ton–proton coupling constants suggest that the five-membered ring exists in a twist–envelope conformation with an OCCO dihedral angle of ~30° and that the preferred conformation is the one in which the group on carbon and the group on phosphorus are as far apart as possible. Calculations[31] based on equations similar to that given in ref 30 indicate that the populations of conformers like A in I and IV are 87 and 90%, respectively. In molecules with groups anti to the substituent on phosphorus (III and the propylene phosphites), the phosphorus–proton and proton–proton coupling constants suggest that the energy difference between the various conformers resulting from pseudorotation of five-membered ring is much smaller than in the anti isomers and the preference for one conformation is not as large as in the case of the anti isomers. This allows a consistent explanation for all nmr data on five-membered ring phosphites (Table IV). In each case where there is a group syn to the group on phosphorus, the data are consistent with the twist-envelope conformation with a preference for conformations like **3A** whereas the data for the examples with groups anti to the group on phosphorus are consistent with a more equal population of conformers like **3A** and **3B**. Not only does this allow a consistent explanation for all the five-membered phosphites, but this is also consistent with the recent data for six-membered ring phosphites,[9] 1,3-dioxalanes,[32] 1,3-oxathiolanes,[33] and ethylene sulfites.[15]

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[31] Values of POCH coupling constants at dihedral angles of 170 and 90° were taken to be 16.0 and 0.5 Hz, respectively.[10] If values other than these are used, slightly different values of *p* will be obtained.

[32] W. E. Willy, G. Binsch, and E. L. Eliel, *J. Amer. Chem. Soc.*, **92**, 5394 (1970), and references therein.

[33] G. E. Wilson, Jr., M. G. Huang, and F. A. Bovey, *ibid.*, **92**, 5907 (1970).

Stereochemistry of Asymmetric Silicon. XXI. Optical Rotary Dispersion and Circular Dichroism of Asymmetric Disilanes Ph$_3$SiSi*X(Ph)(Me) and a Case of Aberrant Cotton Effect Behavior[1,2]

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Abstract: Ultraviolet (uv), optical rotatory dispersion (ORD), and circular dichroism (CD) spectra are reported for eight optically active Ph$_3$SiSi*X(Ph)(Me) compounds in which X = H, F, OH, OCH$_3$, Cl, Br, and (−)-OMen. The uv spectrum of each of these compounds displays a primary absorption maximum in the wavelength range 236–242 nm which is attributable to the chromophoric Ph–Si–Si grouping. The corresponding ORD and CD spectra give sizable Cotton effects in the vicinity of this absorption maximum and are considered to be closely associated with it. These interesting Cotton effects are discussed with respect to the assigned relative configurations of the compounds. This reveals that one of the compounds (X = H) displays striking aberrant Cotton effect sign behavior relative to the collective and internally consistent Cotton effect sign behavior of all of the other compounds. This aberration provides a clear example of the extraordinary sensitivity of ORD and CD spectra to subtle structural changes and advises only circumspect use of such spectra for configurational assignments of Ph$_3$SiSi*X(Ph)(Me) and similar structures.

A previous paper[3] in this series reported the preparation of a family of optically active 1,2,2,2-tetraphenyl-1-methyldisilanes, Ph$_3$SiSi*X(Ph)(Me), which permitted study of the dynamic stereochemistry of a silicon center bonded to a second silicon atom.[3] For optically active Pb$_3$SiSi*X(Ph)(Me) structures in which X = H, F, OH, OCH$_3$, Cl, Br, and (−)-OMen, firm assignments of relative configuration were achieved[3] by means of stereochemical principles and reasoning based on the known stereochemical behavior of monosilicon centers.[4] These studies revealed that for a wide variety of substitution reactions the dynamic stereochemistry of the asymmetric disilicon center is identical with that of monosilicon centers.

Concurrent with our interest in the stereochemistry of disilanes, there has developed an interest on the part of other investigators in the electronic nature of the silicon–silicon bond.[5] Work on compounds containing silicon–silicon bonds has led to the conclusion that such bonds have conjugating properties and are capable of giving absorption in the ultraviolet.[5] In the case of phenyl-substituted disilanes, Hague and Prince[6] were able to show that the Ph–Si–Si grouping is responsible for the intense uv absorption of such compounds near 245 nm. Simple Hückel MO treatment of the uv absorption spectra of phenyl- and vinyl-substituted polysilanes indicates that the data can best be accommodated

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[1] For the preceding paper in this series, see L. H. Sommer, L. Arlie Ulland, and G. A. Parker, *J. Amer. Chem. Soc.*, **94**, 3469 (1972).

