechanism of lowest activation energy (threshold mechanism) in $C_6D_5NO_2$ is a three-ring flip with an activation barrier $\Delta G^{\ddagger} = 18.4$ kcal mol^{-1}.[3a] Rotational barriers for several enols $Mes_2C{=}C(R)OH$ **4** (including R = H) were also investigated. The threshold mechanism, except when R = H, was a two ring-flip and the rotational barriers were correlated with the bulk of the α-alkyl or silyl group R and with the magnitude of the Mes–C=C torsional angles.

Table 1 Bond angles α, torsional angles φ, and C=C bond lengths for **6**–**9**, **11** and **12** in the solid state (refs. 6*a*, 9, 10)

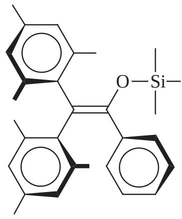
Compound	R	α_1/°	α_2/°	α_3/°	φ_1/°	φ_2/°	φ_3/°	φ_T/°	d(C=C)/pm
6	$SiMe_2Bu^t$	120.4	125.5	111.6	58.0	58.3	43.7	9.8	134.5
7	$P(OEt)_2$	120.8	127.7	111.1	59.4	55.0	44.1	11.5	134.4
8	$P(O)(OEt)_2$	119.7	128.6	111.6	59.7	55.2	33.7	10.4	135.1
9	$P(O)(OPh)_2$	120.6	129.1	111.1	59.7	54.2	37.2	11.5	133.7
11	P(O)(Me)Ph	121.8	128.2	112.4	57.0	54.2	38.2	15.7	134.0
12	H	121.5	129.1	109.9	65.7	62.4	33.3	9.3	134.0

$Mes_2C{=}C(OH)Mes$
3

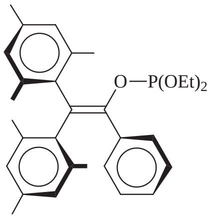
$Mes_2C{=}C(OH)R$
4a R = H
4b R = Et
4c R = Bu^t
4d R = $SiMe_3$

Mes: mesityl

In the present study, the structures of several *O*-substituted derivatives of stable simple enols have been investigated in the solid state and in solution. These include groups whose dynamic behaviour and structures have not been hitherto investigated, *e.g.* silyl enol ethers **5**, **6** and the enoxy phosphorus compounds



5 R′ = Me
6 R′ = Bu^t



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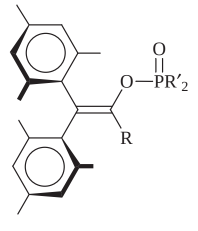
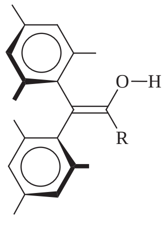


8 R = Ph, R'_2 = $(OEt)_2$
9 R = Ph, R'_2 = $(OPh)_2$
10 R = Bu^t, R'_2 = $(OEt)_2$
11 R = Ph, R'_2 = Me, Ph



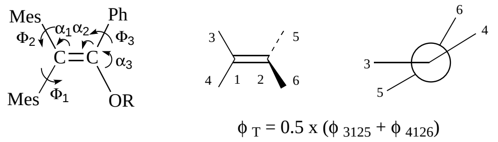
12 R = Ph
13 R = p-$Me_2NC_6H_4$

7–**11**. These compounds were prepared by derivatisation of the appropriate enols, as described elsewhere.[6] The enols **12** and **13**[7] were studied for comparison.

Results

Solid state structures of 6–9, 11 and 12

The solid state structures of the 1-phenyl-2,2-dimesityl enol derivatives **7** and **8** were determined by X-ray crystallography † and those of other derivatives were taken from the literature[6a,9,10] (Table 1). All compounds exist in a propeller conformation in which all the aryl rings are twisted in the same sense. The torsional angles between the Mes ring and the double bond system C=C–Mes cover only a narrow range: φ_1 = 57.0–59.7° and φ_2 = 54.2–58.3°, except for enol **12** which displays higher angles of 65.7 and 62.4°, respectively. Except for silyl enol ether **6**, the angle φ_1 is always larger than φ_2, as found also for 2,2-dimesitylethenol.[3b] The Ph–C=C torsional angles are significantly smaller than the Mes–C=C angles (φ_3 = 33.3–44.1°). The bond angle Mes–C=C (α_1) for the ring *cis* to the phenyl ring is nearly constant and close to the ideal sp^2 angle of 120°, whereas the other Mes–C=C angle is opened up (125.5–129.1°). The double bond length is nearly constant (d = 133.7–135.1 pm). An interesting probe for the steric effect that the olefinic substituents exert on the C=C bond is the torsional angle φ_T (see Fig. 1) of the double bond itself (C=C) that measures the deviation of the olefin from planarity resulting from twisting and out-of-plane-bending.[11] In our systems the values of φ_T range around 10° with 9.8° (**6**) and 15.7° (**11**) being the extremes.



