The Effective 'Size' of the Tris(trimethylsilyl)silyl Group in Several Molecular Environments

Joseph Frey,[a] Etti Schottland,[a] Zvi Rappoport,*,[a] Dmitry Bravo-Zhivotovskii,[b] Moshe Nakash,[b] Mark Botoshansky,[b] Menahem Kaftory*,[b] and Yitzhak Apeloig *,[b]
[a] *Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel*
[b] *Department of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel*

The effective size of the tris(trimethylsilyl)silyl group in several molecular environments has been estimated. 2,2-Dimesityl-1-tris(trimethylsilyl)silylethanol **1g** has been prepared and its structure determined by X-ray crystallography. The Mes–C=C torsional angles are 59.6 (φ_2) and 63.3° (φ_2) and the C=C–Si bond angle α_4 is 133.8°. The two-ring flip barrier for the correlated rotation of the two mesityl rings around the Mes–C= bonds is $\Delta G_c^{\ddagger} = 10.2$ kcal mol^{-1}. The structures of enols Mes$_2$C=C(OH)R, R = H, Me, Et, Pr^i, Bu^t (**1a–1e**), Me$_3$Si (**1f**), (Me$_3$Si)$_3$Si (**1g**) and (Me$_3$Si)$_3$C (**1h**) and the two-ring flip barriers have been calculated by the MM2* force-field. The calculated and the experimental values are in good agreement, except for somewhat lower calculated α_4 for **1b–1e** and a shorter =C–Si distance in **1g**. From the linear correlations between the observed cos φ_2 or $\Delta G_c^{\ddagger}$ values and E_s values for the enols **1a–1e** and the values observed for **1g** an average E_s value of -1.46 has been calculated for (Me$_3$Si)$_3$Si. MM2* calculations gave an A value for (Me$_3$Si)$_3$Si of 4.89 kcal mol^{-1}. These steric parameters resemble those for the Bu^t group ($E_s = -1.54$; $A = 4.9$ kcal mol^{-1}) indicating a similar effective size for the Bu^t and (Me$_3$Si)$_3$Si groups in these specific environments. (Me$_3$Si)$_3$C is significantly larger ($A = 13.3$ kcal mol^{-1}; estimated $E_s = -3.7$).

One of the most fundamental properties of a substituent is its 'size'—a property which is expected to depend on the specific molecular environment in which the group is placed.[1] Over the last years we have been interested in comparing the 'size' of the trimethylsilyl group with that of a methyl or a *tert*-butyl group. Apeloig and Stanger concluded on the basis of the similar solvolysis rates of 2-trimethylsilyl- and 2-methyl-adamant-2-yl (Ad) *p*-nitrobenzoate, coupled with model *ab initio* and force-field calculations, that the solvolysis of the silicon derivative proceeds without significant steric acceleration and thus that in this molecular environment the Me$_3$Si and the methyl groups have similar 'sizes'.[2] Allen *et al.*,[3] who studied the solvolysis of (2-trifluoromethyl)adamant-2-yl 4-methylbenzenesulfonate (tosylate) suggested a steric acceleration of the solvolysis by the CF$_3$ group and pointed out that their results suggest that steric effects may accelerate also the solvolysis of the 2-Me$_3$Si-adamantyl derivative relative to the 2-Me derivative.[3] In a more recent paper, Apeloig *et al.* provided further evidence for their earlier conclusion that the solvolysis rate of the adamant-2-yl derivatives is not sterically accelerated by a 2-Me$_3$Si group in contrast to strong steric rate acceleration by a 2-Bu^t group.[4] The conclusion was that at the adamant-2-yl position the Me$_3$Si and the Me groups have similar effective sizes, although the van der Waals size of the silyl group is much larger considering that a Si–C bond is much longer than a C–C or a C–H bond.

The higher homologue in the silicon series—the tris(trimethylsilyl)silyl group, (Me$_3$Si)$_3$Si,[5]—also referred to as 'supersilyl',[6a] has recently attracted considerable interest[6-10] due to its remarkable combination of steric and electronic properties. Thus, the first kinetically stable silene at room temperature (Me$_3$Si)$_2$Si=C(OSiMe$_3$)Ad was synthesized *via* a photochemical rearrangement of (Me$_3$Si)$_3$SiC(=O)Ad.[7] Also the first stable formylsilane, (Me$_3$Si)$_3$SiCHO[8a] and iminoborane (Me$_3$Si)$_3$SiB=NCMe$_3$[8b] contain the 'supersilyl' group. Numerous organometallic derivatives of the (Me$_3$Si)$_3$Si-group have been synthesized and characterized[9] and (Me$_3$Si)$_3$SiH is gaining popularity as a novel reducing reagent.[10] Bock *et al.* have demonstrated that the 'supersilyl' group can serve both as an efficient electron-donor and electron-acceptor.[6a] Compari-

son of the molecular structure of (Me$_3$Si)$_3$Si–Si(SiMe$_3$)$_3$[6] with the formal alkyl analogue (Me$_3$C)$_3$Si–Si(CMe$_3$)$_3$ reveals that the central Si–Si bond is significantly longer in the latter, *i.e.* 2.70 Å, than in (Me$_3$Si)$_3$Si–Si(SiMe$_3$)$_3$, *i.e.* 2.40 Å,[6] indicating that the Bu^t group is significantly bulkier by this measure than the (Me$_3$Si)$_3$Si-group. This can be expected as Si–Si distances (*ca.* 2.37 Å) are 0.5 Å longer than C–Si distances (*ca.* 1.87 Å) and the latter are approximately 0.3 Å longer than C–C distances (*ca.* 1.54 Å).[11]