[2] We are grateful to the National Science Foundation for support of this work.

[3] L. H. Sommer and K. T. Rosborough, *J. Amer. Chem. Soc.*, **91**, 7067 (1969).

[4] L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965.

[5] For reviews, see H. Gilman, W. H. Atwell, and F. K. Cartledge, *Advan. Organometal. Chem.*, 4, 1 (1966); M. Kumada and K. Tamav, *ibid.*, 6, 19 (1968).

[6] D. N. Hague and R. H. Prince, *J. Chem. Soc.*, 4690 (1965).

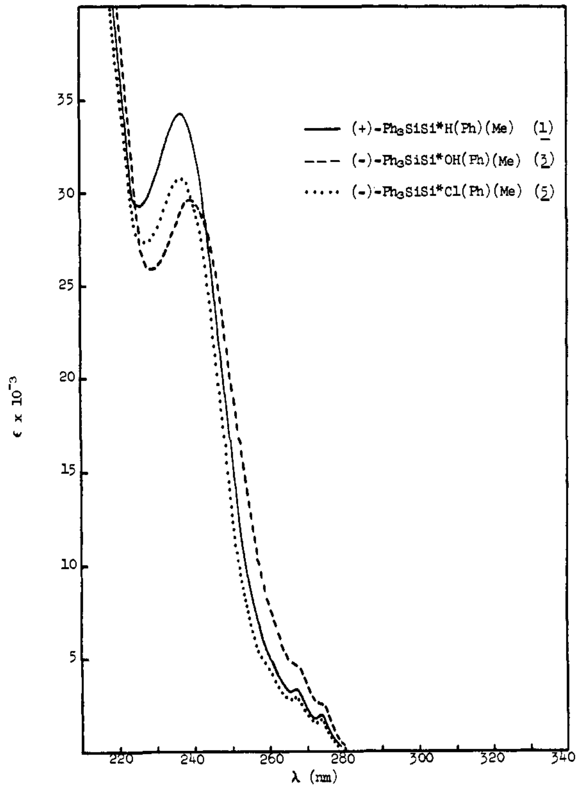

Figure 1. Ultraviolet absorption spectra of compounds **1**, **3**, and **5** (in pentane).

Table I. Ultraviolet Absorption of $Ph_3SiSi^*X(Ph)(Me)$ Compounds[a]

$Ph_3SiSi^*X(Ph)(Me)$[b]	Compd[c]	Absorption characteristics[d]
(+)-SiSi*H	**1**	*274* (1900), *266* (3300), *236* (34,200)
(−)-SiSi*F	**2**	*274* (1850), *267* (3000), *236* (31,000)
(−)-SiSi*OH	**3**	273 (2500), 266 (4800), *239* (29,500)
(−)-SiSi*OCH_3	**4**	273 (2500), 266 (4600), *239* (31,000)
(−)-SiSi*Cl	**5**	*274* (1800), *267* (2900), *236* (30,800)
(−)-SiSi*Br	**6**	272 (1900), 265 (3100), 236 (20,900)
(−)-SiSi*O(−)-Men[e]	**7**	274 (2800), 266 (5400), *240* (23,600)
(+)-SiSi*O(−)-Men	**8**	274 (2700), 266 (5200), *242* (22,700)

[a] Purified pentane solvent was used for all cases and, for a 1-mm path length, sample concentrations ranged from *ca.* 10^{-2} to 10^{-4} *M*. [b] All of the compounds have been reported previously (ref 3). The spectra of the optically pure enantiomers of compounds **1**, **5**, and **6** were determined and the data reported herein for **1**, **5**, and **6** are derived from those spectra. The ORD and CD spectra reported for compounds **1**, **5**, and **6** are, in a mirror image fashion, signed opposite to the observed spectra of their respective enantiomers. This is done for convenience in presentation and discussion. [c] Compound numbers herein assigned for reference in the discussion. [d] Wavelengths are in nm; molecular absorptivities (ϵ) are in parentheses; maxima are in italics while other values refer to shoulders; the first two spectral features listed refer to the secondary absorption bands while the last feature listed refers to the primary absorption band. [e] Minimum diasteromeric purity 77%.

using a mixture of silicon orbitals (possibly, but not necessarily, d orbitals) and an unoccupied orbital (π^*) of the phenyl or vinyl group as the excited state.[7]