$\phi_T = 0.5 \times (\phi_{3125} + \phi_{4126})$

Fig. 1 Definition of the torsional angles φ_1–φ_3, the bond angles α and the C=C bond torsional angle φ_T (ref. 11)

Static and dynamic stereochemistry

Static stereochemistry. The NMR spectra of **5**–**13** in CD_3COCD_3 at 233 K and of **6** in $CDCl_3$ at 243 K display a separate signal for each methyl group and each aromatic proton of the mesityl rings. This is consistent with frozen rotation of these rings about the Mes–C=C bonds. In contrast, the phenyl ring adopts a conformation in solution which is not frozen as can be seen in the dynamic NMR spectra of enol **13** above 220 K since the protons of the *p*-(*N*,*N*-dimethylamino)phenyl group are split to two doublets pointing to an AA′BB′ system. In the case of a frozen conformation about the phenyl group an ABCD system should appear. Below 220 K the doublets in **13** begin to decoalesce as evidenced by a broadening of the signals. At low temperatures the NMR spectra of enol phosphinate **11** exhibit two different sets of signals in a ratio of about 10:1 indicative of a chirality centre at the phosphorus atom.

The ^1H NMR spectrum of the silyl enol ether **6** in $CDCl_3$ at 243 K is depicted in Fig. 2 and shall be described in more detail. The six mesityl-Me groups appear at distinct resonances between 1.5 and 2.5 ppm, four separate mesityl-H protons show up at 6.57 (1 H), 6.66 (2 H) and 6.88 (1 H) ppm. Obviously, two mesityl-H protons are accidentally isochronous, as can be seen from the data in Table 2 since in [$^2H_6$]acetone silyl enol ether **6** displays four separate Mes-H signals. The two methyl groups attached to silicon appear at distinct resonances δ 0.29 and −0.87 ppm indicating that they are diastereotopic. In addition, the protons of the Bu^t group appear as a singlet at 0.87 ppm and the Ph-H protons as a multiplet between 7.09 and 7.30 ppm. The NMR shifts of diastereotopic signals for compounds **6**–**13** at 233 K are provided in Table 2.

Dynamic behaviour. When the temperature of a solution of **6** in $CDCl_3$ is gradually raised the typical changes of a dynamic NMR (DNMR) behaviour are observed. Two pairs of the *o*-Me and two pairs of the *m*-H mesityl signals as well as the two Me–Si signals first broaden and then coalesce at different temperatures. This behaviour is consistent with reversal of helicity due to rotation around the C_{sp2}–C_{aryl} bonds.[3a] A similar pattern of coalescence is obtained in $(CD_3)_2CO$ and for the other compounds as well (Table 4). The coalescence pattern

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† The crystal structures exhibit final R indices [$I > 2\sigma(I)$] for enolphosphite **7** (R_1 = 0.0650) and enolphosphate **8** (R_1 = 0.0601) which are rather high because of disordered ethyl groups. Hence, we do not intend to publish the data, but use them only for comparison.[8]

