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Conformational Analysis of Triarylsilanes

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Abstract: Ground-state geometries and relative strain energies of several methyl-substituted triphenylsilanes have been obtained by full relaxation empirical force field calculations. The C-Si-C bond angle in trimesitylsilane is found to be significantly expanded, in parallel with similar previous findings for trimesitylmethane and trimesitylphosphine. The equilibrium conformer population of tris(*o*-tolyl)silane consists almost entirely of the exo$_3$ and exo$_2$ forms, in approximately equal proportion, whereas in the case of tris(*m*-tolyl)silane all four conformers populate the equilibrium mixture to a significant extent. The experimentally determined dipole moments of the triarylsilanes are in reasonable accord with the quantities calculated by vectorial summation of partial moments based on ground-state geometries and taking into account conformer populations. A marked similarity is noted between the computed geometries and conformational preferences of triarylsilanes and of structurally related phosphine derivatives.

In the course of our work[2] on the stereochemistry of three-bladed molecular propellers of the type Ar$_3$Z and Ar$_3$ZX[2] we had occasion to develop an empirical force field program,[3] which proved to be successful in computing the ground-state conformations of triphenylmethane, trimesitylmethane, and congeners.[4] The present study was undertaken in order to use this method as a means for estimating populations of diastereomeric conformers in molecules of this type in which the three aryl groups (Ar) have the same constitution, but lack a local C_2 axis. As a representative system we chose a series of methyl-substituted triphenylsilanes, since a force field had previously been employed to similar ends in a conformational analysis of tetrakis(*o*-tolyl)silane.[5]

Results and Discussion

Ground-state geometries and energies were computed employing the previously described[3,5] full relaxation empirical force field method, together with the appropriate parameters.[6]

In an exploratory study, ground-state conformations were computed for three molecules of the type Ar$_3$SiH, in which Ar has a local C_2 axis:[8] triphenylsilane (**1**), tris(*p*-tolyl)silane (**2**), and trimesitylsilane (**3**). It was found that all three molecules have $\mathbf{C}_3$ symmetry and that **1** and **2** have identical (within the precision of the method) bond angles (C-Si-C = 110.8°) and dihedral angles of twist[9] (H-Si-C-C′ = 32.7°).[10] In contradistinction, the expanded C-Si-C bond angle of 114.9° computed for **3** (H-Si-C-C′ = 42.1°) is a manifestation of significant nonbonded interaction among the three bulky mesityl groups and parallels the expansion of central bond angles found for trimesitylmethane[3,4a] and trimesitylphosphine.[12] The same effect results in a slight lengthening of the Si-C bond in **3** (1.88 Å) as compared to **1** and **2** (1.86 Å).[13]

Tris(*o*-tolyl)silane and Congeners. Eight conformational stereoisomers (four *dl* pairs) are possible for molecules of the type Ar$_3$SiH, in which the three aryl groups are constitutionally the same but lack a local C_2 axis.[14] Tris(*o*-tolyl)silane (**4**) is a member of this class. The four diastereomers differ in the number of methyl groups which are proximal or distal to the Si-H hydrogen atom[15] and, by analogy with the corresponding phosphines, they may be designated[16] as **4**-exo$_3$, **4**-exo$_2$, **4**-exo$_1$, and **4**-exo$_0$, according as to whether three, two, one, or none of the three methyl groups are proximal (exo). The sense of the propeller (helicity) determines the configuration (*P* or *M*) of the enantiomers in each of the four *dl* pairs.

Structural parameters computed for the four diastereomers are given in Table I. The skeletal structures of **4**-exo$_3$ and **4**-exo$_0$ closely resemble those of **1** and **3**, respectively. Evidently, the bond stretching and bending suffered by **4**-exo$_0$, as compared to **4**-exo$_3$, is similar to that suffered by **3**, as compared to **1**, and for the same reason: in **4**-exo$_0$, as in **3**, three methyl groups are forced into the endo position of the molecular pyramid[15] and are jammed against the nether face of the benzene rings. The resulting congestion is reflected not only in severe deformation of bond angles and lengths, but also in an increase of 3.63 kcal/mol in strain energy (E_T)[17] for **4**-exo$_0$, as compared to **4**-exo$_3$. In harmony with this model, it is found (Table I) that structural deformation and strain energy, which are at a minimum in **4**-exo$_3$, both increase in direct relation to the number of endo groups.

Whereas **4**-exo$_3$ and **4**-exo$_0$ both have $\mathbf{C}_3$ symmetry, the isomers with a mixed distribution of exo and endo groups (**4**-exo$_2$ and **4**-exo$_1$) are asymmetric. Nevertheless, the basic propeller property remains, for although the magnitudes of the three dihedral angles differ appreciably, the sense of twist of each phenyl ring in the triphenylsilane skeleton remains the same.

