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CONFORMATIONAL ANALYSIS

XVII*. CONFORMATIONS OF SILYL-, METHYLSILYL- AND DIMETHYLSILYLARENES

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SUMMARY

The chemical shifts of the silicon bound hydrogens of arylsilanes, methylarylsilanes and dimethylarylsilanes, where the aryl group is phenyl, 1-naphthyl and 2-naphthyl, have been determined in dilute solutions of carbon tetrachloride at 34°. The changes in the chemical shifts with respect to aryl structure increase in the series $SiH_3 < SiH_2CH_3 < SiH(CH_3)_2$. Quantitative correlations of the chemical shifts with relative anisotropic contributions of the aromatic ring are examined as a function of the molecular parameters of bond angles, bond lengths, and dihedral angles. From these correlations it is established that in solution the preferred conformation of the α-silicon is one in which a silicon–hydrogen bond is coplanar with the aromatic ring. It is suggested that d_π–p_π bonding may be responsible for the high field chemical shift of arylsilanes and vinylsilane.

INTRODUCTION

The utility of the point dipole approximation[2-4] in calculating the effect of the anisotropy of aromatic rings and its use in determining the conformation of side chains has been demonstrated[5]. It was shown that the preferred conformation of the α-carbon of ethylarenes is one in which a carbon–hydrogen bond is coplanar with the aromatic ring. In 2-naphthyl-type compounds two isoenergetic in-plane conformations in nonequivalent magnetic deshielding environments are populated whereas in 1-naphthyl-type compounds only the conformation with a carbon–hydrogen bond coplanar with the aromatic ring and *syn* to the *peri* position is populated. A similar conclusion was arrived at for the isopropylarenes of the 2-naphthyl-type structure. However, the isopropyl methine protons of 1-naphthyl-type compounds are more deshielded than predicted from the $\Sigma I \cdot R^{-3} \cdot (1-\cos^2\theta)$ function even for the in-plane conformation with the methine proton *syn* to the *peri* position. It was proposed that the deviation is due to the differential anisotropic contributions of the *peri* C–H bond**, the σ-bond contribution.

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[*] For Part XVI see ref. 1.

[**] Early workers assumed that $\Delta\chi$ for C–H was zero or negligible[6-8]. However, it has been shown to be in the same order of magnitude for $\Delta\chi$ of C–C[9-13].

In questioning the generality of the anisotropy function of aromatic rings, and the differential anisotropic contribution of the *peri* C–H bond on methine protons of 1-naphthyl-type compounds, it was decided to examine the silicon analogs of some of the compounds. Since the atomic radius of silicon is larger than that of carbon, the distance *R*, between the α-proton and the center of the ring of arylsilane compounds is greater than that of alkylarenes.

RESULTS AND DISCUSSION

The chemical shifts of the silicon bound protons of silyl, methylsilyl, and dimethylsilylarenes for the aryl groups phenyl, 2-naphthyl, and 1-naphthyl are given in Table 1. An examination of the data for the three series of compounds reveals trends similar to those observed previously for methyl-, ethyl-, and isopropylarenes. The change in the chemical shifts of protons on α-silicon caused by changes in the aryl group increases in the order silyl < methylsilyl < dimethylsilyl. In addition the changes are greatest for 1-naphthyl compounds as compared to the 2-naphthyl compounds. The trends can be qualitatively interpreted by preferred conformations in which the protons on α-silicon of the arylsilane are replaced by methyl groups in such a manner as to leave the remaining protons closer to the plane of the aromatic ring on a time average basis. Furthermore, the large change observed for the 1-naphthyl compounds suggests that the protons remaining on the α-silicon after methyl substitution reside in positions *syn* to the *peri* position of adjoining rings.

TABLE 1

CHEMICAL SHIFTS[a] OF SILANES

Compounds	*Si–H*
Phenylsilane	417
2-Naphthylsilane	430
1-Naphthylsilane	444
Phenylmethylsilane	431
2-Naphthylmethylsilane	444.5
1-Naphthylmethylsilane	465
Phenyldimethylsilane	441
2-Naphthyldimethylsilane	455
1-Naphthyldimethylsilane	485
Vinylsilane	386

[a] At 100 MHz in Hz downfield from TMS.