What is the size of the (Me$_3$Si)$_3$Si group in other molecular environments? Can its steric effect be defined quantitatively relative to the lower silicon member, Me$_3$Si, as well as relative to the formal alkyl analogue, (Me$_3$Si)$_3$C? In this paper we address these questions in relation to crowded polyaryl substituted enols **1**, of which **1a–1f** were previously studied extensively by one of us.[12] We found that for 2,2-dimesityl-1-R-ethenols, **1a–1e**, the keto–enol equilibrium constants,[13] the barrier for the two-ring flip correlated rotation of the mesityl rings around the Mes–C bonds,[14] and crystallographic parameters such as the cosines of the R–C=C bond angles or the Mes–C=C torsional angles[15] show linear correlation with Taft's steric parameter E_s.[16] We have therefore suggested[12-15] that the above parameters and processes provide a set of sensitive probes to the steric effects of various groups R in a crowded environment.

$$\text{Mes}_2\text{C=C(OH)R}$$
$$\mathbf{1}$$

a R = H; **b** R = Me; **c** R = Et; **d** R = Pr^i; **e** R = Bu^t; **f** R = SiMe$_3$; **g** R = Si(SiMe$_3$)$_3$; **h** R = C(SiMe$_3$)$_3$
$$\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2 \text{ (mesityl)}$$

Indeed, when the internal rotation of the mesityl groups in the trimethylsilyl derivative **1f** was investigated,[17] the threshold mechanism was found to be a two-ring flip with a rotation barrier of 11.1 ± 0.2 kcal mol^{-1},† a value intermediate between

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† 1 cal = 4.184 J.

Table 1 Dynamic NMR data for the rotation of the mesityl rings of **1g** in $(CD_3)_2CO$ [a]

Process	$\delta\,(\Delta\nu,\,180\ \text{K})$ [a,b]	k_c/s^{-1}	T_c/K	$\Delta G_c^{\ddagger}/\text{kcal mol}^{-1}$	δ^c (ppm)
o-Me $\rightleftharpoons$ o-Me	1.60, 2.43 (330.5)	734	226.3	10.3	2.11
o-Me $\rightleftharpoons$ o-Me	1.70, 2.51 (326.2)	725	230.0	10.3	2.20
Mes-H $\rightleftharpoons$ Mes-H	6.56, 6.84 (114.2)	254	215.6	10.1	6.78
Mes-H $\rightleftharpoons$ Mes-H	6.66, 6.93 (105.3)	254	215.6	10.1	6.79

[a] Measured at 400 MHz. [b] At slow exchange. [c] δ of the average signal at fast exchange. Owing to the temperature dependence of the average signals, their assignment to the process given is not unequivocal.
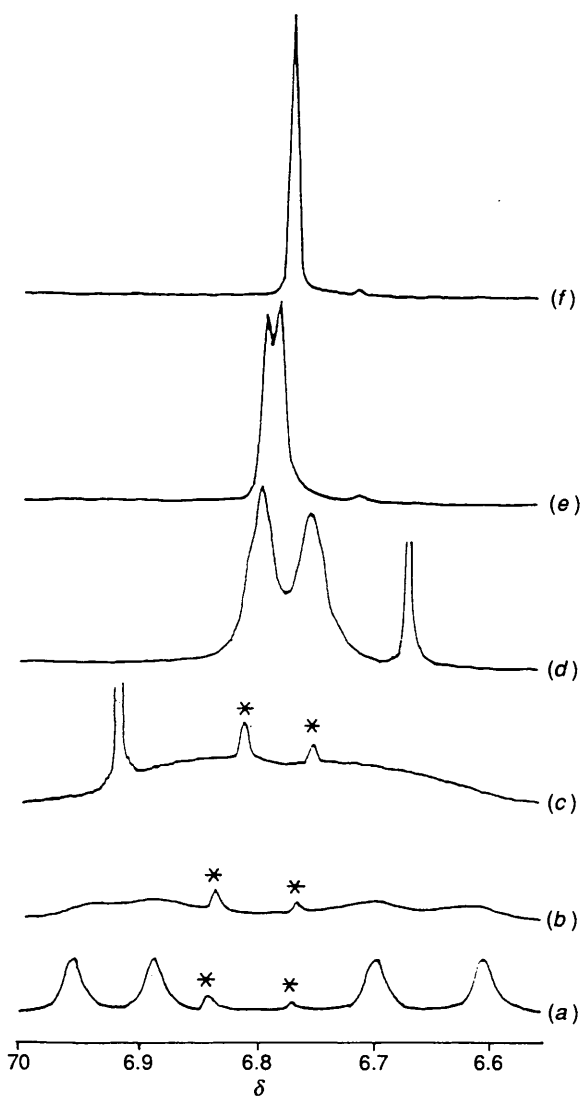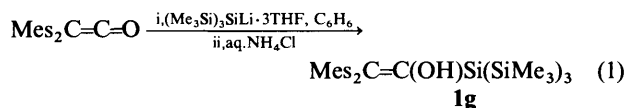

Fig. 1 Dynamic NMR experiment of the Mes-H signals of **1g** in CD_3COCD_3. (a) at 197 K (slow exchange); (b) at 211.5 K (signal broadening); (c) at 214 K (coalescence); (d) at 242 K (build up of new signals); (e) at 292 K (sharpening and temperature-dependent shift of new signals); (f) at 305 K (accidental overlap of average signals). Signals marked with an asterisk are due to impurities. The truncated singlet is the OH signal which is shifted as the temperature is increased.

those measured for **1d** and **1e**,[14] in line with the A values[18] of the Pr^i, Bu^t and Me_3Si-groups (2.1, 4.9 and 2.5 kcal mol^{-1}, respectively). Note, however, that the van der Waals radius of Me_3Si is similar[19a] or slightly larger[19b] than that of Bu^t. In a related study we have shown that due to its electronic effect a silyl substituent destabilizes (relative to methyl) the enol much less than it destabilizes its carbonyl analogue,[20] and this prediction was indeed verified experimentally.[20a,21]

In this paper we apply several of the above mentioned criteria in order to estimate the 'size' of the 'supersilyl' group in a crowded molecular environment. The structure of the $(Me_3Si)_3$-Si-substituted enol **1g** was determined by X-ray crystallography and the correlated rotation barrier of the mesityl groups around the Mes-C bonds was determined. The studies were complemented by force-field calculations which were also used to determine the A value of the $(Me_3Si)_3Si$ group.

