Stereochemistry of Asymmetric Silicon. XI. Optical Rotatory Dispersion and Circular Dichroism of α-NpPhMeSi*X Compounds[1,2]

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Abstract: Optical rotatory dispersion (ORD), circular dichroism (CD), and ultraviolet absorption spectra are reported for ten α-NpPhMeSi*X (designated R_3Si^*X) compounds where X = H, F, Cl, OH, SH, OCH_3, SCH_3, SSi^*R_3, OSi^*R_3, and $NHSi^*R_3$. The ultraviolet absorption of these compounds, which is dominated by the naphthyl chromophore, has associated with it a number of Cotton effects observed in the ORD and CD spectra. These Cotton effects are discussed with respect to configurational assignments based on X-ray and stereochemical data. In combination the ORD and CD Cotton effect data are consistent with those configurational assignments. Although variance of X in R_3Si^*X affects the uv absorption spectrum very little, interesting and substantial changes occur in the ORD and CD spectra. These changes are of general interest because they reflect the very great sensitivity of ORD and CD spectra to relatively minor structural changes in a series of closely related optically active molecules.

The first paper[3] in this series reported the preparation of a family of optically active α-naphthylphenylmethylsilyl compounds, α-NpPhMeSi*X (designated R_3Si^*X below), where X = H, F, Cl, Br, OH, OK, and OCH_3. At the same time, correlations of configuration based on physical methods, including X-ray analysis and stereochemical evidence, were achieved. This work provided a starting point for extensive study of the dynamic (reaction) stereochemistry of asymmetric silicon.[4]

Among the methods brought to bear on the determination of configuration at asymmetric silicon was optical rotatory dispersion (ORD). It was determined[3] that configurational assignments based on the signs of the plain dispersion curves (589–340 mμ) of R_3Si^*X (where X = H, F, Cl, OH, and OCH_3) are in complete harmony with assignments of absolute and relative configurations based on the other lines of physical and chemical evidence.

With the instrumentation available to us at that time, a cutoff point of 340 mμ in the ORD curves was necessary in order to avoid the hazard of possible errors introduced by incursion of high absorbance due to the naphthyl group at lower wavelengths.[5] However, ORD and circular dichroism (CD) behavior at wavelengths below 340 mμ has yielded valuable structural data for a wide variety of optically active compounds containing asymmetric centers other than silicon.[6-8] Thus it was deemed important to extend optical studies of asymmetric silicon to lower wavelengths. This circumstance, plus the availability of greatly improved instrumentation, pointed to the present work. Further interest was provided by the increased number and variety of optically active R_3Si^*X compounds, *e.g.*, with nitrogen[9] and sulfur[10] groups bonded to asymmetric silicon.

Herein are reported ORD and CD data, in conjunction with uv spectral data, for ten R_3Si^*X compounds. This comprises a study of variation in ORD and CD curves resulting from systematic structural changes. The effects of such changes on those portions of the curves showing Cotton effects are of special interest.

General Spectral Properties. Compounds containing the α-naphthylphenylmethylsilyl group, R_3Si^*–, have ultraviolet absorption spectra displaying the features characteristic of a substituted naphthalene.[11] Table I assigns reference numbers to the R_3Si^*X compounds studied and gives data for the main ultraviolet spectral features of these compounds. Figure 1 includes the spectra of (+)-R_3Si^*H and (−)-$R_3Si^*OSi^*R_3$, which are typical of the R_3Si^*X compounds, all of the compounds having very similar uv spectra. These spectra are comprised of the three band systems characteristic of naphthalene and typical of benzenoid hydrocarbons in general.[11,12] Using Clar's notation,[11,12] these three band systems are denoted α, *para*, and β. They are listed in the order of decreasing wavelength, and they are successively more intense in that direction.

For monosilicon compounds, the α-band system normally includes a faint shoulder at 324 mμ leading to a first maximum at 318 mμ (ε 330–530) and a more intense, second maximum at 313 mμ (ε >500). This is followed by steeply rising shoulders leading to a series of three maxima, the central of which is normally at 284–285 mμ and is the most intense of them (ε 8800–10,600). It serves as the central *para* band. The *para* absorption subsides below 260 mμ and this is followed by a steep rise to the

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(1) For the preceding paper in this series, see L. H. Sommer and H. Fujimoto, *J. Amer. Chem. Soc.*, **90**, 982 (1968).

(2) We are grateful to the National Science Foundation for support of this work.

(3) L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Amer. Chem. Soc.*, **86**, 3271 (1964).

(4) L. H. Sommer, "Stereochemistry, Mechanism, and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

(5) Reference 4, Chapter 7.

(6) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

(7) P. Crabbé, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1965.

(8) L. Velluz, M. Legrand, and M. Grosjean, "Optical Circular Dichroism," Academic Press, Inc., New York, N. Y., 1965.

(9) L. H. Sommer and J. D. Citron, *J. Amer. Chem. Soc.*, **89**, 5797 (1967).

(10) L. H. Sommer and J. McLick, *ibid.*, **89**, 5806 (1967).

(11) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962, Chapter 13.

(12) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen and Co., Ltd., London, 1963, Chapter 6.