The correlation line relating the chemical shifts of the methylarenes and silylarenes shown in Fig. 1 has a slope of 0.85. That the slope is less than unity is consistent with the expectation that the longer bonds of the silanes would give rise to smaller changes in chemical shifts due to the anisotropy of the aromatic rings. However, quantitative calculations are necessary to ascertain whether in fact 0.85 reflects only differences in anisotropic contributions as a function of distance. The methyl reso-

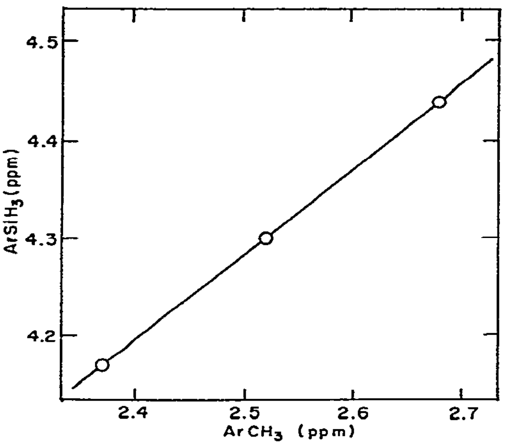
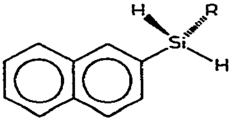


Fig. 1.

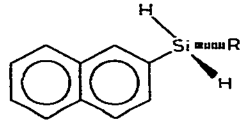
nances of substituted trimethylphenylsilanes have been shown to be smaller than the hydrocarbon analogs but detailed comparisons were not made[14].

In order to assess the conformational features of arylmethylsilanes, the computer program previously described was used[5]. While molecular dimensions of arylmethylsilane are unavailable it can be reasonably assumed that the Si–H bond lengths are not significantly different from those of alkylsilanes which are 1.48 Å[15]. The C_{ar}–Si bond length of 1.84 Å was chosen to be 0.02 Å shorter than for alkylsilanes to account for shortening expected by the increased *s* character of the bond. The bond angles chosen for C_{ar}–Si–H used are 111°, 109.4° and 108° for the silyl, methylsilyl, and dimethylsilylarenes, respectively.

Rotation of a single proton which was located in a plane containing the aromatic ring *anti* to additional aromatic rings and designated as a zero degree dihedral angle, was carried out in 15° increments and in a clockwise fashion toward the adjacent aromatic ring. The $\Sigma I \cdot R^{-3} \cdot (1-3\cos^2\theta)$ anisotropic function was determined for the proton and averaged with the functions for the other protons attached on the α-silicon but located at other dihedral angles dictated by molecular geometry to obtain an output corresponding to a time average value of all protons which could interchange positions to yield the identical conformation. Since the program only gave families of values for single conformations at specific dihedral angles it was necessary to consider isoenergetic conformers of nonequal magnetic contributions which when mixed by a time averaging process would give an average $\Sigma I \cdot R^{-3} \cdot (1-3\cos^2\theta)$ term. For example, the two conformations of 2-naphthylsilane designated (Ia) and (IIa) should be of nearly equal energy and their $\Sigma I \cdot R^{-3} \cdot (1-3$



