

Figure 1. Schematic representation of the two-ring flip mechanism for a triarylsilane, looking along the Si-H bond.

into the expected doublet ($\Delta\nu$ 23.0 Hz). The Gutowsky-Holm approximation⁶ yielded a rate constant k_c for exchange of magnetic environments of the ortho methyl groups of 50.6 sec^{-1} at the coalescence temperature (-47°).

Isomerization of triarylsilane derivatives may be interpreted in terms of an extension of the flip mechanisms postulated by Kurland, *et al.*, for triarylcation ions.^{2,7} Studies in analogous systems⁸ indicate that the two-ring flip is the stereoisomerization pathway of lowest energy. In this mechanism, two aryl rings rotate through two planes perpendicular to the reference plane defined by the three carbon atoms attached to silicon and the third ring rotates through an orientation in which the normal to the ring which passes through the carbon atom attached to silicon lies in a plane perpendicular to the reference plane and containing the C-Si bond (Figure 1). Assuming that the triarylsilanes discussed herein also isomerize by this mechanism, the rate of enantiomerization equals $3k_c$. Thus, the free energy of activation for enantiomerization of **2** by a two-ring flip mechanism is ΔG^\ddagger_{-47} 10.9 kcal/mol, as calculated from the Eyring equation.

In view of this surprisingly low value, it was decided to reinvestigate the ^1H nmr spectrum of **1**. This compound, prepared from **2** by bromination in CCl_4 followed by treatment of the resulting mixture of halides with aqueous HF in ethanol, did indeed exhibit a para methyl singlet and an ortho methyl doublet at ambient temperature, as reported.³ However, at lower temperatures, the doublet collapsed and split into an upfield singlet and a downfield doublet partially obscured by the para methyl signal. This behavior suggested that the doublets were due to long-range H-F coupling; spectra run at both 60 and 100 MHz, as well as fluorine decoupling and INDOR experiments,⁹ confirmed this suggestion. In order to facilitate line-shape analysis, the spectroscopically irritating para methyl absorption was eliminated as follows. Tris(2,6-xylyl)fluorosilane (**3**) was synthesized by a route analogous to that for **1**, and its temperature dependent ^1H nmr spectrum was measured (Figure 2). Spectra were calculated using DNMR2¹⁰ which matched the observed spectra at various temperatures, and the rates obtained were used to determine a barrier of ΔG^\ddagger_{-21} 12.1 kcal/mol for enantiomerization. Similarly, tris(2,6-xylyl)chlorosilane (**4**), prepared by treatment of the corresponding silane (**5**) with sulfuryl chloride,

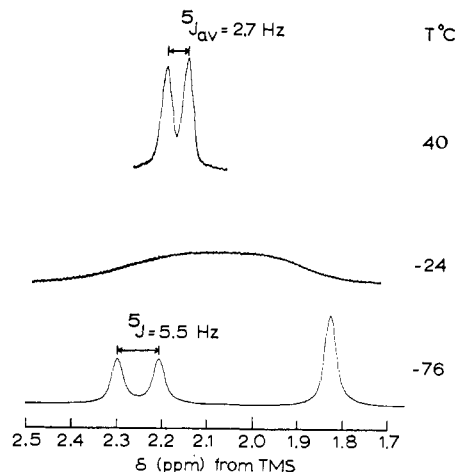


Figure 2. Temperature-dependent ^1H nmr spectrum of tris(2,6-xylyl)fluorosilane (**3**) in CS_2 solution.

exhibited a barrier of ΔG^\ddagger_{-13} 12.5 kcal/mol, as compared to ΔG^\ddagger_{-43} 11.1 kcal/mol for **5**.

It is thus clear that barriers to enantiomerization in trimesitylsilanes are much too low to permit facile resolution. This result brings into question the reported⁴ isolation of diastereomeric tetra-*o*-tolylsilanes. This question is laid to rest in the communication immediately following.¹¹

(11) M. G. Hutchings, C. A. Maryanoff, and K. Mislow, *J. Amer. Chem. Soc.*, **95**, 7158 (1973).

(12) NIH Postdoctoral Fellow, 1972-1973.