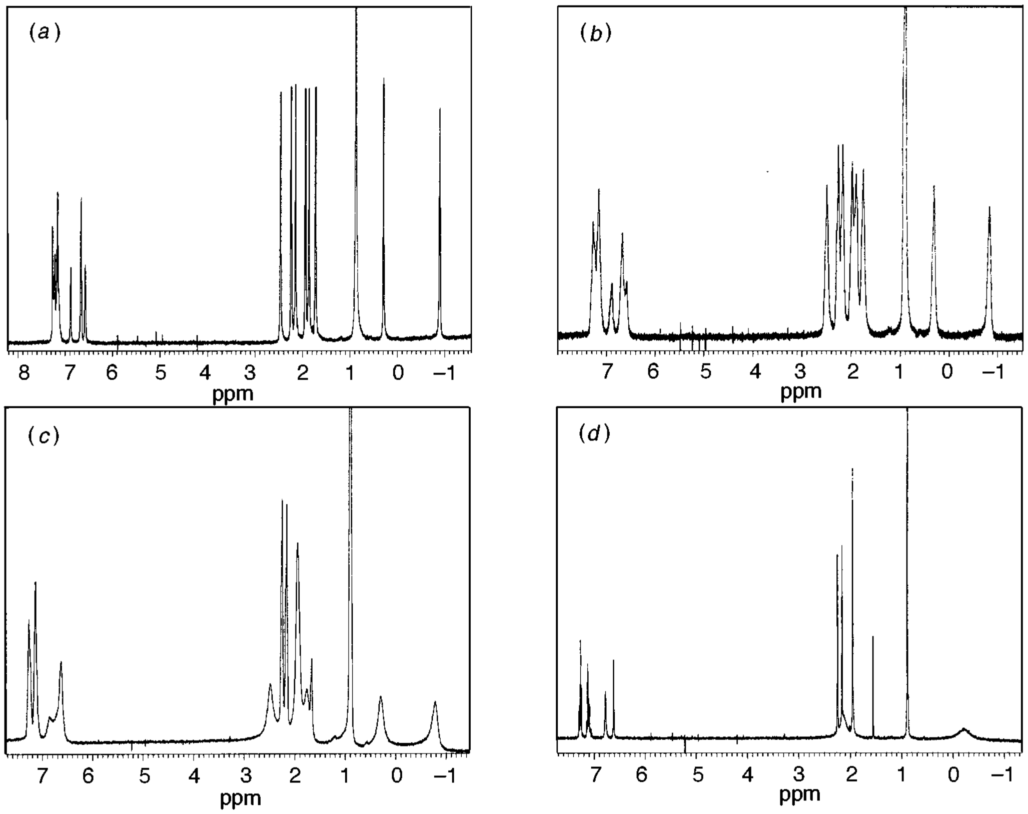


Fig. 2 200 MHz ^{1}H NMR spectra of silyl enol ether **6** in $CDCl_3$ at (*a*) 243, (*b*) 263, (*c*) 273 and (*d*) 298 K

Table 2 ^{1}H NMR data (in ppm) for enol derivatives **5**–**13** in $(CD_3)_2CO$ at 233 K. The pairs of signals which coalesce are separated from each other by line spaces.

Assignment	5	6	6[a]	7	8	9	10	11[b]	12	13
Mes-*o*-CH_3	1.87	1.86	1.87	1.90	1.91	1.93	1.94	1.99	1.89	1.83
Mes-*o*-CH_3	1.93	2.00	1.95	1.97	2.07	2.07	2.40	2.13	1.90	1.92
Mes-*o*-CH_3	1.70	1.74	1.73	1.74	1.82	1.83	1.83	1.93	1.69	1.63
Mes-*o*-CH_3	2.44	2.49	2.47	2.48	2.49	2.47	2.65	2.25	2.51	2.46
Mes-*p*-CH_3[c]	2.12	2.10	2.15	2.13	2.11	2.12	2.16	2.07	2.13	2.12
	2.22	2.21	2.24	2.22	2.21	2.13	2.17	2.07	2.21	2.18
Mes-H	6.60	6.59	6.57	6.63	6.63	6.66	6.63	6.79	6.61	6.63
Mes-H	6.71	6.68	6.66	6.70	6.72	6.78	6.89	6.97	6.70	6.68
Mes-H	6.71	6.72	6.66	6.73	6.72	6.74	6.63	6.73	6.66	6.63
Mes-H	6.95	6.95	6.88	6.97	7.00	7.28	6.89	7.05	6.92	6.89
R[d]		−0.83 0.36 $Si(CH_3)_2$	−0.87 0.29 $Si(CH_3)_2$	*e*	*e*		*e*			6.45 7.14 (d, 2 H, *J* 7.0 Hz)

[a] In $CDCl_3$. [b] Only the signals of the major diastereoisomer are indicated. [c] Not involved in coalescence phenomena. [d] Diastereotopic protons in the R group attached to O which show coalescence. The phenyl protons in **5**–**9**, **11** and **12** only give rise to complex multiplets which cannot be analysed. [e] Data for ethyl groups, see Table 3.

Table 3 ^{1}H NMR data (in ppm) for the ethyl groups in **7**, **8** and **10** in $(CD_3)_2CO$ at 233 K. In each case, CH_2 and CH_3 show coalescence.