(Ia) R=H
(Ib) R=CH_3



(IIa) R=H
(IIb) R=CH_3

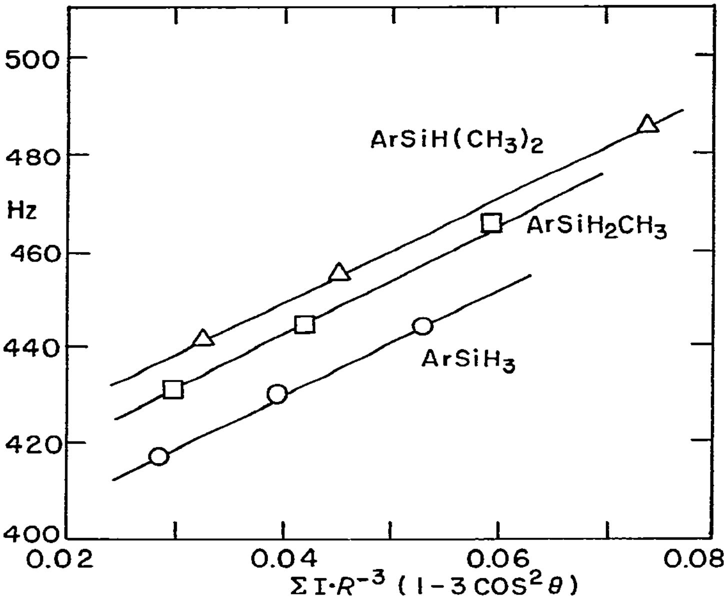
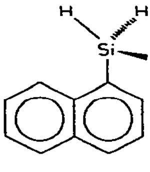


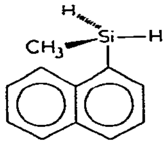
Fig. 2.

$\cos^2\theta$) terms which in turn are composites of a time average of the three consituent protons, must be averaged. Therefore, two in-plane conformations for the 2-naphthyl compound were averaged. Although it is less clear a priori that the same should be done for the 1-naphthyl compound, the resulting value fits well with the phenyl and 2-naphthyl values as was observed as well in the alkylarenes. Independent of the dihedral angle the correlation lines for mixtures of isoenergetic conformers such as outlined above for C–Si–H angle of 111° were identical. The identity of correlation lines independent of the conformation is a result of the symmetry of the SiH_3 group. Since phenylsilane like toluene possesses a six fold rotational barrier which is expected to be small[16], the assignment of a preferred conformation is not meaningful in the context of this study. The slope of 11.0 (Fig. 2) must represent the relationship of the relative anisotropic contributions of the aromatic rings and must be duplicated for all other ring substituents containing Si–H bonds in less symmetric structures if the correct conformation is chosen. The correlation line depicted in Fig. 2 is given by eqn. (1), with $r = 0.9997$.

$$\delta(\text{ppm}) = 11.0\,\Sigma[\text{I}\cdot R^{-3}\cdot(1-3\cos^2\theta)] + 3.86 \tag{1}$$

As in the case of the analogous ethylbenzene a three fold barrier of some magnitude would be expected for methylphenylsilane. As a consequence conformational analysis is possible. As expected by the changed symmetry, the protons on α-silicon of arylmethylsilanes experience marked differing anisotropic contributions as a function of dihedral angle. The correlation lines have the best correlation coefficients and the lowest slope (Fig. 2) for the conformations in which one Si–H bond is coplanar with the aromatic ring. In the case of 2-naphthyl compounds the two in-plane conformations depicted by (Ib) and (IIb) are considered isoenergetic and their functions averaged. The individual functions for conformations (Ib) and (IIb) are an average of the two protons on α-silicon as they can be interchanged to magnetically equivalent positions by 120° rotations. In the case of the 1-naphthyl compound the two conformations (III) and (IV) are certainly not isoenergetic and in fact are associated with dramatically different anisotropic functions. While a small population of (IV) can be tolerated within the limitations of the experimental error, progressively increasing the population of (IV) and similar conformers in other compounds decreases the correlation coefficients and increases the slope over that of the standard established for arylsilanes. The correlation line depicted in Fig. 2 is given by eqn. (2) with $r = 0.9999$.


(III)


(IV)

$$\delta(\text{ppm}) = 11.4\,\Sigma[\text{I}\cdot R^{-3}\cdot(1-3\cos^2\theta)] + 3.97 \tag{2}$$

The protons on α-silicon of aryldimethylsilanes experience dramatically different anisotropic contributions to their chemical shift as a function of dihedral angle. The correlation line in Fig. 2 is for conformations in which the Si–H bond is coplanar with the aromatic ring. In the case of the 2-naphthyl compound the two in-plane conformations are considered isoenergetic and their anisotropy functions are averaged. In the case of the 1-naphthyl compound the conformation with the Si–H bond *syn* to the *peri* hydrogen gave reasonable values. A correlation line is shown in Fig. 2 and is given by eqn. (3) with $r = 0.9997$.

$$\delta(\text{ppm}) = 10.6\,\Sigma[\text{I}\cdot R^{-3}\cdot(1-3\cos^2\theta)] + 4.06 \tag{3}$$

The slopes of the correlation lines for the three series of compounds are not in as close agreement as for the slopes for the alkylarenes. However, only three compounds in each series were prepared whereas in the alkylarenes eight compounds in each series were prepared. Therefore, the average slope for the silicon compounds may be taken as 11.0. This value is somewhat larger than the 9.2 observed for alkylarenes but the ring current model accounts in major part for the effect of aryl groups on the chemical shifts of the silicon compounds.