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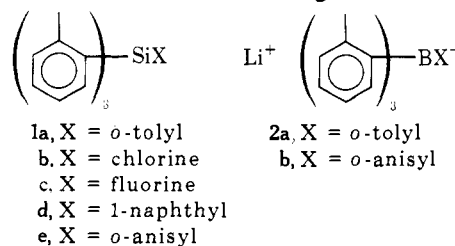
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Dynamic Stereochemistry of Tetraarylsilanes and Borate Salts

Sir:

In the preceding communication,¹ a question was raised concerning a report² claiming the isolation of different conformational stereoisomers of tetra-*o*-tolylsilane (**1a**) at ambient temperatures. We now wish to report results, part of an ongoing study of hindered rotation in tetraaryl molecules of type Ar_4Z , which have the effect of invalidating the earlier claim.²



The ^1H nmr spectrum of **1a** (mp $228\text{--}230^\circ$)³ in $\text{CDCl}_3\text{--CS}_2$ shows the methyl group as a sharp singlet

(1) R. J. Boettcher, D. Gust, and K. Mislow, *J. Amer. Chem. Soc.*, **95**, 7157 (1973).

(2) G. N. R. Smart, H. Gilman, and H. W. Otto, *J. Amer. Chem. Soc.*, **77**, 5193 (1955).

(3) Compound **1a**⁴ was prepared from *o*-tolyllithium and **1b** (3% yield), **1c** (67% yield), or tetramethoxysilane (9% yield).

(4) All compounds exhibited analytical and spectral data consistent with the given structural assignments.

(6) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(7) R. J. Kurland, I. I. Schuster, and A. K. Colter, *J. Amer. Chem. Soc.*, **87**, 2279 (1965).

(8) See ref 2 and references cited therein.

(9) We thank Mr. D. F. Hillenbrand, University of Wisconsin, Madison, Wisconsin, for performing the INDOR and corroborative ^{19}F decoupling experiments.

(10) G. Binsch, *J. Amer. Chem. Soc.*, **91**, 1304 (1969).

at δ 1.95 ($W_{1/2} = 1.4$ Hz) which broadens slightly at -113° ($W_{1/2} = 3.0$ Hz). Further cooling causes viscosity broadening and ultimate precipitation at *ca.* -125° . Since it is likely that **1a** assumes a ground-state conformation of S_4 symmetry, the methyl groups are necessarily isochronous, as found. However, substitution of a 1-naphthyl group for one of the *o*-tolyl groups (**1d**)⁵ lowers the molecular symmetry to C_s or C_1 and thus introduces the potential for anisochrony. Indeed, although the ^1H nmr spectrum of **1d** in CS_2 also displays a sharp singlet for the methyl protons at ambient temperature (δ 1.89), this signal broadens at lower temperatures and splits into two lines at δ 1.74 and 1.95 in the intensity ratio of 1:2 ($T_c = -14^\circ$, $\Delta\nu = 13.0$ Hz). Further cooling causes splitting of the more intense peak to a 1:1 doublet ($T_c = -40^\circ$, $\Delta\nu = 1.25$ Hz). Theoretical line shapes in agreement with those observed experimentally were calculated using a random exchange matrix to describe the methyl group permutations.⁶ The calculated $\Delta G^{\ddagger}_{-14}$ is 13.5 kcal/mol. Further detailed comment on the processes responsible for this dnmr behavior is deferred to a general paper on the static and dynamic stereochemistry of tetraaryl systems of type Ar_3Z .

What is the relevance of this finding to the main question of conformational mobility in **1a**? In a previous and related study on conformational dynamics in triarylborane systems,⁷ it was found that with respect to hindrance of rotation about the bond linking the aryl group to the central atom, the steric effect of the benzo substituent appears to be only slightly less than that of the *o*-methyl substituent. Accordingly, on the assumption that the ground-state conformations of **1a** and **1d** are similar, we may estimate the barrier of the former at not much above 13.5 kcal/mol, and an upper limit of *ca.* 16 kcal/mol may be placed with confidence.

Related tetraarylborate salts⁸ show parallel dnmr behavior. Compound **2a** in CD_3OD exhibits a singlet (δ 1.59) for the methyl protons down to *ca.* -55° , below which viscosity broadening becomes severe. The presumed S_4 symmetry is reduced by substitution of an *o*-anisyl group for one of the *o*-tolyl groups (**2b**). This compound in CD_3OD shows partial splitting of the *o*-methyl resonance even at ambient probe temperatures. An increase in temperature causes coalescence to a singlet (δ 1.61), whereas cooling brings about splitting to a sharp 2:1 doublet, δ 1.53 and 1.59 ($T_c = 42^\circ$, $\Delta\nu = 3.4$ Hz). The calculated ΔG^{\ddagger}_{42} is 17.7 kcal/mol.⁶ By contrast the analogous silane **1e**⁹ shows partial splitting of the C- CH_3 proton signal only at temperatures below *ca.* -80° reflecting the smaller steric effect of *o*-methoxy relative to *o*-methyl and benzo substituents.