It is instructive to note that in related systems, structures analogous to **4**-exo$_3$ have been observed in the solid state. In tris(*o*-tolyl)phosphine and its oxide, the molecule exhibits virtual $\mathbf{C}_3$ symmetry and all three methyl groups occupy exo positions;[18,19] the torsional angles of the tolyl groups in the phosphine[19] (36.7-49.0°) and its oxide[19] (36.7-53.3°) are comparable in magnitude to those found for **4**-exo$_3$ (39.3°).

Table I. Geometries, Relative Strain Energies, and Equilibrium Distribution Calculated for the Conformational Diastereomers of Tris(*o*-tolyl)silane (**4**)

Conformational isomer[a]	Si-C,[b] Å	C-Si-C,[c] deg	H-Si-C-C',[b,d] deg	Rel strain energy (ΔE_T), kcal/mol	ΔG_{298}, kcal/mol	Equilibrium mole fraction (N)
4-exo$_3$	1.86_2	111.2	39.3	0.00	0.00	0.49
	1.86_2	111.0	39.4			
	1.86_2	111.1	39.3			
4-exo$_2$	1.86_4	111.5	−159.6	0.66	0.01	0.48
	1.86_7	113.5	60.5			
	1.86_6	111.7	51.7			
4-exo$_1$	1.86_9	113.7	−151.2	2.27	1.62	0.03
	1.86_9	115.1	−129.8			
	1.86_2	111.2	42.1			
4-exo$_0$	1.86_8	114.8	−136.8	3.63	3.63	0.001
	1.86_9	114.5	−138.5			
	1.86_8	114.6	−138.2			

[a] For definition, see text. [b] For each entry, the index of C (and therefore of the corresponding tolyl group) is defined as (1), (2), and (3), reading from top to bottom. [c] For each entry, C-Si-C refers to (1)-Si-(2), (2)-Si-(3), and (1)-Si-(3), reading from top to bottom. [d] Ref 9.

Table II. Geometries, Relative Strain Energies, and Equilibrium Distribution Calculated for the Conformational Diastereomers of Tris(*m*-tolyl)silane (**5**)

Conformational isomer[a]	Si-C,[b] Å	C-Si-C,[c] deg	H-Si-C-C',[b,d] deg	Rel strain energy (ΔE_T), kcal/mol	ΔG_{298}, kcal/mol	Equilibrium mole fraction (N)
5-exo$_3$	1.85_8	110.9	34.3	0.27	0.83	0.10
	1.85_9	110.8	34.1			
	1.85_9	111.0	34.4			
5-exo$_2$	1.85_8	110.8	33.2	0.19	0.10	0.34
	1.85_7	110.8	−147.0			
	1.85_7	110.8	33.2			
5-exo$_1$	1.85_8	110.8	−148.4	0.09	0.00	0.40
	1.85_7	110.8	−148.4			
	1.85_8	110.9	33.9			
5-exo$_0$	1.85_8	110.8	−149.0	0.00	0.56	0.16
	1.85_8	110.9	−147.7			
	1.85_8	111.0	−148.7			

[a-d] See footnotes in Table I.

Similarly, tris(*o*-tolyl)germane assumes the conformation of a molecular propeller with all three methyl groups in exo positions.[20] On the other hand, sufficient encumbrance at the apex of the pyramid[15] may force one of the exo methyls into an endo position, as observed for tris(*o*-tolyl)phosphine sulfide and selenide.[18,19,21] Our finding that the angle of torsion of the endo tolyl group in **4**-exo$_2$ (20.4°) is substantially smaller than those of the exo groups (51.7 and 60.5°) closely resembles the observation[19] that in tris(*o*-tolyl)phosphine sulfide and selenide, the torsional angles of the endo group (3.4-17.0°) are much smaller than those of the exo groups (52.6-66.9°). Evidently, the steric effects in the silane and phosphine systems are quite similar.