Results

Synthesis.—2,2-Dimesityl-1-tris(trimethylsilyl)silylethenol **1g** was prepared by the reaction of dimesitylketene[22] with tris(trimethylsilyl)silyllithium·3THF[23] at room temperature [eqn. (1)]. The ^1H NMR spectrum of **1g** at room temperature in

$$Mes_2C=C=O \xrightarrow[\text{ii,aq.NH}_4\text{Cl}]{\text{i,}(Me_3Si)_3SiLi\cdot3THF,\ C_6H_6}$$

$$Mes_2C=C(OH)Si(SiMe_3)_3 \quad (1)$$
$$\mathbf{1g}$$

$(CD_3)_2CO$ displays seven singlets: a 27 H $(Me_3Si)_3Si$ signal at δ 0.14, three methyl signals in a 2:1:3 ratio at δ 2.11, 2.18 and 2.20 ascribed to o-, p- and o + p-mesityl methyls, two 2 H signals at δ 6.78 and 6.79 for the m-hydrogens of the two different mesityl rings and an OH signal at δ 6.14.

Dynamic NMR Measurements.—When the temperature of a sample of **1g** in $(CD_3)_2CO$ is lowered to 180 K decoalescence at both the Me and the aromatic region increases the number of signals to 12 at slow exchange. These include a broad $(Me_3Si)_3Si$ singlet at δ 0.09, six methyl singlets at δ.1.60 (o-), 1.70 (o-), 2.11 (p-), 2.14 (p-), 2.43 (o-), 2.51 (o-), four aromatic singlets at δ 6.56, 6.66, 6.84 and 6.93 and a hydroxy singlet at δ 7.25. When a solution of **1g** in 3:7 CS_2-CD_2Cl_2 was cooled to 150 K, broadening of the signal of the $(Me_3Si)_3Si$ group was observed. This may indicate a slow rotation of the $(Me_3Si)_3Si$ group at a low temperature, but complete decoalescence was not achieved.

On raising the temperature gradually to 320 K all the signals except for the OH signal broaden and those for the m-H and the o-Me coalesce. Four coalescence processes were observed, two at the methyl region and two at the aromatic region. Pairs of signals undergoing coalescence were identified by saturation transfer.[24] The signals at δ 1.60 and 2.43 pertain to one ring and those at δ 1.70 and at 2.51 to the other. The two pairs of methyl signals coalesce at close temperatures, whereas those for the two pairs of the aromatic protons coalesce at the same temperature. The rate constant k_c at the coalescence temperature T_c was calculated from the Gutowsky-Holm approximation[25] and the rotation barrier $\Delta G_c^{\ddagger}$ was calculated from the Eyring equation. The data are given in Table 1 and the spectral changes at the aromatic region which show two coalescence processes are plotted in Fig. 1. As the temperature is raised above the coalescence temperature the average peaks display temperature-dependent shifts to different extents and the two resolved
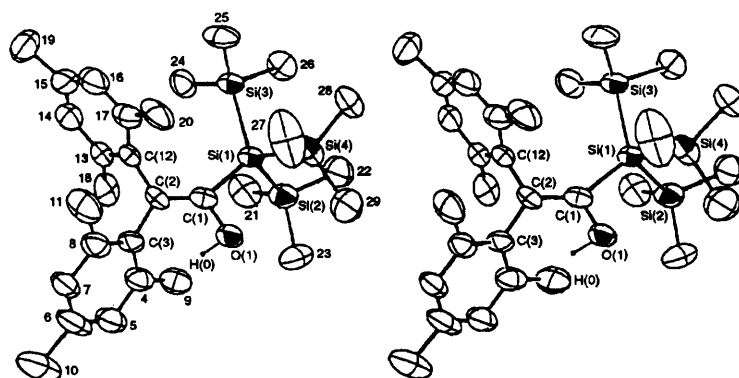
Fig. 2 Numbering scheme for the atoms in the ORTEP stereoview drawing of compound **1g**. The four silicon atoms and the enolic oxygen have been picked out for ease of reference.
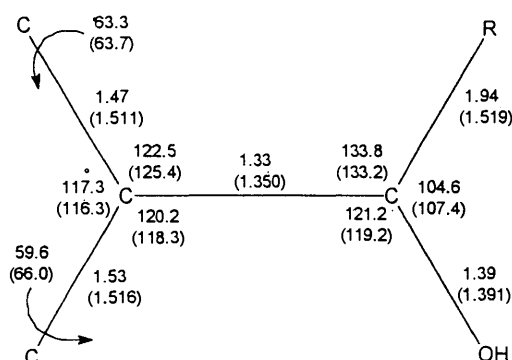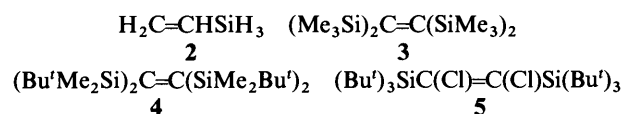

Fig. 3 Comparison of the main (experimental) structural parameters for enols **1g** [R = (Me₃Si)₃Si] and **1e** (R = Buᵗ). Values for the latter are given in parentheses.

signals appearing at 291.6 K merge to a single signal at 305 K [Fig. 1(e), (f)]. We also note that the signals shift with temperature as shown for the non-coalescing p-Me signals. The most significant temperature-dependent shift is of the OH group which shifts from δ 6.14 (180 K) to 7.25 (295 K). Consequently, the positions of the average signals after coalescence are not at the average δ value of the coalescing signals at slow exchange.