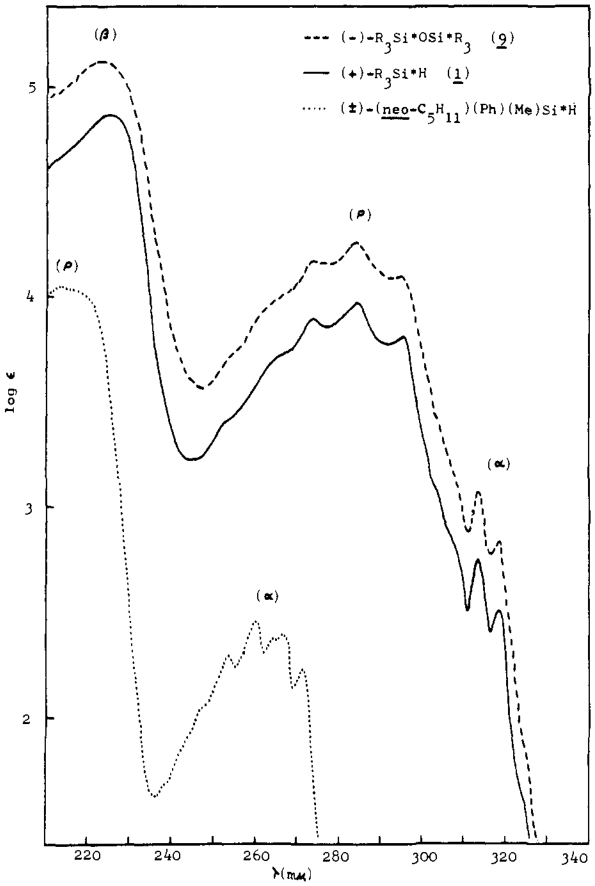

Figure 1. Ultraviolet spectra in cyclohexane of (+)-R_3Si*H, (−)-$R_3Si*OSi*R_3$, and (±)-(*neo*-pentyl)(Ph)(Me)Si*H.

Table I. Ultraviolet Absorption of α-NpPhMeSi*X Compounds[a]

R_3Si*X[b]	Compd[c]	Absorption characteristics[d,e]
(*R*)-(+)-Si*H	**1**	318 (330), 284 (9470), 225 (71,500)
(*S*)-(+)-Si*F	**2**	318 (440), 284 (8800), 224 (69,700)
(*S*)-(−)-Si*Cl	**3**	318 (530), 284 (9380), 224 (66,200)
(*S*)-(+)-Si*OH	**4**	318 (330), 284 (9000), 225 (68,700)
(*S*)-(−)-Si*SH[f]	**5**	318 (410), 285 (9600), 224 (65,500)
(*S*)-(+)-Si*OCH_3	**6**	318 (350), 284 (10,600), 225 (71,300)
(*S*)-(−)-Si*SCH_3[f]	**7**	318 (400), 285 (9750), 224 (64,700)
(*S*)-(−)-$(Si*)_2S$	**8**	318 (870),[g] 287 (18,200), 222 (112,000)
(*R*)-(−)-$(Si*)_2O$	**9**	318 (690), 284 (18,300), 223 (128,000)
(*S*)-(−)-$(Si*)_2NH$	**10**	318 (550), 284 (17,200), 223 (122,000)

[a] Cyclohexane solvent used in all cases. [b] Absolute configurations assigned previously. For **1–4** and **6**, see ref 3; for **5**, **7**, and **8**, see ref 10; for **9**, see L. H. Sommer, C. L. Frye, and G. A. Parker, *J. Amer. Chem. Soc.*, **86**, 3276 (1964); for **10**, see ref 9. [c] Numbers herein assigned to compounds for reference. [d] Selected absorbances: first long-wavelength maximum (α band), major secondary maximum (*para* band), and primary maximum (β band), listed in that order. For complete tabulation of spectral data, see J. McLick, Ph.D. Thesis, University of California, Davis, 1968. [e] Wavelengths, listed first, are in mμ; molecular absorptivities (ε) are in parentheses; all values listed refer to maxima, unless otherwise noted. Values of ε were calculated assuming 100% monomeric species in solution. [f] The spectra of the optically pure enantiomers of compounds **5** and **7** were determined, and the data reported herein derive from those spectra. The ORD and CD spectra reported for **5** and **7** are, in a mirror-image fashion, signed opposite to the observed spectra of their respective enantiomers. This is done for convenience of presentation and discussion. [g] Shoulder.

very intense (ε 64,700–71,500) β absorption located around 224–225 mμ. Following this maximum, a shoulder is observed near 213 mμ. The compounds containing two R_3Si* moieties have spectra very similar to those of the mono-R_3Si* compounds, except the molecular absorptivities of the former are approximately twice as large.

For purposes of general discussion, the β absorption will be referred to as the primary absorption, while the *para* and α absorptions will be referred to as secondary and long-wavelength absorptions, respectively.

The ORD and CD data obtained for R_3Si*X compounds in cyclohexane solvent are given in Tables II and III, respectively. For monosilicon compounds **1–7**, a very weak Cotton effect corresponding to the first long-wavelength uv maximum at 318 mμ is observed. The anomolous ORD curves are superimposed on significant background curves and do not cross the zero axis. These are complemented by weak, but significant, CD maxima which clearly designate the Cotton effect sign.

Immediately following the first uv maximum, CD measurements and, in turn, ORD measurements become unreliable on going to shorter wavelengths, due to increasing light absorption. The nonzero ORD signals do not clearly indicate a Cotton effect corresponding to the second long-wavelength maximum at 313 mμ; however, such could be masked by the background rotation. The ORD data become unreliable near 305 mμ with the onset of the secondary absorption. In this absorption region, sample concentrations which are just dilute enough to allow sufficient light transmittance for measurements (absorbance less than *ca.* 2) afford optical rotation and differential absorption readings which fall within the range of experimental error, *i.e.*, the ratios [φ]/ε and [θ]/ε are prohibitively low. On this account, the ORD and CD spectra in the secondary absorption region were not determined.