The equilibrium distribution of the four diastereomers is governed by the free energy differences, ΔG. The enthalpy differences, ΔH, are reasonably equated with ΔE_T, since we are comparing stereoisomers, and no correction need be made for the entropy of mixing,[22] since all four isomers exist as *dl* pairs. However, the effect of the entropy contribution due to symmetry[22] ($-R \ln 3$) is to lower ΔG for the two asymmetric diastereomers by 0.65 kcal/mol at 25 °C, relative to the isomers with C_3 symmetry. As a result, the equilibrium mixture of conformers of **4** is seen (Table I) to consist almost entirely (>97%) of **4**-exo$_3$ and **4**-exo$_2$ in nearly equal proportion; depopulation of the former due to symmetry is almost exactly compensated for by depopulation of the latter due to internal strain.[23] The equilibrium is mobile, since **3** is known[24] to undergo enantiomerization with $\Delta G^{\ddagger} = 10.9$ kcal/mol, and the barrier is expected to decrease in molecules with fewer ortho substituents,[2] such as **4**.[25]

Tris(*m*-tolyl)silane and Congeners. Four conformational *dl* pairs are also possible for tris(*m*-tolyl)silane (**5**), but in contrast to **4** the skeletal structures of all four are essentially indistinguishable from each other and from **1** (Table II). What is apparent from an inspection of molecular models is thus borne out quantitatively by the calculations: the methyl groups in **5** do not suffer any significant nonbonded interaction. For the same reason, it is not surprising that the relative strain energies of the four conformational diastereomers differ by less than 0.3 kcal/mol (Table II), although it is worth noting that methyl groups are slightly *less* strained in the endo than in the exo position. Because of the very small values of ΔH, the $T\Delta S$ term (0.65 kcal/mol) now becomes the dominant contribution to ΔG. As a result of these effects, **5**-exo$_2$ and **5**-exo$_1$ in combination constitute the major proportion of the mixture. In summary, our calculations indicate that all four diastereomers of **5** populate the mobile equilibrium[25] mixture to a significant extent, with the asymmetric conformers somewhat in preponderance.[23]

A comparison with structurally related molecules is illuminating. In the solid state, tris(*m*-tolyl)phosphine[27] has the exo$_2$ conformation, whereas the corresponding phosphine

Table III. Slopes for the Dependence of Static Dielectric Constant and Square of Refractive Index on Mole Fraction (a_0 and a_D, respectively) with Infinite Frequency Intercepts (a_∞), Critical Frequencies (ν_m), Atomic Polarizations (P_A), and Dipole Moments (μ (25 °C))

	a_0	a_D	a_∞	ν_m, GHz	P_A, cm^3	μ, D[a]
Triphenylsilane (**1**)	1.796	1.015	1.264	4.1	4.3	0.62
Tris(*p*-tolyl)silane (**2**)	2.468	1.044	1.260	2.7	4.4	0.93
Trimesitylsilane (**3**)	1.965	1.253	1.532	2.0	5.7	0.56
Tris(*o*-tolyl)silane (**4**)	1.551	1.182	1.395	4.7	4.3	0.33
Tris(*m*-tolyl)silane (**5**)	2.363	1.052	1.315	3.5	5.0	0.87

[a] The estimated accuracy is ±0.03D.

oxide, sulfide, and selenide all have the exo$_1$ conformation.[21a] These observations are consistent with the conformational preferences calculated for **5**.

Dipole Moments of Triarylsilanes. As a test of the reliability of the preceding analysis and of the attendant assumptions and approximations, the dipole moments (μ) of **1–4** were measured and compared with quantities calculated for **3–5** on the basis of computed geometries and energies.

The dipole moments were experimentally determined at 25 °C in dilute benzene solution, employing the microwave technique[28-30] (see Experimental Section). The results are collected in Table III. The measured dipole moment of **1** is in good agreement with 0.66D previously determined[31] in *p*-xylene solution at 25 °C by the same method, and with the values of 0.66 ± 0.04 (CCl_4)[32] and 0.70D (C_6H_6)[11] determined at 25 °C by the classical technique.[28,33]

From the value of μ for **1** (0.62D) and the Si-H bond moment (1.0D[34]), a value of 0.41D was computed for the partial moment acting along the silicon–phenyl bond axis (μ_{Si}), based on the fully relaxed geometry of the molecule. This value is in good agreement with μ_{Si} = 0.45D calculated from μ = 0.25D for phenyltrimethylsilane[31,35] and a Si-CH_3 moment of 0.2D.[34] Since **1** and **2** have the same geometries, the partial moment acting along the phenyl–methyl bond axis (μ_C) was simply derived[16] from the differences in dipole moments, 0.31D: given the H-Si-C bond angle of 108.1°, it follows that μ_C = 0.34D, in excellent agreement with 0.35D found for the dipole moment of toluene[36] and with μ_C = 0.36D employed in our previous calculations.[16]

The molecular moments of **3–5** were calculated by vectorial summation of partial moments using the coordinates calculated in the empirical force field program. The results are collected in Table IV.