X-Ray Structure of Compound **1g**.—The atom numbering scheme of **1g** [R = (Me₃Si)₃Si] is given in the ORTEP stereoview drawing (Fig. 2). Tables of atomic coordinates, bond lengths and bond angles, and thermal parameters have been deposited at the Cambride Crystallographic Data Centre.†

The main features of the X-ray data of **1g** are detailed below. As the most relevant structure comparison is with **1e** (R = Buᵗ), we collect in Fig. 3 the main geometrical parameters of **1e** and **1g**: (a) The structure of **1g**, as that of other diarylvinyl systems [15] is a propeller-type with a Mes–C=C torsional angle of 63.3° for the β-ring (*cis* to the Si) and 59.6° for the β'-ring (*trans* to the Si). The former angle is practically identical with that of 63.7° for **1e**, while the latter is larger (66.0°) for **1e**. The O–H and the C=C moieties are essentially *syn*-coplanar [the torsional C(2)C(1)OH angle = 1.9°]. (b) The widest bond angle of 133.8° is found for C(2)C(1)R. This is the largest known bond angle for enols [133.2° in **1e** (R = Buᵗ)].[14,15] (c) The smallest bond angle around the double bond is RC(1)O, which is 104.6° for **1g** (107.4° for **1e**).[14] (d) The β-MesC(2)β'-Mes and the β'-MesC(2)C(1) bond angles in both enols **1e** and **1g** differ by only

† For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1994, Issue 1.

1–1.9° while the β-MesC(2)C(1) angle and the C(2)C(1)O angle are 2.9° smaller and 2° larger, respectively for **1g**. (e) The C(1)–C(2) bond length is longer by 0.02 Å in **1e** than in **1g**. (f) The =C–Si distance is 1.94 Å. This value is 0.08 Å longer than the value in vinylsilane **2**,[26a] 0.01–0.02 Å longer than in the less congested tetrasilylethylenes **3**[26b] and **4**[26c] but 0.02 Å shorter than in the apparently more congested 1,2-disilylethylene **5**.[26d] (g) The torsional bond angle of the double bond [OC(1)C(2)-C(3)] is 9.2°.

$$H_2C{=}CHSiH_3 \quad (Me_3Si)_2C{=}C(SiMe_3)_2$$
$$\mathbf{2} \qquad\qquad\qquad \mathbf{3}$$

$$(Bu^tMe_2Si)_2C{=}C(SiMe_2Bu^t)_2 \quad (Bu^t)_3SiC(Cl){=}C(Cl)Si(Bu^t)_3$$
$$\mathbf{4} \qquad\qquad\qquad\qquad \mathbf{5}$$

Force-field Calculations.—Method. The force-field calculations were carried out with the MacroModel program[27] which uses the MM2* force-field which treats electrostatics and conjugation differently[28] than the original MM2.[29] There are also some small differences in the parameters of the MM2 and MM2* force-field and they are responsible for the small differences found between various geometrical values reported in Table 2 and those reported previously by some of us[14] using the MM2 (85) force-field. In some of the studied cases 'high-quality' optimized parameters do not exist and we have used the recommended 'low-quality' parameters [e.g. 109.5° for the CSiSi bond angle in the (Me₃Si)₃Si fragment].[27] We find that in general, the MM2* results are in better agreement with experiment than the MM2 results (see below). The MM2* calculated rotation barriers of the mesityl groups in **1a–1h** are reported in Table 3 together with the available experimental values.

Structures and rotation barriers of enols **1**. The MM2* force-field method was used for calculating the ground state geometries of **1** and the rotation barriers for the correlated rotation of the mesityl rings. The main geometrical parameters of the ground states of enols **1**, which include bond angles around the double bond, bond lengths to C(1) and C(2), the mesityl-C=C torsional angles φ₁ and φ₂ and the C=C-O-H torsional angles, as well as the definitions of the geometrical parameters are given in Table 2.

Table 2 also contains the experimental parameters for all the enols (except for **1f** and **1h**) in the solid state.[14] The calculated parameters given in Table 2 are for both the *syn* and *anti* conformers, with regard to the C=C-O-H dihedral angle. The energy differences between the conformers are not large (Table 2) and the changes in the geometrical parameters upon rotation around the =C-OH bond are minor and therefore they will not affect our analysis.

The geometrical parameters for **1a–1e** were previously

Table 2 Calculated (MacroModel, V3.5X, MM2*) and experimental (in parentheses) bond angles, torsional angles and bond lengths for enols 1 [a]

Angle (deg)

R	α_1	α_2	α_3	α_4	α_5	α_6	φ_1	φ_2	φ [b]	$\Delta(s-a)$ [c]
H	120.0	120.5	119.5	119.7	114.9	125.4	57.6	50.7	5.2,[d] 165.8[e]	−1.78
	(118.1)[f]	(121.0)[f]	(120.8)[f]	(118.1)[f]	(118.7)[f]	(123.0)[f]	(56.7)[f]	(50.2)[f]	g	
Me	121.9	119.0	119.1	123.3	114.1	122.6	56.5	59.8	5.6,[d] 136.5[e]	0.54
	(121.8)	(118.2)	(119.9)	(126.0)	(112.4)	(121.6)	(57.5)	(55.7)	g	
Et	121.7	118.5	119.7	123.3	113.3	123.5	57.2	61.0	6.3,[d] 137.9[e]	0.55
	(119.9)	(120.6)	(119.4)	(127.4)	(109.0)	(123.4)	(59.7)	(58.3)	h	
Pr[i]	121.7	118.4	119.8	123.0	113.6	123.2	57.3	63.3	5.1,[d] 129.6[e]	0.24
	(120.4)	(121.2)	(118.4)	(127.7)	(110.0)	(121.8)	(62.8)	(60.1)	h	
Bu[t]	125.4	116.4	118.2	128.8	111.2	120.7	57.2	68.9	8.0,[d] 137.5[e]	0.26
	(125.4)	(116.3)	(118.3)	(133.2)	(107.4)	(119.2)	(66.0)	(63.7)	h	
Me₃Si	122.6	118.4	118.9	127.9	108.4	123.6	56.9	67.8	5.2,[d] 142.1[e]	−1.06
									h	
(Me₃Si)₃Si	126.9	115.2	117.8	132.4	107.1	120.6	60.2	67.4	6.0,[d] 141.0[e]	−1.36
	(122.5)	(117.3)	(120.2)	(133.8)	(104.6)	(121.2)	(59.6)	(63.3)	h	
(Me₃Si)₃C	129.2	110.3	120.5	135.0	110.2	114.8	61.4	68.0	8.2,[d] 132.5[e]	−2.46