The above-mentioned interesting aspects of the silicon–silicon bond together with our continuing interest in the Cotton effect behavior and structural stereochemistry of asymmetric silicon compounds have led us to investigate the optical rotatory dispersion (ORD) and circular dichroism (CD) of the asymmetric disilanes $Ph_3SiSi^*X(Ph(Me)$ studied in our previous work. Our particular objectives were to determine whether the chromophoric Ph–Si–Si grouping present in these structures is optically active, and, if so, to determine the extent to which the attendant Cotton effects provide data useful for assignments of relative configuration. This latter goal was desired because our earlier ORD and CD studies on optically active monosilanes indicated the very great sensitivity of ORD and CD spectra to relatively minor structural changes in a series of closely related asymmetric silicon compounds, and thereby advised the use of considerable caution in the use of such spectra for configurational assignments.[8]

In this paper we report the results of our ORD and CD studies on optically active disilanes, which include (1) data for ultraviolet Cotton effects which are attributable to the conjugated Ph–Si–Si chromophore, and (2) disclosure of a case of aberrant Cotton effect behavior within a family of closely related molecules $Ph_3SiSi^*X(Ph)(Me)$.

Presentation and Discussion of Spectra. Table I assigns reference numbers to the optically active $Ph_3SiSi^*X(Ph)(Me)$ compounds studied and reports the uv absorption properties of these compounds. Figure 1 presents the absorption spectra which were obtained for three of the compounds (X = H, OH, and Cl) and which are typical of $Ph_3SiSi^*X(Ph)(Me)$ absorption spectra in general. Examination of these spectra indicates that while variance of X in $Ph_3SiSi^*X(Ph)(Me)$ causes some changes in λ_{max} and ϵ values, these changes are relatively minor and that all of the spectra include (a) two relatively weak absorbances (maxima or shoulders), one in the range 272–274 nm (ϵ 1800–2800) followed by the other in the range 265–267 nm (ϵ 2900–5400), *which herein will be referred to as the secondary bands;* (b) subsequently at shorter wavelength, an intense absorption maximum (except for **6** which displays a shoulder) in the range 236–242 nm (ϵ 20,900–34,200) *which herein will be referred to as the primary band;* and (c) at still shorter wavelengths, a steep rise in the absorption below *ca.* 220 nm.

Comparison of the uv absorption characteristics of $Ph_3SiSi^*X(Ph)(Me)$ compounds in Table I with those previously reported for other phenyl-substituted disilanes, *e.g.*, for $Ph_3SiSiPhMe_3$[5] and $Ph_3SiSiPh_3$,[6] shows a great overall similarity. On the basis of similar structures and similar absorption characteristics, it is logical to attribute the uv absorption bands of the $PhSiSi^*X(Ph)(Me)$ compounds to the same chromophores as those responsible for the analogous absorption bands of the closely allied model phenyl-substituted disilanes. Therefore, based on the conclusions of Hague and Prince,[6] we attribute the primary absorption bands of the $Ph_3SiSi^*X(Ph)(Me)$ spectra to the chromophoric Ph–Si–Si group. Additionally, and as suggested by Hague and Prince,[6] we consider the secondary absorption bands of the $Ph_3SiSi^*X(Ph)(Me)$ spectra to be benzenoid (^1L_B) in orgin.

Observation of the intense absorption maximum attributable to the Ph–Si–Si grouping in Ph_3SiSi^*X-(Ph)(Me), plus incorporation of an asymmetric silicon atom in that grouping, would, on the basis of a potential inherently dissymmetric chromophore, predict sizable attendant Cotton effects in the ORD and CD

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(7) C. Pitt, L. L. Jones, and B. G. Ramsey, *J. Amer. Chem. Soc.*, **89**, 5471 (1967).

(8) L. H. Sommer and J. McLick, *ibid.*, **91**, 2001 (1969).

Table II. Optical Rotatory Dispersion Properties of Asymmetric Disilanes[a]

Figure	Compd	$c \times 10^3$	$[\phi]_{300}$[b]	Dispersion characteristics[c]								
2	**1**[d]	1250–9.75	+1220	275 pk (+3,900)	273 tr (+3,140)	268 pk (+4,380)	276 tr (+3,750)	253 pk (+6,400)	247 (0)	234 tr (−32,400)		215 (−4,000)
2	**2**	2000–20.0	−1700	275 tr (−7,180)	273 pk (−6,860)	268 tr (−9,330)	267 pk (−8,970)	254 tr (−15,300)	247 (0)	236 pk (+53,500)		227 (+33,700)
2	**3**	2000–6.25	−1940		273 sh (−8500)			262 tr (−11,800)	251 (0)	237 pk (+37,700)		223 (+13,000)
3	**4**	1150–7.20	−2340		273 sh (−8300)		267 sh (−9700)	262 tr (−11,400)	249 (0)	233 pk (+43,800)		220 (+27,000)
3	**5**[d]	1000–7.80	−1070		274 sh (−3240)		268 sh (−5100)	252 tr (−13,400)	244 (0)	232 pk (+35,200)		215 (+1000)
	6[d]	1140–17.8	−650				267 sh (−2900)	253 tr (−8,000)	246 (0)	235 pk (+11,600)	225 (0)	225 (0)
	7[e]	4045–8.00	−4300	276 tr (−13,900)	274 pk (−13,500)	269 tr (15,600)	276 pk (−14,800)	261 tr (−17,200)	251 (0)	230 pk (+66,000)	218 (0)	215 (−24,000)
	8	5000–6.25	+5400	276 pk (+26,900)	274 tr (+25,200)	270 pk (+31,300	266 tr (+29,100)	260 pk (+36,200)	251 (0)	230 tr (−176,000)	218 (0)	216 (+58,000)