Upon subsidence of the secondary absorption near 260 mμ, ORD and CD measurements are again possible, and compounds **1–7** display moderately intense Cotton effects in the vicinity of the primary absorption band, *i.e.*, below 240 mμ. The ORD curves and complementary CD curves which comprise these primary Cotton effects are included in Figures 2–7 and the data pertaining to them are summarized in Table IV.

It is important to note here that further CD data indicate that R_3Si*X compounds generally, but with the apparent exception of R_3Si*H, give Cotton effects adjacent (at shorter wavelengths) to the first primary Cotton effect and of *opposite* sign. However, satisfactory quantitative measurements were precluded by unfavorable [θ]/ε ratios. Since these Cotton effects also occur in the vicinity of the primary absorption band, it should be understood that the primary Cotton effects reported in the present work are, unless otherwise noted, the *first* primary Cotton effects encountered below 240 mμ. It is believed that multiple primary Cotton effects are generally an important feature of the over-all Cotton effect behavior of R_3Si*X (see below).

Tables I–IV also include uv, ORD, and CD data for disilicon compounds **8**, **9**, and **10**. Compounds **8** and **9**, the disilthiane and the disiloxane, are especially notable since they have Cotton effect activity measurable through all three regions of their spectra. This includes multiple Cotton effects (most clearly seen in the CD spectra) in the

Table II. Optical Rotatory Dispersion of R$_3$Si*X Compounds[a, b]

Fig	Compd	$c \times 10^3$	$[\phi]_{340}$[c]	Dispersion characteristics[d]							
2	**1**	1000–6.2	+520	319 pk (+745)	316 tr (+580)	307[e] (+775)	260[f] (+4400)	230 pk (+36,000)	225 (0)	216 tr (−58,000)	210 (−48,000)
2	**2**	1000–8.0	+720	317 pk (+1090)	315 tr (+1080)	304[e] (+1650)	260[f] (+2900)	236 pk (+19,000)	232 (0)	226 tr (−50,000)	224 (−28,000)
2	**3**	2000–3.6	+90[g]	318 pk (+380)	316 tr (+330)	307[e] (+770)	260[f] (+5500)	236 pk (+16,000)	233 (0)	229 tr (−30,000)	227 (−22,000)
4	**4**	2000–7.0	+360	318 pk (+635)	316 tr (+500)	307[e] (+710)	260[f] (+1100)	238 pk (+11,000)	233 (0)	230 tr (−29,000)	228 (−12,000)
4	**5**[p]	1000–5.0	−360	321 tr[h] (−425)	319 pk (−415)	309[e] (−550)	260[f, i] (−3000)	230 tr (−42,000)	228 (0)	225 pk (+48,000)	224 (+17,000)
6	**6**	1000–7.3	+430	318 pk (+780)	315 tr (+720)	304[e] (+1050)	260[f] (+2000)	238 pk (+17,000)	232 (0)	227 tr (−42,000)	226 (−37,000)
6	**7**[p]	2000–4.7	−230	321 tr[h] (−310)	318 pk (−270)	307[e] (−430)	260[f, j] (−5500)	230 tr (−52,000)	227 (0)	223 pk (+75,000)	221 (+55,000)
8	**8**	500–2.7	−4700		316 sh (−15,800)	305 tr[k] (−27,000)	263 tr (+22,700)	238 pk (+198,000)	234 (0)	221 tr (−372,000)	216 (−73,000)
8	**9**	2000–3.1	−130[l, m]		313 sh (+1220)	299 pk[n] (+5100)	265 in (−17,500)	238 tr (−63,000)	233 (0)	227 pk (+254,000)	220 (+92,000)
..	**10**	2220–5.5	−530	316 tr (−1640)	314 pk (−1580)	301 tr[o] (−3300)	255[f] (+4800)	241 pk (+18,000)	236 (0)	231 tr (−31,000)	229 (−12,000)

[a] Compound numbers assigned in Table I. [b] Concentration, *c*, in g/100 ml in cyclohexane. The range employed is given. [c] Unless otherwise noted, at longer wavelengths the curve is plain to 700 mμ, rotations decrease and do not cross the zero axis. [d] Wavelengths in mμ; molecular rotations in parentheses. Abbreviations: peak (pk), trough (tr), shoulder (sh), inflection (in). Last value listed is last reliable rotation obtained in the short-wavelength region. [e] Last reliable reading upon entry into secondary (*para*) absorption region (see text). [f] A first reading upon subsidence of the secondary absorption (see text). [g] Also 460–450 broad tr (−25), 370 (0). [h] Probably a turning point in negative plain curve upon entry into peak. [i] Also 250 sh (−3800), 245 broad tr (−4300), 240 pk (−3600); these features are not clearly defined. [j] Also 245 sh (−8500), not clearly defined. [k] Also 299 (0), 297 pk (+8300), 296 tr (+6600), 286 pk (+37,500), 280 sh (+34,000), 267 sh (+24,700); see Figure 8. [l] Corrected to 100% enantiomeric purity, assuming 92% optical purity. [m] Also 360–370 broad tr (−190), 331 (0). [n] Also 295 (0), 291 sh (−2900), 281 tr (−13,800), 274 pk (−13,200); see Figure 8. [o] Also 297 (−250), last reliable reading in the secondary absorption. [p] Footnote *f*, Table I.