A feature of the correlation line of the arylsilanes which at first appears unusual is the intercept of 3.86 ppm. In the case of the methylarenes, the intercept of the correlation line is close to the chemical shift of the methyl resonance of propene which is an excellent model for the predicted chemical shift in the absence of anisotropic contributions due to ring currents. A direct determination of the silyl resonance of vinylsilane (Table 1) gives a value of 386 Hz which is equal to that of the intercept. The methyl resonance of propene is deshielded with respect to ethane due to the anisotropy of the vinyl group by approximately 1.3 ppm. Thus the intercept for the arylsilanes would be expected to be equal to that of vinylsilane. The chemical shift of vinylsilane should be at lower field than methylsilane (3.66 ppm) by a smaller amount than that observed for the carbon analogs due to increased bond distances. A deshielding of approximately 0.8 ppm appears qualitatively reasonable. The net deshielding of the hydrogen attached to silicon caused by the vinyl group is only 20 Hz instead of a predicted 80 Hz. An upfield shift due to d_π–p_π bonding of approximately 60 Hz may account for this difference.

If d_π–p_π bonding effects are being observed in the compounds studied, different contributions of the vinyl and various aryl groups could account for the larger slope of 11.0 over that of 9.2. The order of decreasing contributions of d_π–p_π bonding would have to be vinyl > phenyl > 2-naphthyl > 1-naphthyl. If the chemical shift contribution caused by such bonding with the vinyl group is approximately 60 Hz then that due to the phenyl group would have to be only 54 Hz. Similarly, the upfield shifts due to d_π–p_π bonding of 2-naphthyl and 1-naphthyl would have to be only 53 Hz and 52 Hz respectively. If the estimated contribution of d_π–p_π bonding to the chemical shift of vinylsilane is changed to a different value then those of the aryl groups would have to be changed proportionately. In any case although all groups attached to silicon cause shifts to high field, the differential effects of d_π–p_π bonding are small.

Due to the symmetry and number of *d* orbitals of silicon the effectiveness of d_π–p_π overlap should be independent of conformation. Therefore, the slope of 11.0 observed for the arylsilanes which is a reflection of both conformationally independent anisotropic contributions of the aryl groups and any differential d_π–p_π contribution should serve as a reference slope for the arylmethylsilanes and aryldimethylsilanes. As shown by the correlation lines of Fig. 2, the slope may be approximated for those conformations containing an in-plane silicon–hydrogen bond. Rotation about the arylsilicon bond yields conformations whose correlation lines have larger slopes than that of the reference. Therefore, the conformational features of silicon compounds parallel those of alkylarenes.

The effect of hyperconjugation of a Si–H bond on the ultraviolet spectra of arylsilanes has been discussed[17]. The hyperconjugative effect is not displayed when hydrogens of SiH_3 are replaced by methyl. This result is consistent with this work in which the Si–H bonds are found to be in unfavorable positions for hyperconjugative interaction when methyl groups are present.

In the previous work on the alkylarenes it was suggested that a σ-bond contribution of the *peri* position gave rise to the observed deviations from the correlation lines for the methine proton of isopropylarenes of the 1-naphthyl-type structure. As was suggested, the longer bonds of the silanes should diminish this effect and indeed there are no deviations from the correlation line.

EXPERIMENTAL

All of the compounds examined in this work were prepared by addition at 0° of the appropriate aryllithium reagent to the appropriate silicon compound given by $Si(CH_3)_n(OCH_3)_{4-n}$ followed by reduction with lithium aluminum hydride.