	7	8	10
O–C*H*$_2$–CH_3	3.99 (2 H)[a]	4.02 (2 H)[a]	3.96 (2 H)[a]
	3.26 (2 H)[a]	3.30 (1 H)[a]	3.28 (1 H)[a]
		2.83 (1 H)[a]	2.74 (1 H)[a]
O–CH_2–C*H*$_3$	1.26 (3 H)[b]	1.26 (3 H)[b]	1.23 (3 H)[b]
	0.93 (3 H)[b]	0.88 (3 H)[b]	0.82 (3 H)[b]

[a] Multiplet. [b] Triplet, $J = 7.0$ Hz.

resembles that of previously studied 2,2-dimesitylvinyl systems, *e.g.* $Mes_2C{=}C(Mes)OH$.[3a] Here and in other cases,[4] saturation transfer experiments were used to identify pairs of *o*-methyl groups and *m*-protons on the same mesityl ring, thus assisting in identifying groups participating in the same coalescence process. Based on this evidence our analysis of coalescence processes has been performed. In some of the compounds studied the non-vinylic *O*-substituent R contains protons which can serve as probes for the molecular environment. This is the case with the ethyl groups of the diethyl phosphite **7** and the diethyl phosphates **8** and **10**, each of which show a unique anisochrony of the two ethyl groups. The two OEt groups display separate signals, indicative of their diastereotopic environment. Interestingly, within the phosphates **8** and **10** one O–CH_2 moiety splits into two separate signals. The spectral changes accompanying the temperature change for **6** are shown in Fig. 2.

Table 4 Coalescence data for compounds **5**–**13** at 200 MHz

Compound	R[a]	Solvent	Process	$\Delta\nu$/Hz	T_c/K	$\Delta G_c^{\ddagger\,b}$/kcal mol^{-1}
5	$SiMe_3$	$(CD_3)_2CO$	Mes-*o*-CH_3	12.4	266	13.8
			Mes-*o*-CH_3	148.0	292	13.7
			Mes-H	21.9	270	13.7
			Mes-H	47.2	276	13.6
6	$SiMe_2Bu^t$	$(CD_3)_2CO$	Mes-*o*-CH_3	28.4	254	12.7
			Mes-*o*-CH_3	151.3	269	12.6
			Mes-H	18.6	252	12.8
			Mes-H	46.6	259	12.7
			Si–CH_3	238.3	274	12.6
6	$SiMe_2Bu^t$	$CDCl_3$	Mes-*o*-CH_3	16.5	253	12.9
			Mes-*o*-CH_3	147.7	268	12.6
			Mes-H	17.8	252	12.8
			Mes-H	43.8	259	12.7
			Si–CH_3	232.5	273	12.6
7	$P(OEt)_2$	$(CD_3)_2CO$	Mes-*o*-CH_3	13.5	272	14.0
			Mes-*o*-CH_3	150.7	296	13.9
			Mes-H	13.3	271	14.0
			Mes-H	48.3	281	13.8
			O–CH_2–CH_3	66.0	282	13.7
8	$P(O)(OEt)_2$	$(CD_3)_2CO$	Mes-*o*-CH_3	30.8	265	13.2
			Mes-*o*-CH_3	131.2	279	13.2
			Mes-H	15.5	260	13.3
			Mes-H	55.8	270	13.2
			O–CH_2–CH_3	76.1	274	13.2
9	$P(O)(OPh)_2$	$(CD_3)_2CO$	Mes-*o*-CH_3	32.0	265	13.2
			Mes-*o*-CH_3	127.8	279	13.2
			Mes-H	24.4	260	13.1
			Mes-H	108.0	274	13.0
10[c]	$P(O)(OEt)_2$	$(CD_3)_2CO$	Mes-*o*-CH_3	92.8	288	13.8
			Mes-H	49.3	277	13.6
			O–CH_2–CH_3	81.6	282	13.6
11[c]	P(O)(Me)Ph	$(CD_3)_2CO$	Mes-*o*-CH_3	63.9	294	14.3
			Mes-H	36.0	287	14.3
12	H	$(CD_3)_2CO$	Mes-*o*-CH_3	2.3	256	14.1
			Mes-*o*-CH_3	164.0	307	14.4
			Mes-H	18.9	277	14.1
			Mes-H	51.6	290	14.2
13[d]	H	$(CD_3)_2CO$	Mes-*o*-CH_3	18.6	276	14.1
			Mes-*o*-CH_3	166.0	302	14.2
			Mes-H	10.3	270	14.1
			Mes-H	52.0	291	14.3

[a] Note that **10** and **13** are not Mes_2C=C(Ph) systems. [b] ±0.2 kcal mol^{-1}. [c] Here, the coalescence temperature for the second pair of methyl groups and of Mes-H cannot be determined because of accidental isochrony with other signals. [d] The coalescence temperature T_c of the aryl protons in *p*-$Me_2NC_6H_4$ is <220 K, thus the barrier of rotation for this ring is $\Delta G_c^{\ddagger} < 10$ kcal mol^{-1}. T_c could not be determined exactly due to unresolved spectra at very low temperatures.