The increase in barrier height on going from the silicon to analogous boron systems is entirely consistent

with the expected increase in steric congestion in the transition state when bonds to the central atom are shortened.¹⁰ A similar correlation between bond lengths and barriers to aryl group rotation in trimesityl compounds of group Va elements has previously been noted.¹³

Granted an upper limit of 16 kcal/mol for the rotation barrier in **1a**, the estimated half-life of a stereoisomer at 25° is no more than 0.06 sec.¹⁴ We are therefore forced to conclude that the barrier to interconversion of stereoisomers in the tetra-*o*-tolylsilane system is much too low to permit separation and isolation of stereoisomeric conformers of this compound at practicable working temperatures. In confirmation of this conclusion, all of our attempts to repeat the earlier work claiming the isolation of four, or possibly five, stereoisomers (mp 145, 228, 300, 344°; 270°)² have invariably led to a single isomer, mp 228–230°, and to no others.

It was originally stated,² without further detail, that "the aromatic groups of tetra-*o*-tolylsilane are not free to rotate about the carbon-silicon bonds and it is possible to construct no fewer than eight models of the molecule, representing four meso compounds and two racemic pairs." In an elaboration of this conclusion, Cahn, Ingold, and Prelog, on the assumption of a threefold potential for rotation about the C-Si bonds, calculated that nine isomers (three meso forms, three racemates) were possible.¹⁵ The present work voids the experimental basis for these conclusions.¹⁶

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(10) In the solid state, the relevant bond lengths have been determined as *ca.* 1.64 Å in Ph_3B^- salts¹¹ and *ca.* 1.86 Å in some phenylsilane derivatives.¹²

(11) (a) M. Di Vaira and A. Bianchi Orlandini, *J. Chem. Soc., Dalton Trans.*, 1704 (1972); (b) C. Floriani, F. Calderazzo, and L. Randaccio, *J. Chem. Soc., Chem. Commun.*, 384 (1973).

(12) (a) P. C. Chieh and J. Trotter, *J. Chem. Soc. A*, 1778 (1969); (b) C. Glidewell and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 2409 (1972).

(13) A. Rieker and H. Kessler, *Tetrahedron Lett.*, 1227 (1969).

(14) Calculated from the Eyring equation, assuming $\Delta S^\ddagger = 0$.

(15) R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, 5, 385 (1966).

(16) These considerations underscore the need for the caveat, repeatedly expressed,^{7,17} that space-filling molecular models grossly exaggerate the energy requirements for the conformational interconversion of compounds of this type.

(17) H. Kessler, A. Moosmayer, and A. Rieker, *Tetrahedron*, 25, 287 (1969).

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Optical Activity Due to Isotopic Substitution. Circular Dichroism of (1R)-[1- ^{2}H]- α -Fenchocamphoronequinone

Sir:

The successful synthesis of (1R)-2- ^{18}O - α -fenchocamphoronequinone (**I**), a molecule which owes its chirality to ^{16}O - ^{18}O asymmetry, has revealed a CD spectrum which differs markedly from the spectra of other optically active α -diketones.¹ Therefore it became of

(1) W. C. M. C. Kokke and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, 94, 7583 (1972).

(5) Compound **1d** (mp 229–230°)⁴ was prepared in 25% yield from the reaction of **1c** and 1-naphthyllithium in ether.

(6) The computer program employed was adapted from one developed by M. Saunders: see M. Saunders in "Magnetic Resonance in Biological Systems," A. Ehrenberg, B. C. Malmström, and T. Vänngård, Ed., Pergamon Press, New York, N. Y., 1967, p 85. We are grateful to Professor Saunders for providing us with a copy of his program.

(7) J. F. Blount, P. Finocchiaro, D. Gust, and K. Mislow, *J. Amer. Chem. Soc.*, 95, 7019 (1973).

(8) Prepared by adaptation of literature procedures; see G. Wittig and W. Herwig, *Chem. Ber.*, 88, 962 (1955).

(9) Compound **1e** (mp 216–217°)⁴ was prepared in 82% yield from **1c** and *o*-anisyllithium. Nmr in CS_2 : δ 1.89 (s, 9 H), 3.18 (s, 3 H).