Bond length (Å)

R	C=C	C–O	=C–Mes(β)	=C–Mes(β′)	=C–R
H	1.345	1.360	1.509	1.507	1.103
	(1.326)[f]	(1.372)[f]	(1.501)[f]	(1.506)[f]	
Me	1.350	1.365	1.508	1.511	1.513
	(1.311)	(1.371)	(1.492)	(1.515)	(1.51)
Et	1.350	1.365	1.509	1.511	1.518
	(1.329)	(1.371)	(1.511)	(1.500)	(1.49)
Pr[i]	1.351	1.365	1.510	1.513	1.524
	(1.359)	(1.371)	(1.505)	(1.493)	(1.494)
Bu[t]	1.354	1.369	1.508	1.520	1.541
	(1.350)	(1.391)	(1.511)	(1.516)	(1.519)
Me₃Si	1.349	1.363	1.507	1.514	1.881
(Me₃Si)₃Si	1.351	1.367	1.509	1.519	1.890
	(1.33)	(1.39)	(1.47)	(1.53)	(1.94)
(Me₃Si)₃C	1.370	1.372	1.511	1.549	1.578

[a] Experimental values are from ref. 14. [b] The C=C–O–H angle. [c] $\Delta(s-a)$ = energy difference (in kcal mol⁻¹) between the *syn* and *anti* conformers. A negative value indicates that the *syn* conformer is more stable. [d] *syn* Conformer. [e] *anti* Conformer. [f] Average of values for four crystallographically different molecules. [g] Only the structure of the ethanolate (1·EtOH), where the C=C–O–H conformation is *anti*, was determined. [h] The conformation of the C=C–O–H moiety is *syn*.

Table 3 Experimental and calculated barriers (kcal mol⁻¹) for the two-ring flips in enols Mes₂C=C(OH)R 1

Compound	R	$\Delta G^{\ddagger}_{exp}$ [a]	ΔE_{calc} [b]
1a	H	14.2	14.6 (16.4)
1b	Me	12.5	13.0 (9.1)
1c	Et	12.0	12.9
1d	Pr[i]	11.7	12.5
1e	Bu[t]	10.4	10.7
1f	Me₃Si	11.1	11.6
1g	(Me₃Si)₃Si	10.2	10.3
1h	(Me₃Si)₃C	c	8.0

[a] Experimental data (referred to in the text as $\Delta G^{\ddagger}_c$) for the first five enols are from ref. 14, for R = SiMe₃ from ref. 17 and for R = (Me₃Si)₃Si from the present work. [b] Calculated with the MM2* force-field. Values in parentheses are those reported in ref. 14. [c] Not available.

calculated by the MM2 (85) program, and while the differences from the present calculations are small, it is noteworthy that the present calculated values are generally closer to the observed values. A consistent, although small difference between the calculated and observed values is found for α_4—the widest

bond angle—for the R alkyl groups. The calculated values are lower by 2.7–4.7° than the observed values. However, the difference is smaller, being only 1.4° for 1, R = (Me₃Si)₃Si.

The transition state energies for mesityl ring rotations were calculated for conformations where both rings were perpendicular to the double bond. All other parameters were fully optimized. In some cases, deviations of the aromatic rings from planarity of up to 4.5° were noted. However, as the resulting changes in energy were very small, the results reported in the tables are for the planar ring structures. Much larger deviations from ring planarity were found when the MM2 force-field was used.[14]

The calculated rotation barriers, ΔE_{calc}, which are the differences in steric energies of the ground state and the transition state for each enol are given in Table 3, together with the experimentally measured $\Delta G^{\ddagger}$ values for the two-ring flips.[14]

Also reported are the previously calculated (MM2) rotation barriers for 1a and 1b. The agreement between the calculated and observed rotation barriers is very good, except that the calculated rotation barriers are consistently higher than the experimental ones by a fraction (0.1–0.9) of a kcal mol⁻¹. The new calculated rotation barriers (MM2*) for 1a and 1b are

Table 4 Experimental and calculated (MM2* and MM2, kcal mol⁻¹) A values of alkyl and silyl substituents

R	A_{exp}[a]	A_{calc} (MM2*)	A_{calc} (MM2)	A_{calc} (lit.)
Me	1.74	1.78	1.78	1.77[b,c]
Et	1.79	1.82	1.82	1.87[b,c]
Pr^i	2.21	1.72	1.72	2.05[b,c]
Bu^t	4.7, 4.9	5.00	4.99	5.41[b,c]
SiH₃	1.45, 1.52	0.95	0.94	1.26,[c] 1.08[d]
Me₃Si	2.5	2.59	2.49	3.41[b]
(Me₃Si)₃Si	e	4.89	4.83	e
(Me₃Si)₃C	e	13.3	10.76	e

[a] Values from ref. 31(a). [b] R. J. Ouellette, D. Baron, J. Stolfo, A. Rosenblum and P. Weber, *Tetrahedron*, 1972, **28**, 2163. [c] N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski and F. A. Van Catledge, *J. Am. Chem. Soc.*, 1968, **90**, 1199. [d] R. J. Unwalle, S. Prefeta, Jr. and F. C. Catledge, *J. Org. Chem.*, 1988, **53**, 5658. The *ab initio* calculated value at MP3/3-21G*//3-21G* is 1.13 kcal mol⁻¹. [e] Not available.