[a] All data were obtained in pentane solvent. The range of concentrations c (in g/100 ml) is given. [b] For all compounds at wavelengths longer than 300 nm the dispersion curve is plain with rotations decreasing in magnitude on going to 700 nm; in no case is the zero rotation axis crossed by the plain curve. [c] Wavelengths in nm; molecular rotations (ϕ) in parentheses. Abbreviations: peak (pk), trough (tr), shoulder (sh). The last value listed is the last reliable reading. [d] Footnote *b*, Table I. [e] Footnote *e*, Table I.

spectra. Sizable Cotton effects are in fact observed, and the present work comprises the first ORD and CD study of a chromophore containing a metaloid–metaloid bond.

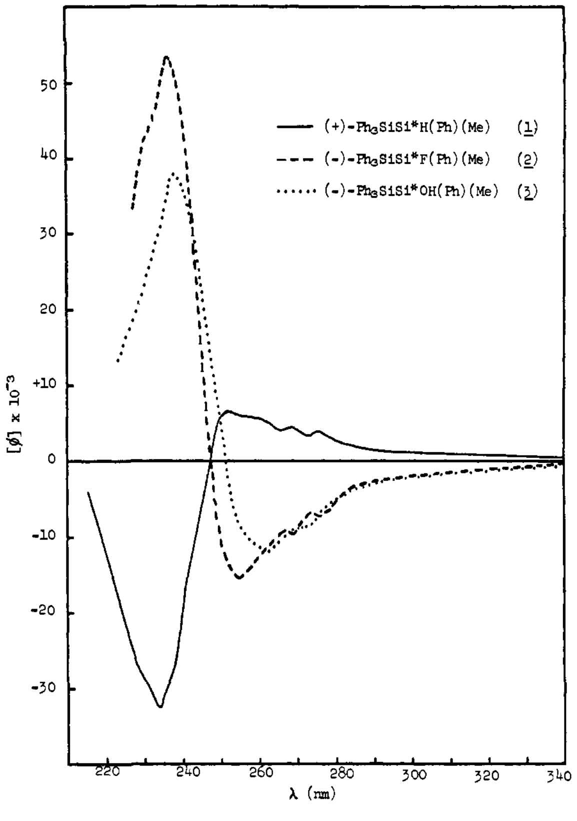

Figure 2. Optical rotatory dispersion curves of **1**, **2**, and **3**. These compounds have been assigned the same configuration based on previous stereochemical data.

Since it happens that all of the compounds studied display rather similar overall ORD and CD spectral properties other than for signs of optical rotation and ellipticity, it is convenient to first discuss the spectra collectively without respect to sign. A subsequent section will then discuss the spectra with respect to sign.

The important ORD spectral data for optically active disilanes **1**–**8** are given in Table II while Figures 2 and 3 present the ORD curves for six of the compounds.[9] It is observed that from 700 nm down to 280 nm all of the compounds display plain dispersion curves. Below