For all compounds four coalescence processes were monitored at each ring, except for **10** and **11** that exhibit only two coalescence processes in the rings due to accidental isochrony of signals at the coalescence point. As stated above, the ^1H NMR spectrum of enol phosphinate **11** contains two sets of signals with a ratio of 10 : 1 indicating the presence of not only enantiomers but also diastereomers. Only the signals of the main diastereomer have been analysed while the coalescence temperatures of the minor diastereomer could not be determined accurately because of a bad noise-to-signal ratio. For **6**–**8** and **10** the coalescence processes due to the group R were also followed. The exchange rates at the coalescence temperatures T_c were calculated by using the Gutowsky–Holm[12] equation and the rotational barriers $\Delta G_c^{\ddagger}$ by using the Eyring equation with the assumption of a transmission coefficient of unity. The data are listed in Table 4. Within experimental error, the various probes provide the same $\Delta G_c^{\ddagger}$ value for each compound.

Discussion

Structural aspects

In line with other 1,1-diaryl- and 1,1,2-triaryl-substituted systems,[3,4,13] the X-ray diffraction results show that in the solid state the silyl enol ethers and the phosphoenols **5**–**11** exist in a propeller conformation. Accordingly, our model compounds should give rise to two enantiomeric forms, except for **11** which contains an additional stereogenic element (*vide infra*). A similar propeller conformation exists in solution because at sufficiently low temperatures the 2,6-methyl groups and the 3,5-H protons of the mesityl rings are diastereotopic as shown by ^1H NMR spectroscopy. The coalescence of several pairs of signals at higher temperature is consistent with the assumption that under these conditions the enantiomeric propellers interconvert rapidly on the NMR timescale.

The torsional angles φ_T may serve as probes for the crowding of crowded olefins.[11] Within some special fulvalene derivatives φ_T is as great as 40°.[11] However φ_T angles for molecular propeller structures are lower, *e.g.* in tetraphenylethylene $\varphi_T = 8.5°$,[14] in $(Mes)_2C$=C(Mes)OAc (**14b**) $\varphi_T = 10.0°$,[3a] and in Ph_2C=$C(Bu^t)_2$ $\varphi_T = 24.0°$.[15] The last case shows that the aryl groups may be more flexible and smaller than the *tert*-butyl group because φ_T in the triarylvinyl structures is substantially lower. The values for φ_T of silyl enol ether **6** and phosphoenols **7**–**9** and **11** are comparable with those of enol acetate **14b** and enol **12**[9] (Table 1). Another probe for steric crowding of olefins is the C=C bond length which is 132 pm in case of uncrowded

Mes_2C=C(OR)Mes

3 R = H ($\Delta G_C^{\ddagger}$ = 18.4 kcal mol^{-1})
14a R = Pr^i ($\Delta G_C^{\ddagger}$ = 15.8 kcal mol^{-1})
14b R = Ac ($\Delta G_C^{\ddagger}$ = 19.0 kcal mol^{-1})

enol ether systems.[16] With increasing steric congestion the C=C bond length increases as can be seen in Ph(Mes)C=CHOH, where the bond length is 133 pm.[17] In even more congested systems like the enol derivatives studied here the bond length is increased up to 134–136 pm as is well known from many examples in the literature as well.[11]

Dynamic behaviour. Barriers for 2,2-dimesityl-substituted enols were previously measured and calculated by molecular mechanics[18] for several α-alkyl, α-silyl (and H) ethenols $Mes_2C=C(OH)R'$ (*e.g.* for **4a**: R′ = H, **4b**: R′-Et, **4c**: R′ = Bu^t, **4d**: R′ = $SiMe_3$). With the exception of **4a** for which the threshold mechanism is a one-ring flip, the threshold mechanism for the other enols **4b**–**4d** is a two-ring flip.[18] In contrast, for **3** the threshold mechanism was a three-ring flip with an 8 kcal mol^{-1} higher rotation barrier for the correlated rotation than for the two-ring flip barrier of **4c**. The effects of substituents on the oxygen on the barriers were only briefly investigated for the trimesitylvinyl derivatives **3**, **14a** and **14b**. The increase in the barriers follow the order Pr^i < H < Ac for R. Calculations have shown[19] that the barrier should be sensitive to the conformation of the group R.

The present compounds enable us to investigate some hitherto unaddressed questions related to the geometry and the barriers of dimesitylvinyl propellers. These include the questions (*a*) what is the rotational mechanism of triarylvinyl propellers with one relatively non-bulky aryl group, (*b*) the effect of a substituent in the aryl group on the barrier, (*c*) the relative effect of the bulk of phenyl and *tert*-butyl substituents on the barriers at the same threshold mechanism, (*d*) the effect of *O*-substituents of different polarity and steric demands on the barriers and (*e*) the effect of these substituents on the geometry of otherwise similar systems.