Table 5 Experimental and calculated (MM2*, kcal mol⁻¹) =C–Si bond lengths of vinyl-Si derivatives

Compound	=C–Si (Å) Exp. (ref.)	=C–Si (Å) Calc.
2	1.853[26a,a]	1.873
3	1.915[26b]	1.897
4	1.915, 1.926[26c]	1.907
5	1.956[26d]	1.887
1g	1.94	1.890

[a] From microwave determination.

much closer to the experimental ones than those previously calculated by MM2.[14] Since the calculated values are activation enthalpies ($\Delta H^{\ddagger}$) while the measured rotation barriers are activation free energies ($\Delta G^{\ddagger}$), the good agreement between the calculated and experimental values may indicate only a small experimental contribution of $\Delta S^{\ddagger}$ to the rotation barriers. Indeed, a $\Delta S^{\ddagger}$ of *ca.* 0 was measured for the mesityl rotation in the more crowded tetramesitylethylene.[30]

A values. The A values, defined as the free energy difference between equatorial and axial substituents on a cyclohexane ring,[31] for the six R groups of **1b–1g** and for SiH₃ and (Me₃Si)₃C were calculated from the computed MM2* differences between the steric energies of the axial and equatorial R groups in cyclohexane. Owing to the central role of A values in discussions of steric effects and substituent 'sizes' we have calculated the A values also with the MM2 force-field which has previously been used extensively in the literature.[32] The calculated A values by both MM2* and MM2 together with the available experimental values and several older calculated values from the literature are given in Table 4.

=C–Si *Bond lengths.* The MM2* computed =C–Si bond length in **1g** is *ca.* 0.05 Å shorter than the experimental value (Table 2). In order to find out if this is due to a deficiency of the MM2* force-field, the =C–Si bond lengths for compounds **2–5** were also computed by MM2*. Comparison of the calculated values and the experimentally determined bond distances (Table 5) indicates lower calculated values (except for **2**), up to a 0.07 Å shorter bond length in the highly congested **5**.

Discussion

The Rotation Mechanism for Compound **1g**.—Three conclusions are derived from the data of Table 1. First, the activation free energy for rotation of the two mesityl rings in

1g, as measured by two probes for each ring are the same, 10.2 ± 0.1 kcal mol⁻¹. Although this can result from two consecutive one-ring flips which have similar rotation barriers, it is more likely that this is due to a single correlated two-ring flip of the two rings. The arguments supporting the two-ring flip mechanism are similar to those discussed previously for other systems **1**,[12,17] and the very good agreement between the observed barriers and the force-field calculated ones for both **1f** and **1g** fully support this conclusion. The transition state for the enantiomerization is shown in eqn. (2), where ⊣▭▯ represents a mesityl ring perpendicular to the C=CO plane.

(2)
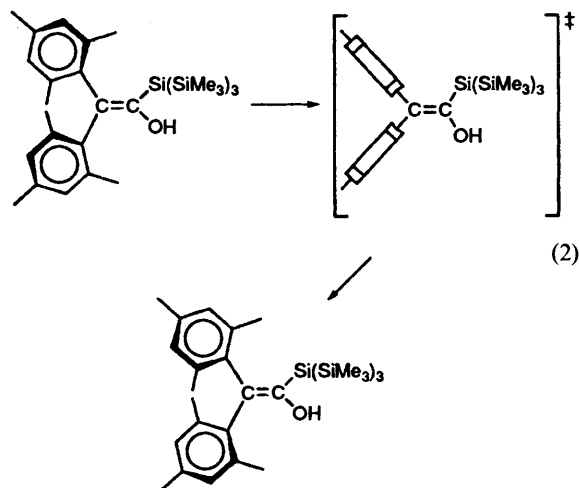
Second, the rotation barrier of 10.2 kcal mol⁻¹ in **1g** is lower by 0.9 kcal mol⁻¹ than the barrier in **1f**, the analogue with the 'smaller' α-Me₃Si substituent. Third, this rotation barrier is slightly smaller, although within the combined experimental errors, than the value for the α-*tert*-butyl analogue **1e**, for which $\Delta G_c^{\ddagger}$ = 10.4 kcal mol⁻¹.[14] The calculations are in full agreement. The calculated barrier for the two-ring flip in **1g** is 10.3 kcal mol⁻¹, by 1.3 and 0.4 kcal mol⁻¹ lower than in **1f** and **1e**, respectively. This agreement is noteworthy in view of the fact that the calculated =C–Si bond distance in **1g** is much shorter than the experimental value.

The interpretation of the two above-mentioned rotation barriers depends on the ground state geometries of **1e**, **1f** and **1g**, since the α-R-substituent exerts severe steric distortions on the systems, especially by affecting the Mes–C=C torsional angles. The experimental Mes–C=C torsional angles for **1e** (66.0, 63.7°) are somewhat higher than for **1g** (59.6, 63.3°), whereas the calculated values for these molecules are even closer (Table 2). In the absence of X-ray data for **1f** we compare the calculated torsional angles, which again do not differ much from those in **1g** (**1f**: 56.9, 67.8°; **1g**: 60.2, 67.4°). We conclude that the difference in the steric effect of the Bu^t and (Me₃Si)₃Si groups on the torsional angles in **1** is small, but that these small differences can partially account for the small differences in their $\Delta G_c^{\ddagger}$ values.