Table III. Circular Dichroism of R$_3$Si*X Compounds[a]

Figure	Compd[b]	CD characteristics[c, d]				
3	**1**	318 max (+170)	314[e] (0)	240[f] (+1700)	225 max (+41,000)	216 (0)
3	**2**	318 max (+130)	316[e] (+40)	248[f] (+1300)	233 max (+34,000)	229 (0)
3	**3**	319 max (+185)	318[e] (+90)	246[f] (+1100)	234 max (+29,000)	230 (0)
5	**4**	318 max (+210)	316[e] (+70)	249[f] (+1220)	233 max (+23,000)	230 (0)
5	**5**[m]	317 max (+150)	315[e] (0)	232[g] (0)	228 max (−33,000)	225 (0)
7	**6**	318 max (+130)	316[e] (+60)	248[f] (+7800)	233 max (+36,000)	229 (0)
7	**7**[m]	317 max (+140)	315[e] (0)	234[f] (−2000)	227 max (−76,000)	220 (0)
9	**8**	320 max (+1850)	318[h] (0)	246[f] (+4000)	233 max (+332,000)	225[i] (0)
9	**9**[j]	...	...[k]	266[f] (−1700)	232 max (−250,000)	226 (0)
..	**10**	319 max (+140)	317[l] (0)	251[f] (+5700)	237 max (+35,000)	233 (+18,000)

[a] Concentration ranges the same as given in Table II for ORD measurements; in all cases cyclohexane solvent was used. [b] Compound numbers assigned in Table I. [c] Wavelengths in mμ; molecular ellipticities given in parentheses (θ); abbreviations: maximum (max), minimum (min); last value listed is last reliable ellipticity obtained, except when noted. [d] At wavelengths longer than the first value listed, the ellipticity diminishes toward zero in an asymptotic manner. [e] Last reliable reading; next reliable reading is obtained after subsidence of the secondary absorption. [f] First reliable reading after secondary absorption subsidence. [g] Also 239 (+2280), footnote *f*; 235 max (+9100). [h] Also 314 max (−3420), 313 min (−3270), 301 max (−36,400), 295 min (−30,600), 292 max (−36,400), 278 (−1700, footnote *e*). [i] Also 215 max (−307,000), 210 (−214,000). [j] Footnote *l*, Table II. [k] First observed feature: 314 max (+700); also 311 min (+420), 296 max (+11,800), 293 min (+9400), 286 max (+13,600), 281 (+3100, footnote *e*). [l] Also 297 max (−3700), 296 (−3300, footnote *e*). [m] Footnote *f*, Table I,

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

	ORD Cotton effect		CD Cotton effect		Uv absorption[f]	
	Midpoint[c]	Amplitude[d]	Maximum[d,e]		λ_{max},	
Compd[b]	mμ	$\times 10^{-3}$	mμ	$[\theta] \times 10^{-3}$	mμ	$\varepsilon \times 10^{-3}$
1	223	94	225	+41	225	71.5
2	231	69	233	+34	224	69.7
3	233	46	234	+29	224	66.2
4	234	40	233	+23	225	68.7
5[g]	228	90	228	−33	224	65.5
6	233	59	233	+36	225	71.3
7[h]	227	127	227	−76	224	64.7
8	230	570	233	+332	222	112
9	233	317	232	−250	223	128
10	236	49	237	+35	223	122

[a] All data obtained in cyclohexane solvent; the data refer to *first* primary Cotton effects, unless otherwise noted. [b] Compound numbers assigned in Table I. [c] Data from Table II. [d] Due to overlap of first primary Cotton effects with second primary Cotton effects, ORD and CD Cotton effect positions and amplitudes must be considered apparent. [e] Data from Table III. [f] Data from Table I. [g] *Second* primary Cotton effect. [h] The Cotton effect listed for **7** is the first observable primary Cotton effect but it is likely that it corresponds to the *second* primary Cotton effect of its close relative **5**, listed above.

secondary absorption region, *i.e.*, below 305 mμ, and high intensity primary Cotton effects.

Discussion of Spectra. Compounds **1–10** have all been previously assigned relative and absolute configurations, and these are designated in Table I. It should be noted that all of the compounds listed are uniformly of the same assigned configuration with an exception of **9**, which has been assigned the opposite configuration. Figures 2–9 afford comparisons of the ORD and CD behavior of these compounds, and these will now be discussed in some detail.

The absolute configurations of (*R*)-(+)-R_3Si*H (**1**) and (*S*)-(+)-R_3Si*F (**2**) were determined by X-ray analysis.[3,13] The two compounds have the same configuration (although having opposite *RS* notation). Compounds **3**, **4**, and **5** were assigned the (+)-R_3Si*H configuration on the basis of physical and chemical correlations.[3]

Figures 2 and 3 compare the ORD and CD curves of **1**, **2**, and **3** (X = H, F, Cl). The positive long-wavelength Cotton effects (CD positive maxima at 318–319 mμ, greatly magnified in Figure 3) and the positive first primary Cotton effects of these compounds are all mutually consistent with their having the same assigned configuration.