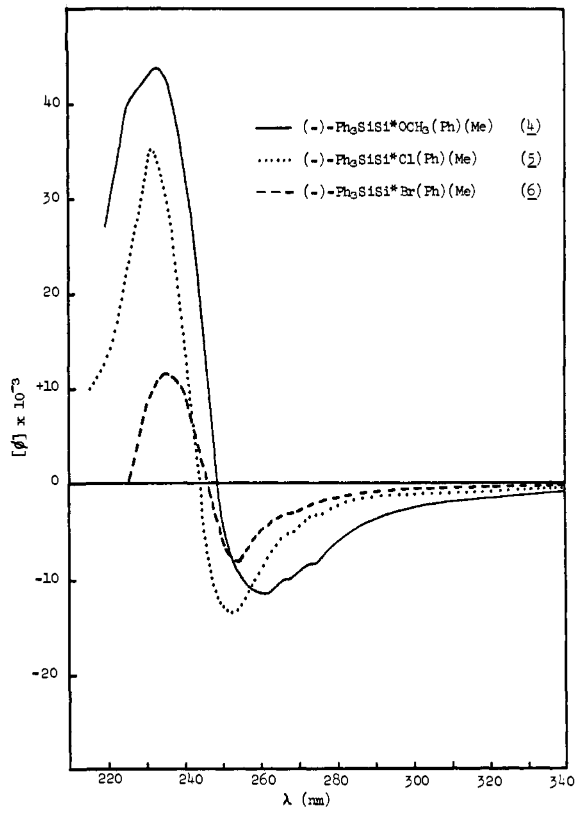

Figure 3. Optical rotatory dispersion curves of **4**, **5**, and **6**. These compounds have been assigned the same configuration based on previous stereochemical data.

(9) The ORD (and CD) spectra obtained for 7 and 8 are not included in figures in this paper for economy of presentation.

Table III. Circular Dichroism Properties of Asymmetric Disilanes

Figure	Compd.	CD characteristics[a]						
4	**1**[b]	274 max (+1730)	272 min (+660)	267 max (+2560)	265 min (+1730)	244 max (+25,800)	235 (0)	*c*
4	**2**	273 max (−1350)	272 min (−1080)		266 sh (−2560)	244 max (−25,000)	234 (0)	*c*
4	**3**	273 sh? (−2000)				249 max (−32,000)	238 (0)	230 max[d] (+11,800)
5	**4**	273 sh (−3180)		266 sh (−6800)		245 max (−30,000)	235 (0)	*c*
5	**5**[b]	275 max (−1130)	273 min (−730)	268 max (−2150)	266 min (−1810)	244 max (−25,400)	233 (0)	*c*
5	**6**[b]	274 sh? (−650)				246 max (−14,500)	235 (0)	*c*
	7[e]	274 sh (−5900)		266 sh (−18,000)		249 max (−44,700)	237 (0)	220 max[f] (+63,000)
	8	274 sh (+18,300)		266 sh (+32,400)		248 max (+104,000)	234 (0)	220 max[g] (−148,000)

[a] Data were obtained in pentane with concentrations given in Table II. Wavelengths are in nm; molecular ellipticites (θ) are in parentheses. Abbreviations: maximum (max), minimum (min), and shoulder (sh). The last value given is the last reliable reading. [b] Footnote *b*, Table I. [c] At wavelengths immediately shorter than that of the zero ellipticity listed in the table, nonzero ellipticity was detected and observed to be opposite in sign to the first primary CD maximum. However, the data were only of qualitative significance. [d] Also 223 (0). [e] Footnote *e*, Table I. [f] Also 215 (+38,000). [g] Also 215 (−88,000).

Table IV. Summary of Primary Cotton Effect Data[a]

Compd	ORD Cotton effect midpoint[b] nm	ORD Cotton effect midpoint[b] Amplitude × 10^{-3}	CD Cotton effect maximum[c] nm	CD Cotton effect maximum[c] $[\theta] \times 10^{-3}$	Uv absorption[d] nm	Uv absorption[d] $\epsilon \times 10^{-3}$
1	244	38.8	244	+25.8	*236*	34.2
2	245	68.8	244	−25.0	*236*	31.0
3	250	49.5	249	−32.0	*239*	29.5
4	248	55.2	245	−30.0	*239*	31.0
5	242	48.6	244	−25.4	*236*	30.8
6	244	19.6	246	−14.5	236	20.9
7	246	83.2	249	−44.7	*240*	23.6
8	245	212	248	−104	*242*	22.7

[a] The data refer to the first primary Cotton effects. [b] From data in Table II. [c] Data from Table III. [d] Data from Table I.

280 nm, two weak ORD Cotton effects are, successively, superimposed upon the rising (in magnitude) plain curves in the wavelength regions 273–276 and 266–270 nm. The locations of these weak Cotton effects suggest that they are associated with the secondary uv absorption bands described above. These secondary Cotton effects are clearly discernable only in the spectra of **1**, **2**, **7**, and **8**, while in the spectra of the other compounds they give rise to shoulders in the background dispersion curves. More importantly, at still shorter wavelengths the ORD curves of all the compounds give large Cotton effects in the vicinity of the primary absorption. For each of the compounds this Cotton effect is denoted the primary ORD Cotton effect. The first extremum of this Cotton effect occurs in the range 252–262 nm, the zero rotation crossing point occurs in the range 244–251 nm, and the second extremum (which is *ca.* two–four times the magnitude of the first for most of the compounds) occurs in the range 230–237 nm. In each of the ORD spectra the long wavelength plain dispersion curve is seen to be a tailing off of the first extremum of the primary ORD Cotton effect.