Before analysing specific results two points are of importance. First, the DNMR investigation enables the determination of the threshold mechanism of enantiomerization. For all compounds studied a correlated flip mechanism was found because the exchange barriers of all different diastereotopic groups of protons within a molecule for the two mesityl rings were the same. Secondly, the solvent effect on the barrier is apparently small as shown by the similar barriers for silyl enol ether **6** in chloroform and acetone.

The largest effect is that observed for the α-*tert*-butyl systems. Substituting the hydrogen of enol **4c** by a $P(O)(OEt)_2$ group, thus converting it to the enol phosphate **10**, results in a significant 3.3 kcal mol^{-1} increase [from 10.4 to 13.7 kcal mol^{-1}, both in $(CD_3)_2CO$] of the rotation barrier. This effect is in the same direction, but much larger in magnitude, when converting **3** to the acetate **14b** in the three-ring flip.[3a] Unfortunately, we have no X-ray data for **10**, so it remains unclear to what extent this is due to a difference in the ground state Mes–C=C torsional angles between the two substrates. This effect seems unique to the *tert*-butyl group since when conducting a similar change for the α-phenyl-substituted enol **12** to enol phosphate **8** the rotational barrier is reduced from 14.2 to 13.2 kcal mol^{-1} and an almost identical change occurs for the enol phosphate **9**. Here, it seems a clear manifestation of an electronic or a steric effect, rather than an indirect steric effect on the Mes–C=C torsional angles. The Ph–C=C angles of both compounds **8** and **12** are nearly identical, whereas the Mes–C=C angles for **8** are 6.0 and 7.2° lower, resulting in increased conjugation energy for **8**.

Because in all our compounds the rotation barriers for the exchange of pairs of protons on different mesityl rings are identical it is clear that the two mesityl rings undergo a flip process and it is highly likely that they rotate in unison. An accidental identity of two independent barriers, one for each ring, still is not unequivocally excluded but based on the accumulating experience with compounds $Mes_2C=CXY$ (X, Y ≠ H) which are almost always displaying concerted rotation of the two rings this possibility is unlikely. The question then arises concerning the behaviour of the phenyl ring during the mesityl ring rotations. Since the processes undergone by all the α-phenyl substituted systems have similar $\Delta G_c^{\ddagger}$ values and the DNMR behaviour looks the same we assume the phenyl group behaves the same in all these cases.

Table 5 Rotational barriers $\Delta G_c^{\ddagger}$ [in $(CD_3)_2CO$] as determined through DNMR spectroscopy, oxidation potentials of the enols and some σ_p values of the R groups (see also ref. 20)

Compound[a]	$\Delta G_c^{\ddagger b}$	σ_p of R	$E_{pa}{}^c$	Ref.
5	13.7	−0.07	0.65	6*a*
6	12.7		0.73	6*a*
6[a]	12.7		0.73	6*a*
7	13.9		0.74	6*b*
8	13.2	+0.53[d]	1.01	6*b*
9	13.1		1.10	6*b*
10	13.7		1.22	6*b*
11	14.3	+0.50[e]	0.97	6*b*
12	14.2	0	0.60	
13	14.2		0.13	7

[a] In $CDCl_3$. [b] In kcal mol^{-1}. [c] The oxidation potential is provided in V *versus* ferrocene/ferrocenium as determined by cyclic voltammetry in acetonitrile. [d] For $P(O)(OMe)_2$. [e] For $P(O)Me_2$.

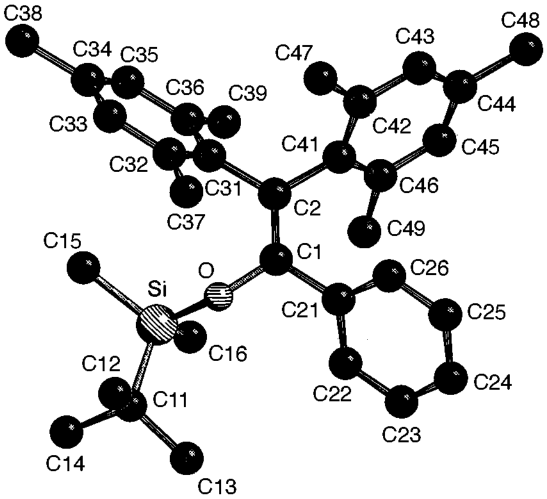


Fig. 3 SCHAKAL plot of silyl enol ether **6** as determined by X-ray structural analysis (ref. 6*a*)