It is important to note that for (+)-R_3Si*H (**1**) the primary ORD Cotton effect midpoint is at 223 mμ, and the primary CD maximum is at 225 mμ, which correlates well with the primary uv maximum at 225 mμ. However, for (+)-R_3Si*F (**2**) and (−)-R_3Si*Cl (**3**), with primary uv maxima also in the range of 224–225 mμ, the Cotton effect midpoints and CD maxima occur in the range 231–234 mμ. While no rigorous explanation is presently available for this apparent red shift of Cotton effects, it is likely due to overlap of these first primary Cotton effects with second and *oppositely* signed Cotton effects at shorter wavelength (remarked on above).[14]

Figures 4 and 5 give the ORD and CD curves of (+)-R_3Si*OH (**4**) and (−)-R_3Si*SH (**5**). Compound **5** has been assigned the same configuration as **4** (*i.e.*, the (+)-R_3Si*H configuration) based on leaving group reasoning.[10] The positive long-wavelength Cotton effect and positive first primary Cotton effect (apparently red shifted) of the silanol **4** correlate with those of compounds **1–3** in uniform positive sign. In turn, the silanethiol **5** also displays a *positive* long-wavelength Cotton effect, as clearly designated by a CD positive maximum at 317 mμ (Figure 5), which is consistent with its assigned relative configuration. It will be noted, however, that for **5** the positive long-wavelength ORD Cotton effect (Figure 4) is superimposed on a negative (rather than a positive) background curve. For **5**, the ORD spectrum below 250 mμ is somewhat complex, but this receives clarification from the corresponding CD spectrum (Figure 5) which discloses a pair of closely spaced, oppositely signed Cotton effects. The first of these two primary CD Cotton effects is located at 235 mμ and is *positive*. It is followed by an adjacent, *negative* Cotton effect at 228 mμ of notably greater intensity which dominates in the ORD spectrum.

In the ORD curve of **5** (Figure 4) a broad trough is observed around 245 mμ, followed by a peak at 240 mμ. The peak probably relates to the first extremum (distorted by background cancellation) of the positive Cotton effect indicated by the CD positive maximum at 235 mμ. The second extremum of this Cotton effect is probably masked by the rapidly falling negative curve associated with the ensuing second (negative) primary Cotton effect. The great value of CD spectra in Cotton effect studies is clearly seen in this circumstance.

If, in Figure 5, the *first* primary Cotton effect (CD positive maximum at 235 mμ), of **5** is compared to that of **4** (CD positive maximum at 233 mμ), then there is proper agreement of Cotton effect signs with assigned same configurations. The *second* (and negative) primary Cotton effect of **5**, which dominates the ORD spectrum, is apparently not comparable to the *first* primary Cotton effect of **4**.

Figures 6 and 7 give the ORD and CD curves of

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[13] Y. Okaya and T. Ashida, *Acta Cryst.*, **20**, 461 (1966).

[14] It is known that two strongly overlapping CD Cotton effects of similar rotatory strength but of *opposite* signs give a resultant CD "couplet" in which the longer wavelength maximum is red shifted relative to its component band, and the shorter wavelength maximum is blue shifted relative to its component band.[15,16] Formation of such couplets involves mutual cancellation of component CD curves, resulting in diminution of observed rotatory strengths. This may account for the smaller observed rotatory strengths of the first primary Cotton effect of **2** and **3**, relative to that of the apparent single primary Cotton effect of **1** (see Figure 3).

[15] K. M. Wellman, P. H. A. Laur, W. S. Briggs, A. Moscowitz, and C. Djerassi, *J. Amer. Chem. Soc.*, **87**, 66 (1965).

[16] J. A. Schellman, *Accounts Chem. Res.*, **1**, 144 (1968).

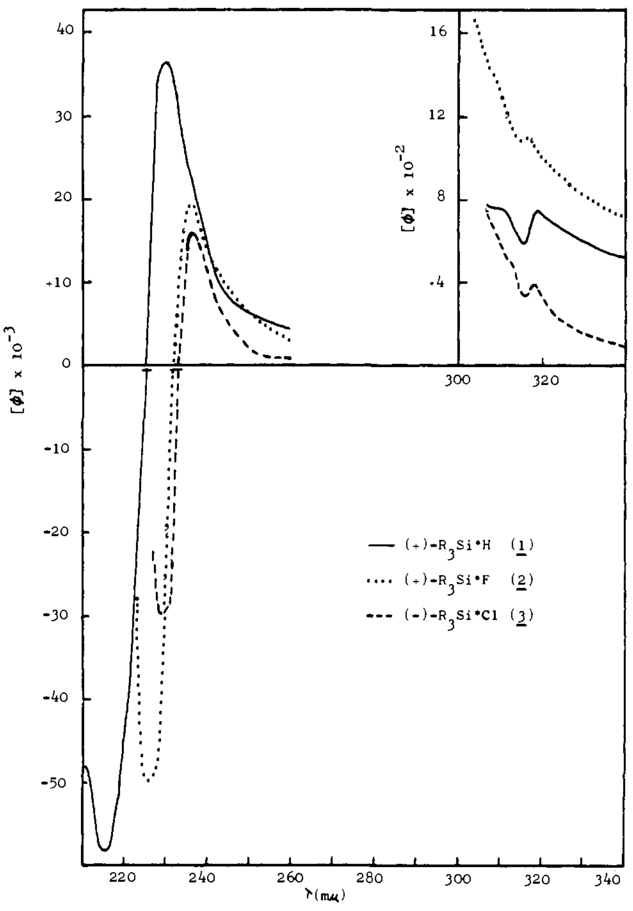

Figure 2. Optical rotatory dispersion curves of (+)-R_3Si^*H, (+)-R_3Si^*F, and (−)-R_3Si^*Cl. These compounds have been assigned the same configuration based on previous evidence.