The important CD data obtained for the optically active disilanes **1**–**8** are given in Table III, while Figures 4 and 5 present the six CD curves corresponding to the six ORD curves included in Figures 2 and 3. At wavelengths longer than *ca.* 300 nm, the molecular ellipticity of the compounds is essentially zero. Below 300 nm, the ellipticity increases in a plain fashion, and below 280 nm two very weak CD Cotton effects occur in the wavelength regions 272–275 and 265–268 nm. These are clearly discerned only in the spectra of **1**, **2**, and **5**, while in the spectra of the other compounds they cause shoulders in the rising (in magnitude) background curves. The locations of these CD Cotton effects indicate that they are associated with the secondary uv bands and correspond to the weak secondary ORD Cotton effects described above. Due to their lack of clarity, these secondary ORD and CD Cotton effects seem to be of little value for configurational purposes. However, on proceeding to wavelengths below those of the secondary Cotton effects, the CD curve of each compound gives a large Cotton effect with the ellipticity maximum in the wavelength range 244–249 nm. This Cotton effect has the same sign as, and a magnitude similar to, the corresponding primary ORD Cotton effect which it complements, and it is denoted the *first* primary Cotton effect. Denotation as such is necessary because it appears to be normally followed by an adjacent *second* CD Cotton effect at shorter wavelength having the opposite sign. Such second primary CD Cotton effects are directly observed in the spectra of **3**, **7**, and **8**, while they may be inferred from the CD data obtained for the other compounds. For these latter compounds, second CD maxima were not observable because of unfavorable $[\theta]/\epsilon$ ratios, but qualitative data indicating nonzero ellipicity were obtained. For **3** (and apparently for these other cases), the second primary CD Cotton effect is rather less intense than the first primary CD Cotton effect. In the case of **7** and **8**,

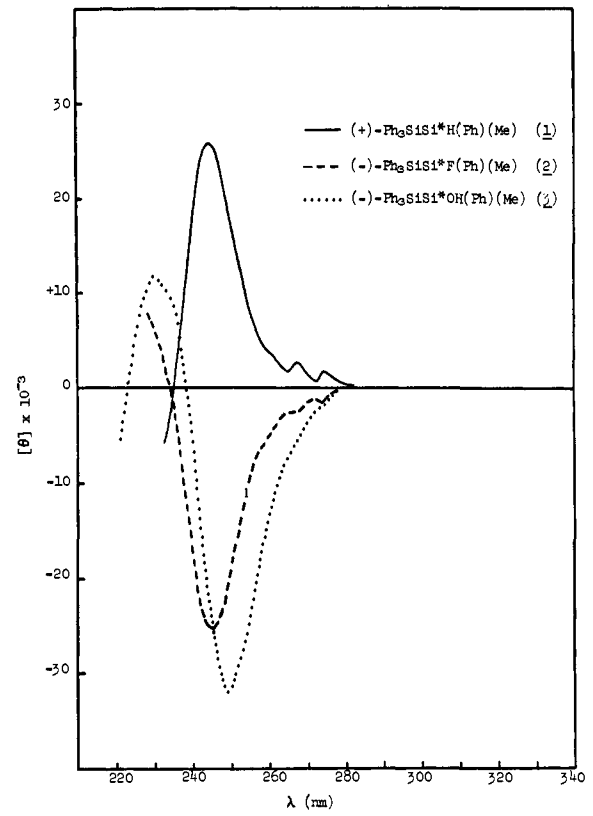

Figure 4. Circular dichroism curves of **1**, **2**, and **3**. These compounds have been assigned the same configuration based on previous stereochemical data.