E_s *Value for the* (Me₃Si)₃Si *Group.*—Assuming that the previously observed linear relationship between $\Delta G_c^{\ddagger}$ for the two-ring flip and the steric parameter E_s of an α-H and α-alkyl substituents in **1** (Fig. 4) also holds for (Me₃Si)₃Si, the calculated E_s value for (Me₃Si)₃Si value from this plot is *ca.* −1.6. This value is very similar to the E_s value of the Bu^t group (−1.54), which is not surprising since the $\Delta G_c^{\ddagger}$ values for Bu^t and (Me₃Si)₃Si are almost the same. This value is much smaller than the E_s values for Me₂(Bu^t)C or Et₃C (−3.9 and −3.8, respectively[16]) although formally, *i.e.* by counting the number of methyl groups and taking into account its symmetry,
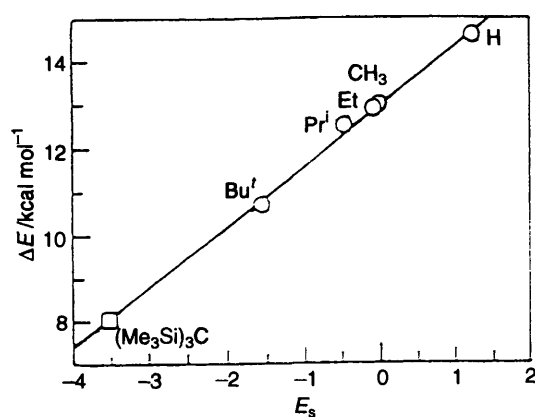
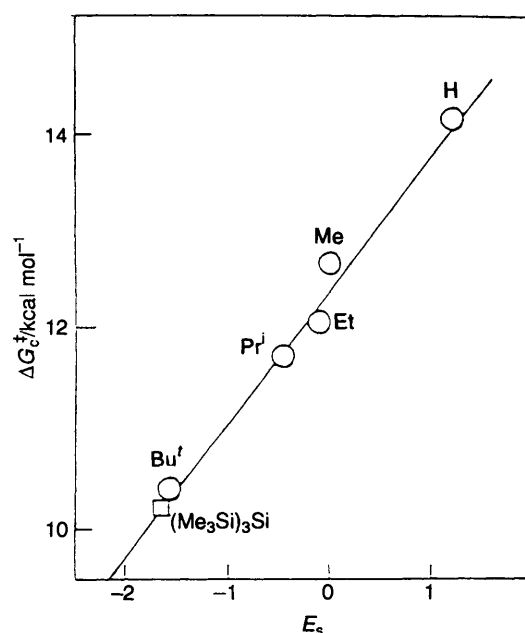Fig. 4 Estimation of the E_s value for the $(Me_3Si)_3Si$ group from a plot of $\Delta G_c^{\ddagger}$ vs. E_s

Fig. 5 Estimation of the E_s value for the $(Me_3Si)_3Si$ group from a plot of $\cos \varphi_2$ vs. E_s

$(Me_3Si)_3Si$ should be much bulkier and hence should have a larger E_s.

Another approach for estimating the E_s value of $(Me_3Si)_3Si$ is based on the linear correlation observed between $\cos \varphi_2$ in enols 1a–1e and E_s.[12a] When the observed $\cos \varphi_2$ value for 1g is added to the plot in Fig. 5, an E_s value of -1.32 is obtained. Again, the bulk of the $(Me_3Si)_3Si$ group in the ground state does not differ much from that of the Bu^t group. The average E_s value of the $(Me_3Si)_3Si$ group from the two approaches is -1.46.

A manifestation that alkyl and silyl substituents obey the same correlation is that the point for 1g perfectly fits the line of the linear $\Delta G_c^{\ddagger}$ vs. α_4 plot (not shown) for enols 1a–1e.

We conclude that both the structural data for 1g and the barrier in the correlated two-ring flip rotation of the dimesitylvinyl moiety indicate that in the molecular environment of 1 the steric bulk of the $(Me_3Si)_3Si$ and the Me_3C groups is very similar and much smaller than might have been deduced from the van der Waals bulk of $(Me_3Si)_3Si$.

A Values.—Another parameter related to the 'size' of groups is their A value. Since the A values are based on axial–equatorial equilibria of cyclohexyl-R derivatives the experimental range of values accessible is not large and values for bulky groups are lacking.

Comparison of our calculated A values with the experimentally available values (Table 4) indicate that the calculations well reproduce the latter values. Most interesting are the calculated values (in kcal mol^{-1}) for Me_3Si (2.59) and Bu^t (5.00) which agree very well with the experimental values of 2.5 and 4.9, respectively. This excellent agreement gives confidence in the calculated value for $(Me_3Si)_3Si$ of 4.89 which is practically identical with that of Bu^t. Consequently, similarly to systems 1, when attached to cyclohexane, the $(Me_3Si)_3Si$ group displays a significantly larger 'size' than that of Me_3Si and close to that of Me_3C.

E_s *and A Values for the* $(Me_3Si)_3C$ *Group.*—The $(Me_3Si)_3C$-group, the 'trisyl' group,[33] is another silicon-containing 'bulky substituent' which has attracted recently considerable interest.[33-35] In particular, Eaborn and co-workers have used the 'trisyl' group extensively in their studies aimed at generating silicenium ions and stable methyl-bridged siliconium ions.[33a] Most recently the organic chemistry of simple 'trisyl' derivatives of the type $(Me_3Si)_3CX$ (X = halogen) was studied[33b] and the X-ray structure of $(Me_3Si)_3CK$ was reported.[34] In view of this interest we have included also the 'trisyl' group in our computational study, but no attempt was made to synthesize the highly strained 1h.

The calculated structure of 1h (Table 2) indicates that the high steric crowding leads to extreme bond angles and bond lengths. Only α_3 has a regular sp^2 value of ca. 120°. Both α_1 and α_4, which are on the same side of the double bond, are substantially widened (to 129.2 and 135.0°, respectively), mostly at the expense of the bond angles α_2 and α_5 between the geminal substituents, which have values close to 110°. All the bonds, especially the C=C and C–R bonds are significantly elongated compared with their calculated distances in the other enols. Surprisingly, the Mes–C=C torsional angles and the double bond torsional angle $[OC(1)C(2)C(3)]$ are only slightly higher than those calculated for 1g.

The calculated A value for $(Me_3Si)_3C$ is 13.3, much higher than the value for $(Me_3Si)_3Si$, reflecting mainly the much shorter bond (C–C vs. C–Si) between the substituent and cyclohexyl ring.