The boiling point, chemical shift of the methyl resonance in τ units, and the mass of the parent ion are given in Table 2. The values in parentheses are the literature reported boiling points and the calculated mass of the parent ion.

The NMR samples were prepared by dissolving 5×10^{-4} mole of the com-

TABLE 2

	B.p. (°C/mm)		$\tau(CH_3)$	*m/e*	
$C_6H_5SiH_3$	71/170	(120/760)[a]			
$C_6H_5SiH_2CH_3$	140/760	(140/760)[b]	9.62 (t)		
$C_6H_5SiH(CH_3)_2$	30/4	(157/744)[c]	9.70 (d)		
$1\text{-}C_{10}H_7SiH_3$	70/0.3	(49.5/0.025)[d]		158.0550	(158.0552)
$1\text{-}C_{10}H_7SiH_2CH_3$	65/0.3		9.52 (t)	172.0705	(172.0708)
$1\text{-}C_{10}H_7SiH(CH_3)_2$	90/0.4		9.54 (d)	186.0863	(186.0865)
$2\text{-}C_{10}H_7SiH_3$	69/0.3			158.0554	(158.0552)
$2\text{-}C_{10}H_7SiH_2CH_3$	75/0.4		9.57 (t)	172.0706	(172.0708)
$2\text{-}C_{10}H_7SiH(CH_3)_2$	74/0.15		9.62 (d)	186.0863	(186.0865)

[a] See ref. 18. [b] See ref. 19. [c] See ref. 20. [d] See ref. 21.

pounds in 1 ml of a solution containing 10% by volume of cyclohexane and 90% carbon tetrachloride. The chemical shifts at 34° were determined relative to the cyclohexane lock signal at 142 Hz using a Varian Associates 100 MHz instrument.

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REFERENCES

1 R. J. Ouellette, J. D. Rawn and S. N. Jreissaty, *J. Amer. Chem. Soc.*, 93 (1971) 7117.
2 J. A. Pople, W. G. Schneider and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance*, McGraw-Hill Book Co., New York, 1959, p. 251.
3 J. W. Emsley, J. Feeney and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Vol. 1, Pergamon Press, London, 1965, p. 142.
4 H. M. McConnell, *J. Chem. Phys.*, 27 (1957) 226.
5 R. J. Ouellette, B. K. Sinha, J. Stolfo, C. Levin and S. H. Williams, *J. Amer. Chem. Soc.*, 92 (1970) 7145.
6 A. A. Bothner-By and C. Naar-Colin, *Ann. N.Y. Acad. Sci.*, 70 (1958) 833.
7 J. I. Musher, *J. Chem. Phys.*, 35 (1961) 1159.
8 A. G. Moritz and N. Sheppard, *Mol. Phys.*, 5 (1962) 361.
9 A. D. Buckingham, W. H. Prichard and D. W. Whiffen, *Chem. Commun.*, (1965) 51.
10 J. Guy and J. Tillier, *J. Chem. Phys.*, 24 (1956) 1117.
11 J. A. Pople, *Discuss. Faraday Soc.*, 34 (1962) 68.
12 D. W. Davies, *Mol. Phys.*, 6 (1963) 489.
13 R. F. Zurcher, *Helv. Chim. Acta*, 44 (1961) 1755.
14 J. F. Jaggard and A. Pidcock, *J. Organometal. Chem.*, 16 (1969) 324.
15 L. Pierce and D. H. Peterson, *J. Chem. Phys.*, 33 (1960) 907.
16 J. W. Fleming and C. N. Banwell, *J. Mol. Spectrosc.*, 31 (1969) 318.
17 J. Nagy and J. Reffy, *Period. Polytech. Chem. Eng. (Budapest)*, 12 (1969) 373.
18 A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 69 (1947) 2692.
19 L. I. Zakharkin, *Izv. Akad. Nauk SSSR*, (1960) 2244.
20 R. A. Benkeser and D. J. Foster, *J. Amer. Chem. Soc.*, 74 (1952) 5314.
21 H. E. Opitz, J. S. Peake and W. H. Nebergall, *J. Amer. Chem. Soc.*, 78 (1956) 292.