The dipole moments of **4** and **5** are weighted composites of the moments of the constituent conformers: $\mu^2 = \sum_i N_i \mu_i^2$, where N_i and μ_i are the mole fraction and the dipole moment of the *i*th conformer. From computed values of N_i (Tables I and II) and μ_i (Table IV), the calculated composite μ's of **4** and **5** were thus found to be 0.46 and 0.98D, respectively, as compared with the experimentally determined values (Table III) of 0.33 and 0.87D. Given the many assumptions underlying the calculated values, the agreement is quite satisfactory.

A more serious discrepancy exists between the calculated and experimentally determined μ values for **3**, 0.76 and 0.56D, respectively. This must at least in part be ascribed to the severe skeletal distortion suffered by **3**. The enlarged C-Si-C bond angle is expected to result in a change in Si-H bond moment due to rehybridization, as previously shown for the parallel case of trimesitylphosphine, where a significant change in the partial moment of the lone pair accompanies expansion of the C-P-C bond angle.[37] In the present case, a change in Si-H bond moment from 1.0 to 0.80D would account for the whole of the observed discrepancy between calculated and found μ values.[38] According to this view, the calculated moment of **4**-exo$_0$ (and, to a lesser extent, of **4**-exo$_1$) is also likely to be overestimated in our calculation, but since the mole fraction of these conformers is negligible at equilibrium, the composite μ of **4** will not be noticeably affected by neglect of this factor.

Table IV. Dipole Moments Computed by Vectorial Summation of Partial Moments

Molecule	Conformation	μ, D
Trimesitylmethane (**3**)		0.76
Tris(*o*-tolyl)silane (**4**)	exo$_3$	0.17
	exo$_2$	0.59
	exo$_1$	0.94
	exo$_0$	1.31
Tris(*m*-tolyl)silane (**5**)	exo$_3$	0.08
	exo$_2$	0.65
	exo$_1$	1.08
	exo$_0$	1.49

Experimental Section

Materials. Triphenylsilane was purified by recrystallization from ethanol, mp 42.5–43.6 °C (lit.[39] 43–44 °C). The tritolylsilanes were prepared by reaction of the appropriate tolylmagnesium bromide with trichlorosilane. Tris(*o*-tolyl)silane, recrystallized from ethanol, had mp 88.6–89.6 °C (lit.[40] 89–90 °C); tris(*m*-tolyl)silane was twice distilled, bp 162–165 °C (0.15 mm) (lit.[41] bp 158–160 °C (0.1 mm)); tris(*p*-tolyl)silane, recrystallized from ethanol, had mp 81.6–83.1 °C (lit.[42] 82.5–83.5 °C). Trimesitylsilane, prepared by reaction of mesityllithium with trichlorosilane and recrystallized from hexane–chloroform, had mp 197.0–198.1 °C (lit.[24] 197–198 °C).

Dipole Moments. Static dielectric constants, ϵ_0, were measured at 2 MHz with a model DM-01 dipolmeter equipped with a DFL-1 cell and refractive indices were determined for the sodium D line. Dielectric constants, ϵ', and losses, ϵ'', were measured at frequencies of ca. 132, 25, and 9 GHz as previously described.[29,43] Error analyses and the experimental details of the microwave techniques have been reported.[29,43,44] The values of ϵ_0, ϵ', ϵ'', and n_D^2 were plotted against the mole fraction of solute in the solution. The slopes of the straight lines thus obtained, a_0, a', a'', and a_D, corresponding to ϵ_0, ϵ', ϵ'', and n_D^2, respectively, were fitted to Cole–cole arcs[45] in the usual fashion[46] to evaluate the critical frequencies,[47] ν_m, and the arc intercepts at infinite frequency, a_∞. Table III contains the pertinent end results derived from the microwave data. Good least-squares linear fits obtained for ϵ' and ϵ'' vs. mole fraction and excellent agreement (0.04%) of the measured ϵ' values of pure benzene with the extrapolated values indicate normal behavior on the part of the solutions examined. In addition, because the 132, 25, and 9 GHz data are so well grouped on the very-high-frequency side of ν_m, the reported a_∞ values, corresponding to the optical dielectric constant, ϵ_∞, appear to be unusually accurate. Therefore, the collective dielectric constant and loss results yielded directly and reliably the differences, $a_0 - a_\infty$, which measure the amplitudes of the respective dispersions associated with the orientation polarizations of the molecules studied. The μ values listed in Table III were calculated employing the Debye equation modified for dilute solutions. The atomic polarization values listed in Table III, as determined from the observed differences, $a_\infty - a_D$, are internally consistent and of normal magnitude.[48]

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