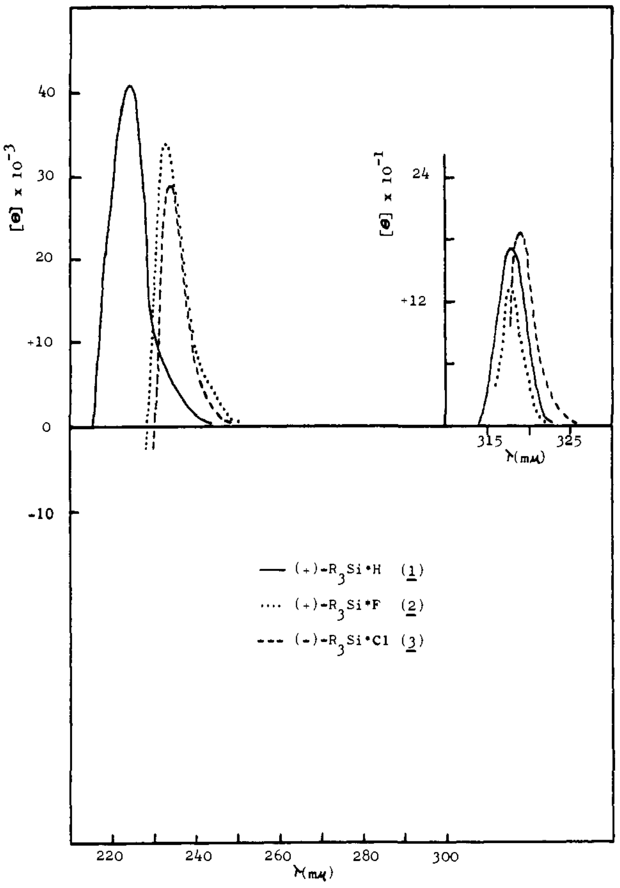

Figure 3. Circular dichroism curves of (+)-R_3Si^*H, (+)-R_3Si^*F, and (−)-R_3Si^*Cl. These compounds have been assigned the same configuration based on previous evidence.

(+)-$R_3Si^*OCH_3$ (**6**) and its sulfur analog, (−)-$R_3Si^*SCH_3$ (**7**). Compound **7** has been assigned[10] the (+)-R_3Si^*H configuration, and, hence, the same configuration as **6**. The positive long-wavelength Cotton effect and positive first primary Cotton effect (apparently red shifted) of **6** correlate in sign with those of **1–4** discussed above. Likewise, **7** displays a *positive* long-wavelength Cotton effect (best seen in the CD spectrum, Figure 7) consistent with its assigned relative configuration. However, similar to the case of **5** above, this weak Cotton effect is superimposed on a *negative* ORD background curve which persists into the primary absorption region and develops into a major, *negative* Cotton effect centered at 227 mμ (Figure 6), verified by a *negative* CD Cotton effect at 227 mμ (Figure 7). In addition, the CD data indicate the possibility of a weak, positive Cotton effect near 235 mμ, which may parallel the positive, first primary CD Cotton effect of **5** at 235 mμ, but due to a low signal/noise ratio the data were inconclusive. The ORD curve shows only a poorly defined shoulder at 245 mμ. However, the otherwise parallel ORD behavior of **7** and its close relative **5**, *including similarly shaped and positioned major primary ORD Cotton effects*, is suggestive of a common basis and leads to the conclusion, similar to the case of **5**, that the dominant, negative primary Cotton effect of **7** at 227 mμ is probably not comparable to the first (and positive) primary Cotton effect of its oxygen analog **6**.

The configuration of (−)-$R_3Si^*SSi^*R_3$ (**8**) is rigorously known to be the same as that of (−)-R_3Si^*SH (**5**) and (−)-$R_3Si^*SCH_3$ (**7**) through synthesis not involving the asymmetric center.[10] Unlike its relatives **5** and **7**, compound **8** displays a *dominant positive* first primary Cotton effect in both the ORD and CD spectra (see Figures 8 and 9). This Cotton effect (CD positive maximum at 233 mμ) correlates in position and sign with the first primary Cotton effects of nonsulfur compounds **2–4**, and **6** (CD positive maxima at 233–234 mμ) of the same assigned configuration. It also probably corresponds to the weak, positive first primary Cotton effect (CD maximum at 235 mμ) of **5** discussed above.[17]

In addition to common positive first primary Cotton effects, a second correlation between **8** and the monosilicon compounds is suggested by a positive CD Cotton effect in the long-wavelength region at 320 mμ (Figure 9).

Figures 8 and 9 compare the ORD and CD curves of **8** and its oxygen analog, (−)-$R_3Si^*OSi^*R_3$ (**9**). Compound **9** has been assigned[18] the configuration *opposite* to **8**, *i.e.*, that of (−)-R_3Si^*H. Comparison of the curves, especially those of CD (Figure 9) is suggestive of parallel, but *oppositely signed* Cotton effect behavior, and this is

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(17) In Figure 9, the positive first primary CD Cotton effect is followed by a negative Cotton effect in an apparent couplet fashion. The latter Cotton effect, with its negative maximum near 215 mμ, is measurable because of its high intensity.

(18) L. H. Sommer, C. L. Frye, and G. A. Parker, *J. Amer. Chem. Soc.*, **86**, 3276 (1964).