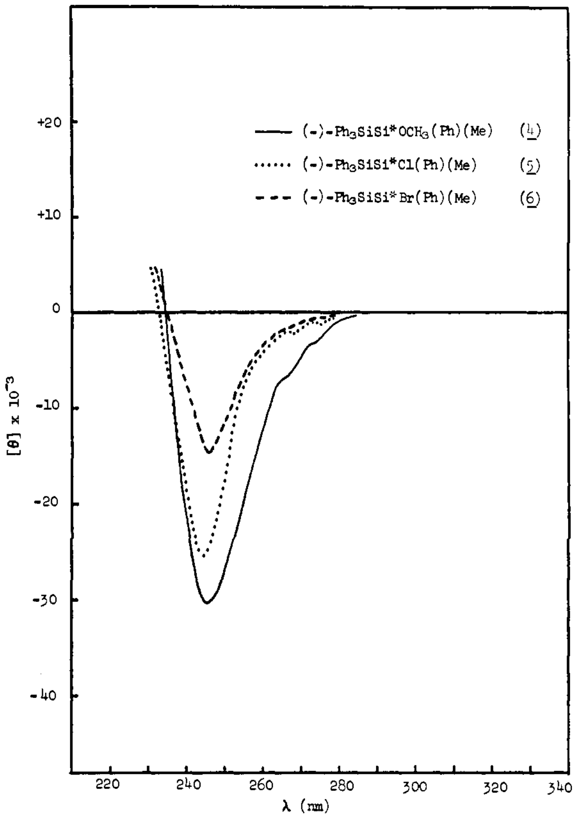

Figure 5. Circular dichroism curves of **4**, **5**, and **6**. These compounds have been assigned the same configuration based on previous stereochemical data.

the reverse is true, namely the second primary CD Cotton effects are more intense than the first.

For purposes of comparison, a summary of the primary ORD and CD Cotton effect data and of the primary uv absorption data are given in Table IV. Based on the overall parallelism in intensities between the CD and absorption curves, *i.e.*, the occurrence of two weak secondary (benzenoid) maxima superimposed in a rising curve leading to greatly more intense maxima at shorter wavelengths,[10] we feel it is reasonable to assume that for each compound the primary Cotton effects are closely associated with the primary absorption band. However, as first noted above, in the primary absorption region the CD curve normally manifests a splitting into two oppositely signed primary Cotton effects. It will now be further noted that in each case the first primary CD maximum is red shifted relative to the absorption maximum, while, when observed, the second primary CD maximum (opposite in sign) is blue shifted relative to the absorption maximum.[11] These facts suggest the possibility that the two primary Cotton effects comprise a rotatory strength couplet.[12] This suggestion is supported by the fact that in each corresponding ORD curve the second extremum of the primary Cotton effect is considerably more intense than the first extremum,[13] a property characteristic of rotatory strength couplets.[12] However, while these aspects of the data suggest the involvement of such couplets, it is evident that the present spectra at best involve nonideal cases since the ideal rotatory strength couplet is comprised of two equal but opposite rotatory strengths. Contrarily, the present spectra appear to involve unequal rotatory strengths and they may involve further complexity. It is interesting to note that for a given $Ph_3SiSi^*X(Ph)(Me)$ structure there are potentially three Ph–Si–Si* contributions and one Si–Si*–Ph contribution to the primary absorption. These contributions may be essentially degenerate in the isotropic uv absorption spectrum but split in the anisotropic absorption spectrum (CD).

Discussion of Cotton Effects with Respect to Configuration. All of the $Ph_3SiSi^*X(Ph)(Me)$ compounds studied in the present work have previously been assigned relative configurations. The compounds are listed with the signs of their respective D line optical rotations in Table I. All of the compounds have the same assigned configuration except the last one listed (*i.e.*, compound **8**) which has been assigned the opposite configuration at silicon. Assignments of the same configuration to compounds **1–7**, and the opposite to **8**, were based on clear reaction stereochemistry data for $Ph_3SiSi^*X(Ph)(Me)$ interconversions which demonstrated extensive and complete harmony with previously

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(10) It is pertinent to note here that simple phenyl ^1L_b Cotton effects are in general comparatively quite weak[8] and the fact that the secondary (benzenoid ^1L_b) Cotton effects in the present ORD and CD spectra of $Ph_3SiSi^*X(Ph)(Me)$ are weak and almost masked by the ORD and CD curves due to activity of the Ph–Si–Si grouping at shorter wavelengths is quite consistent with this.

(11) The second primary CD maximum is directly observed in the cases of **3**, **7**, and **8**, and inferrable in the other cases as mentioned earlier in the text.

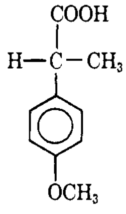
(12) J. A. Schellman, *Accounts Chem. Res*, 1, 144 (1968)

(13) An exception to this is the case of **6** in which the second extremum is only slightly more intense than the first. It should be noted here that third extrema of the primary ORD Cotton effects, which could possibly furnish a further parallel with the ideal rotatory strength couplet, were not observable because of unfavorable $[\phi]/\epsilon$ ratios.

established principles concerning the mechanism behavior of organosilicon reaction centers.