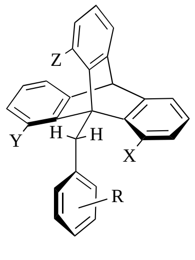
Since the barriers of rotation within the different compounds are quite similar (12.7–14.3 kcal mol^{-1}) the electronic effect on the barrier exerted by the ether group O–R is rather small. This is in sharp contrast to the electronic effect which can be probed by electrochemical means. In this regard, the oxidation potentials of the enol phosphite **7** (E_{pa} = 0.74 V *vs.* ferrocene/ferrocenium) and of the enol phosphate **8** (E_{pa} = 1.01 V *vs.* ferrocene/ferrocenium) differ significantly.[6b] Also, (*i*) the oxidation potentials of the silyl enol ethers **5** and **6** and the enol phosphates **8**–**10** and (*ii*) the Hammett substituent constants σ_p of $SiMe_3$ and $P(O)(OMe)_2$ differ significantly (Table 5).

Obviously, the barriers are almost completely unaffected by the electronic properties of the *O*-substituent R. Similarly, their steric requirements exert only a small influence on $\Delta G_c^{\ddagger}$, at least in a direct way. Indirectly, the shape of R influences the torsional angles φ, thus affecting the barrier through changing the energy of the ground state (*vide infra*). A large direct steric effect of R can be ruled out because the substituent is pointing away from the aryl groups as can be seen in the X-ray crystal structures (Fig. 3). Interestingly, when comparing the enols **12** and **13** it can be seen that the *p*-dimethylamino group on the phenyl ring does not affect the barrier of helicity reversal, as well. Here, the influence of the different electronic situation in the α-aryl groups of **12** and **13**, as can be probed by electrochemical means (Table 5), on the barriers $\Delta G_c^{\ddagger}$ was not observed.

Important mechanistic information related to this question can be deduced from the behaviour of the OR moiety. Some of the R groups possess diastereotopic sets of protons such as the $SiMe_2$ unit in **6** or the $P(OEt)_2$ groups in **7**, **8** and **10** which split into separate signals at low temperatures. This anisochrony is not due to restricted C_{sp2}–O bond rotation since no conformers which may be due to such restricted rotation have ever been observed at a temperature >213 K. Such conformers were indeed observed by Biali and Rappoport[3a] for trimesitylvinyl acetate **14b** at very low temperatures, but it was reported that when one mesityl ring is exchanged by a phenyl ring in either the α- or the β-position the acetyl side group becomes flexible as judged by the dynamic NMR studies. The splitting is therefore ascribed to the presence of the chiral environment of the propeller moiety, the lifetime of which is determined by the rate of helicity reversal. Hence, the diastereotopic groups can be seen as stereochemical probes for the chiral environment. By this line of reasoning any non-flip mechanisms can be ruled out because it would lead to topomerization and not to enantiomerization.[3a]

The question whether the phenyl group in our systems participates in the flipping process can be addressed by investigating the enol system $Mes_2C{=}C(p\text{-}Me_2NC_6H_4)OH$ **13** because here, the dynamic behaviour of the proton signals of the aryl group (AA′BB′ system) in the α-position can be analysed accurately whereas the unsubstituted phenyl group only gives rise to complex multiplets in the ^1H NMR spectrum. We find that the barrier for the C(olefin)–$C_{ipso}(p\text{-}Me_2NC_6H_4)$ rotation (<10 kcal mol^{-1}) is much lower than the barrier of the C(olefin)–C_{ipso}(Mes) rotations which is 14.2 kcal mol^{-1}. Consequently, the last process is a two-ring flip of the mesityl rings because these rings rotate in unison and their rotation is accompanied by an isolated rotation of the $p\text{-}Me_2NC_6H_4$ group. This result can be extended to the 2,2-dimesityl-1-phenyl system because the difference of the steric requirements of phenyl and $p\text{-}Me_2NC_6H_4$ should not affect the mechanism for helicity reversal (Fig. 4). Interestingly, with this kind of mechanism (mesityl two-ring-flip, isolated phenyl rotation) the barrier $\Delta G_c^‡$ within the unsubstituted enol **12** (14.2 kcal mol^{-1}) is equal to the mesityl two-ring-flip barrier of 14.2 kcal mol^{-1} in $Mes_2C{=}C(H)OH$ (**4a**).[18]

Some years ago, work by Mislow[21] and Oki[22] and their coworkers concerning rotations in 9-benzyltriptycenes revealed a similar mechanistic behaviour because two molecular processes take place, a correlated rotation (gear motion) and an isolated rotation of the aryl group. The gear motion is characterised by a rotation by 120° about the C_9–CH_2 bond which is always accompanied by 180° rotation about the CH_2–C_{ar} bond.