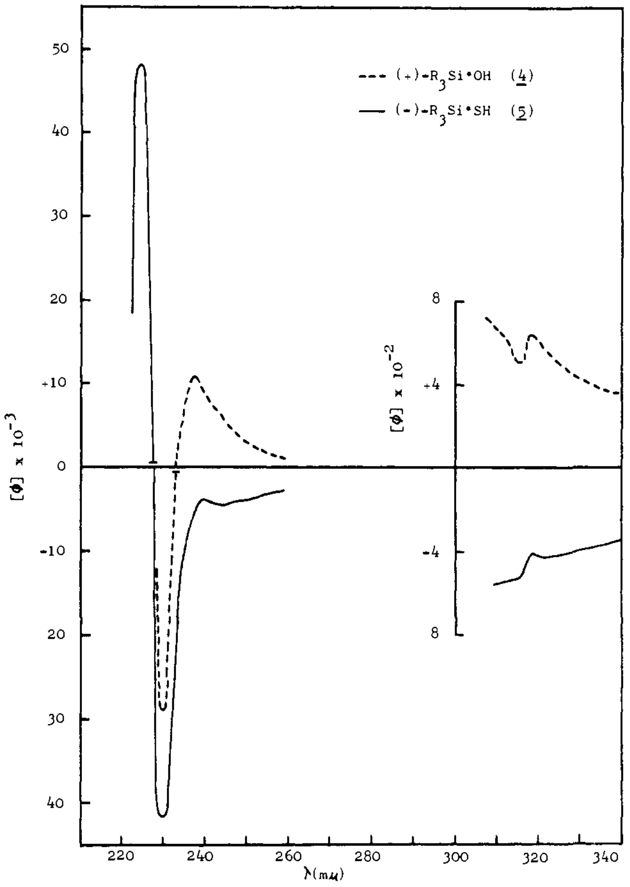

Figure 4. Optical rotatory dispersion curves of (+)-R_3Si^*OH and (−)-R_3Si^*SH. These compounds have been assigned the same configuration based on previous evidence.

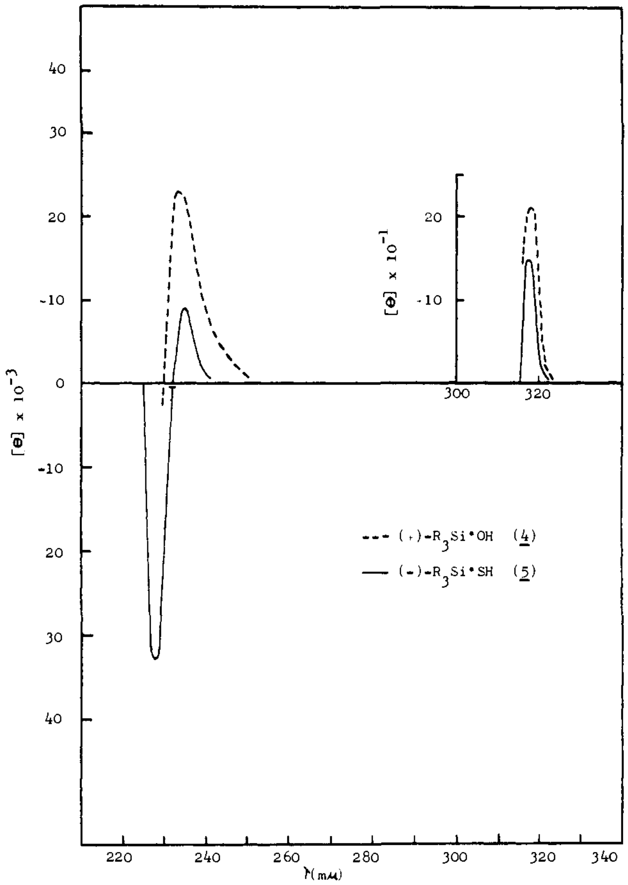

Figure 5. Circular dichroism curves of (+)-R_3Si^*OH and (−)-R_3Si^*SH. These compounds have been assigned the same configuration based on previous evidence.

consistent with assigned opposite configurations.[19]

The disilazane, (−)-$R_3Si^*NHSi^*R_3$ (**10**), has a previously assigned[9] (+)-R_3Si^*H configuration, and its Cotton effect behavior relative to that of the disilthiane **8** is consistent with the same assigned configuration, *i.e.*, Cotton effects of the same sign as those of **8** in all three regions of the spectrum, although with considerably less intensity and some difference in positioning (see Tables II–IV).

Thus, the Cotton effect behavior of the disilicon compounds **8**, **9**, and **10** is mutually consistent with their assigned relative configurations and is also suggestive of positive correlation with the monosilicon compounds especially in the short-wavelength region, where positive first primary Cotton effects are associated with the (+)-R_3Si^*H configuration. However, the significant secondary Cotton effects of the disilicon compounds distinguish them from the simple monosilicon compounds, whose Cotton effect activity in the secondary absorption region is, at best, very weak. The secondary Cotton effects of the disilicon compounds are noted to be uniformly *opposite* in sign to the first primary Cotton effects encountered at shorter wavelengths. These secondary Cotton effects have a notable effect on the plain dispersion curves at longer wavelengths: they determine the sign of the long-wavelength plain curves (including D line rotation) of the disilthiane **8** and the disilazane **10**, while they cause a sign change in the curve of the disiloxane **9**. All of these compounds ultimately go on to first primary Cotton effects opposite in sign to these intervening secondary Cotton effects.