It is interesting to note that the A values calculated with MM2* and MM2 are very similar for all substituents R, except for R = $(Me_3Si)_3C$ for which the MM2 value (10.8 kcal mol^{-1}) is significantly smaller than the MM2* value (13.3 kcal mol^{-1}). However, the actual A value of $(Me_3Si)_3C$ might be even higher than 13.3 kcal mol^{-1} as the calculated MM2* C–Si distances are somewhat too long. For example, the bond length of 1.905 Å calculated for (H)C–Si in $(Me_3Si)_3CH$ is by 0.017 Å longer than the measured value.[36]

The high calculated A value for $(Me_3Si)_3C$ raises interest in the unavailable E_s value for this group, which can be roughly estimated from our calculations. From the excellent correlation ($r = 0.9961$) between the MM2* calculated activation energies (ΔE) for the correlated rotation of the mesityl rings of 1a–1g and the E_s values of R (Fig. 6) and the calculated ΔE value for $Mes_2C=C(OH)C(SiMe_3)_3$, E_s for $(Me_3Si)_3C$ is -3.6. From the fair correlation ($r = 0.9581$, not shown) between the calculated α_4 and E_s, $E_s[(Me_3Si)_3C] = -3.8$. We believe that the average value, *i.e.* -3.7, can be taken as a reasonable estimate for the E_s value of the $(Me_3Si)_3C$ group. This E_s value is much larger than E_s for $(Me_3Si)_3Si$ (-1.46) and similar to the values for Et_3C (-3.9) and $Me_2(Bu^t)C$ (-3.8).[16]

The fact that the A and E_s values for $(Me_3Si)_3C$ are much larger than for $(Me_3Si)_3Si$ is consistent with the recently reported cone angles (θ)[37a] of these groups $(\theta = 216$ and 199°, respectively[37b]). The very large calculated A and E_s values for the $(Me_3Si)_3C$-group are consistent with the severe inhibition to bimolecular substitution that the trisyl group imposes at
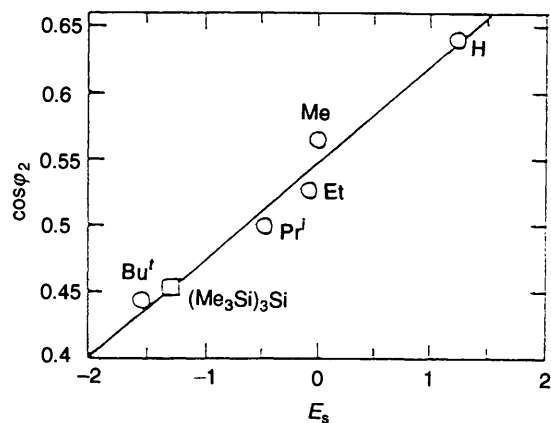
Fig. 6 Plot of the calculated (MM2*) barriers ΔE for the two-ring flip vs. E_s values

silicon directly bonded to it. A dramatic example is the resistance of $(Me_3Si)_3CSiCl_3$ to prolonged boiling in methanol and its lack of reactivity with organolithium reagents.[35]

Experimental

Preparation of 2,2-Dimesityl-1-tris(trimethylsilyl)silylethenol **1g**.—$(Me_3Si)_3SiLi\cdot3THF$[23] (2.2 g, 4.7 mmol) in dry benzene (20 cm³) was placed in a Schlenk flask under vacuum, and dimesitylketene (1.17 g, 4.2 mmol) in dry benzene (10 cm³) was added. After stirring at room temperature for 2 h, saturated aqueous NH_4Cl (20 cm³) was added to the mixture, the organic layer was separated and dried ($MgSO_4$), the volatile materials were evaporated under vacuum and then the crude product was isolated by column chromatography on silica gel with 10:1 hexane–diethyl ether as eluent. The major fraction was an oily product from which colourless crystals of the title compound **1g** (1.5 g, 73%) were separated in the cold and used for the X-ray analysis, m.p. 121–122 °C; $\delta_H(CDCl_3)$ 0.92 [27 H, s, $(Me_3Si)_3Si$], 2.10, 2.15, 2.20 (3 × 3 H, 3 s, Mes-Me), 6.73, 6.80 (2 × 1 H, 2 s, Mes-H); m/z (EI) 436 (M^+ − Me_3Si) (Found: C, 67.3; H, 9.9. Calc. for $C_{29}H_{50}OSi_4$: C, 66.09; H, 9.56%).

Dynamic NMR Measurements.—These were conducted with a Bruker AMX-400 spectrometer operating at 400.13 MHz. Temperature measurements were based on the chemical shift separation of the protons of methanol and the use of known temperature shift correlations.[38] The sample was equilibrated thermally at the reaction temperature for 15 min before measurements. Pairs of coalescing diastereotopic signals were assigned by saturation transfer at slow exchange.

X-ray Structure Determination of Compound **1g**.—Intensity was measured with a Philips PW1100 four-circle diffractometer with graphite-monochromated Mo-Kα radiation (0.710 69 Å) in the ω-2θ method. The crystal structure was solved and refined by SHELXS.[39] The refinement procedure was carried in separate blocks; the heavy atoms, anisotropically in one, and the hydrogen atoms, isotropically with their atomic displacement parameters riding on their bonded heavy atoms in the other one.

$C_{29}H_{50}OSi_4$; colourless cubic crystals crystallize in monoclinic space group Cc; $a = 23.503(10)$, $b = 16.894(8)$, $c = 8.932(4)$ Å, $\beta = 110.64(2)°$, $D_x = 1.04$ g cm⁻³ for four molecules in the unit cell. At the end of the refinement the discrepancy factors are $R = 0.090$ and $R_w = 0.093$ for 2324 observed reflections $[F_o > 3.0\sigma(F_c)]$.

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MM2* uses an improper torsion while MM2 uses a pyramidalization distance; (3) the way conjugation is handled: MM2* uses specific V_1-V_3 torsional terms for various conjugated systems whereas MM2 uses an SCF π-calculation. Further information can be obtained from ref. 27 and the user's Manual of MacroModel.

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