Interestingly, even in β,β-dimesityl-α-(3′,5′-disubstituted aryl)ethanols the α-aryl group displays an uncorrelated rotation of the three rings.[23] Hence, it seems reasonable to assume that the threshold mechanism for enantiomerisation within the β,β-dimesityl-α-phenyl enols is a β,β-dimesityl-two-ring-flip as long as no *ortho* substituents other than H/D are present at the α-phenyl ring. However, when methyl groups are present as *ortho* substituents at the α-aryl ring, such as in $Mes_2C{=}C(Mes)OH$ **3**, the three-ring flip becomes the threshold mechanism for enantiomerisation having a lower activation barrier than a process involving an uncorrelated rotation of the α-mesityl ring.[3a]

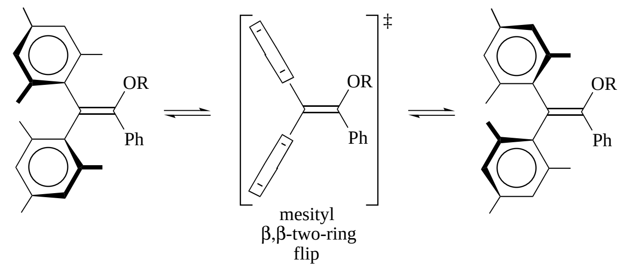


Fig. 4 Mechanism of helicity reversal in enol derivatives **5**–**11** and enols **12**, **13** (in **10**, Ph is substituted by a Bu^t and in **13** by $p\text{-}Me_2NC_6H_4$)

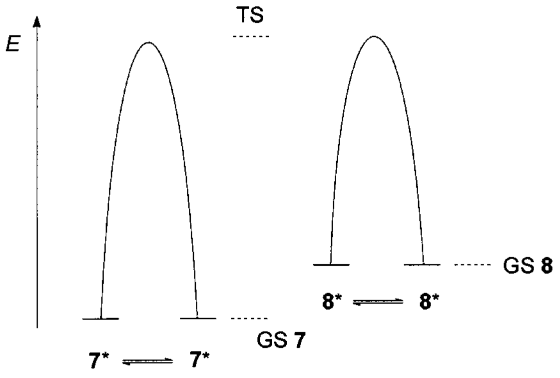


Fig. 5 The higher ground state energy for **8** leads to a lower activation barrier $\Delta G_c^‡$ for the helicity reversal, in comparison with **7**

The question arises why the sterically more congested silyl enol ether **6** (12.7 kcal mol^{-1}) has a lower activation barrier for helical reversal than **5** (13.7 kcal mol^{-1}). The same is true for the enol phosphate **8** (13.2 kcal mol^{-1}) and phosphite **7** (13.9 kcal mol^{-1}). This can be explained in terms of a ground state effect (Fig. 5) because the sterically more encumbered systems have a higher ground state as can be seen by the torsional angles φ. A similar effect was shown by Rappoport and coworkers for the sterically more encumbered system $Mes_2C{=}C(Bu^t)OH$ (**4c**) exhibiting a lower activation barrier $\Delta G_c^‡$ (10.4 kcal mol^{-1}) for the two-ring-flip than $Mes_2C{=}C(Pr^i)OH$ ($\Delta G_c^‡ = 11.7$ kcal mol^{-1}) and $Mes_2C{=}C(Et)OH$ ($\Delta G_c^‡ = 12.0$ kcal mol^{-1}).[13,24]

In conclusion, systems $Mes_2C{=}C(Ph)$–OR exhibit two different kinds of dynamic processes as deduced by DNMR spectroscopy. First, an isolated rotation of the phenyl ring with a low activation barrier and, secondly, a correlated rotation of the two β-mesityl rings with a substantially higher barrier. A severe electronic influence of the residue R attached at the enol ether oxygen atom on the rotation barrier seems not to be present.

Experimental

General methods

^1H NMR spectra were recorded on a Bruker AC-200 pulsed FT spectrometer operating at 200 MHz. The ^1H NMR samples were prepared by dissolving *ca.* 20 mg of the substrate in 0.5 ml of solvent. Temperature measurements were based on the chemical-shift separation of the protons of an CH_3OH sample. The $\Delta G_c^‡$ values were determined from the exchange rate constant at T_c.

Materials

The compounds were synthesised as described elsewhere; for **5** and **6**, see ref. 6*a*, for **7**–**11**, see ref. 6*b*, for **12** see ref. 9 and for **13** see ref. 7. The deuteriated NMR solvents were commercial samples and were used without further purification.

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