Although the data of Table IV suggest that the primary Cotton effects of compounds **1**–**8** derive from a common optically active chromophore (*i.e.*, the conjugated Ph–Si–Si chromophore) and it might be expected that such a chromophore would manifest largely uniform Cotton effect behavior with respect to configuration over the range of functional groups X involved, this expectation proves to be invalid. Specifically, compound **1** exhibits primary ORD and CD Cotton effects which are signed completely opposite to the corresponding Cotton effects of all the other compounds having the same assigned configuration (compounds **2**–**7**).[14] In view of the fact that compound **1** displays primary Cotton effect sign behavior opposing the collective and internally consistent Cotton effect sign behavior of compounds **2**–**8**, *we consider the Cotton effect behavior of compound* **1** *to be aberrant.* This aberrant behavior is best illustrated in Figure 4 which compares the CD spectra of **1** with the corresponding spectra of **2** and **3**. Particularly striking is the comparison between the CD curves of **1** and **2** which are almost enantiomeric in appearance in spite of the fact that the compounds have the same assigned configuration. However, the corresponding ORD curves (Figure 2) do not have such a striking enantiomeric appearance.

This is not the first report of aberrant Cotton effect behavior, there being at least two cases known involving acyclic organic compounds containing asymmetric carbon centers bonded to phenyl groups.[15] One of these cases involves compounds **9** and **10**. These give



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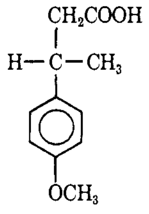

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CD Cotton effect curves which are nearly mirror images of each other as well as ORD curves which have been described as "quasi-enantiomeric" in appearance.[15b] Yet, it is known with certainty that configuration at the asymmetric carbon atoms in **9** and **10** is the same. The present case involving **1** *vs.* **2**–**8** comprises another striking example of such behavior.

At present we are only able to speculate briefly on the possible basis of the disilane Cotton effect aberration. It occurs in compound **1** for which X = H in Ph$_3$SiSi*X(Ph)(Me), and the aberration is relative to the collective behavior of the other compounds in which X = F, OH, OCH$_3$, Cl, Br, and (−)-OMen. Compared to these other functional groups, H is the smallest X group and at the same time it is the only X group which does not contain nonbonding electrons. These features offer some clues to the basis of the aberration. Possible explanations include (1) that the aberration is due to a conformational difference between **1** and the other compounds owing to the small size of H, and (2) that the aberration is due to electronic factors owing to the absence of nonbonding electrons in **1** and the presence of nonbonding electrons in all of the other compounds. These possibilities are not mutually exclusive and there may be others. Molecular models have not afforded any clear predictions and we presently prefer 2 as a leading possibility because there is a theoretical basis to expect that the optical activity of π–π^* transitions can be affected by mixing with n–π^* transitions or transitions involving d orbitals.[16] Furthermore, changing X from H to F, OH, etc., seems to represent a potentially more drastic electronic change than a conformational change in structures such as Ph$_3$SiSi*X(Ph)(Me).

Previous ORD and CD studies[8] revealed that in the optically active α-NpPhMeSi*X system the hydride (X = H) derivative manifests noticeably different (although not classified aberrant) primary Cotton effect behavior relative to derivatives in which X = F, Cl, OH, and OCH$_3$. In that system the hydride derivative manifests a simple primary Cotton effect (assigned to the naphthyl chromophore) while the other derivatives exhibit a splitting in the primary CD curves with a red shift of the first CD maximum in each case. The fact that the hydride derivatives of both the α-NpPhMeSi*X system and the present Ph$_3$SiSi*X(Ph)(Me) system exhibit distinctive behavior relative to that of the other derivatives may not be purely coincidental and warrants further study.

The present work serves to show that for Ph$_3$SiSi*X(Ph)(Me) structures ORD and CD Cotton effect data faithfully reflect relative configuration over a variance of X incorporating the halogens and alkoxy groups, with the latter ranging in size from OH to OMen. However, in the present case if the sign of the primary Cotton effect of **1** had been used for assignment of configuration relative to that of the halogen and alkoxy compounds, that assignment would have been incorrect and would have incurred serious invalid conclusions in the framework of reaction stereochemistry studies. By way of the striking aberrant Cotton effect behavior of compound **1**, *this study demonstrates how extraordinarily sensitive ORD and CD spectra can be to subtle changes in molecular structure and it thus warns against the wholesale use of such spectra for configurational assignments.*

Experimental Section

All uv, ORD, and CD spectra were determined on a Durrum-JASCO ORD/UV/CD-5 instrument. The solvent used was *n*-pentane (Phillips Petroleum Co.) purified by extraction with concentrated sulfuric acid followed by passage through a column of silica gel. Operating techniques and calculations have been described previously in detail.[8]

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(14) In addition, the primary Cotton effects of **1** are of the *same* signs as those of **8** although the latter has the *opposite* assigned configuration.

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