It is important to note that further work in its preliminary stages[20] indicates that this behavior is not necessarily limited to the disilicon compounds, but that it also may occur with simple branching in the X group (*e.g.*, $X = OC(CH_3)_3$).

For purposes of comparison with R_3Si^*X, it was of interest to determine the spectral properties of an available asymmetric silane in which the naphthyl group is absent, and (*neo*-pentyl)(Ph)(Me)Si*H was chosen for this purpose. The uv spectrum of this silane, in its racemic form, is included in Figure 1. As expected, the compound displays a typical phenyl chromophore spectrum,[12,21] with the α band system centered at 260 mμ (ε 290) and the more intense *para* absorption at 213–217 mμ (ε 11,000). The phenyl β band probably occurs at shorter wavelength (below 200 mμ) and is not observed. The observed α and *para* bands correspond to the benzene ^1L_b and ^1L_a transitions, respectively.[12,21]

It is noted that the spectral comparison between R_3Si^*H

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[19] Curiously, first long-wavelength and second primary CD Cotton effects (corresponding to those of **8**) were not observable for **9**.

[20] L. H. Sommer and J. McLick, unpublished work.

[21] Reference 11, Chapter 12.

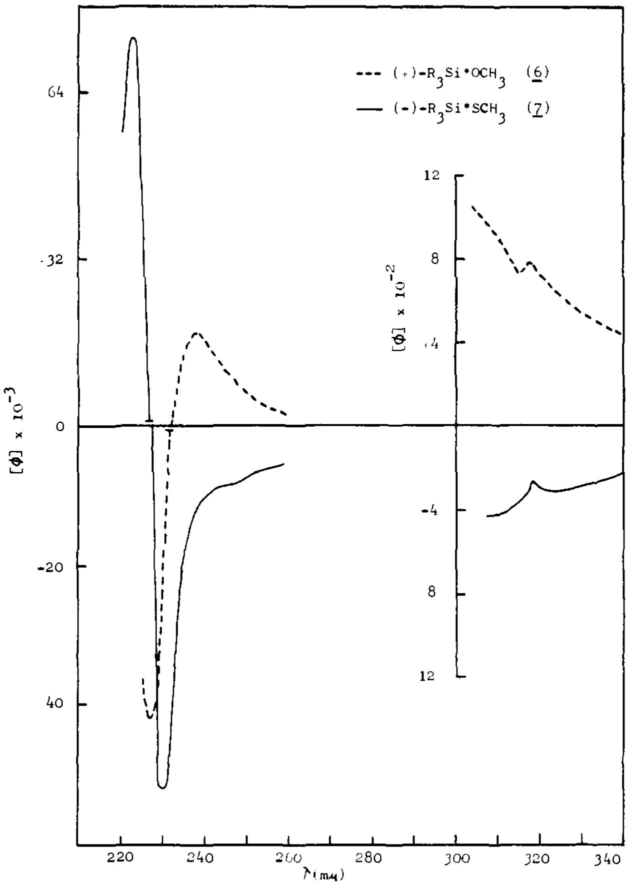

Figure 6. Optical rotatory dispersion curves of (+)-$R_3Si^*OCH_3$ and (−)-$R_3Si^*SCH_3$. These compounds have been assigned the same configuration based on previous evidence.

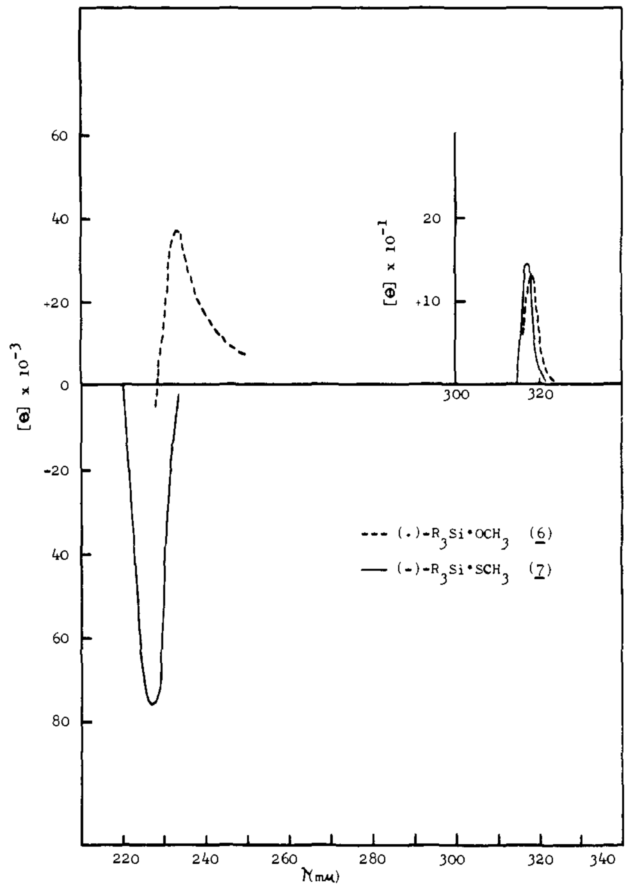

Figure 7. Circular dichroism curves of (+)-$R_3Si^*OCH_3$ and (−)-$R_3Si^*SCH_3$. These compounds have been assigned the same configuration based on previous evidence.

and (*neo*-pentyl)(Ph)(Me)Si*H in Figure 1 is similar to a comparison between benzene and naphthalene themselves, the naphthalene absorption being greatly more intense than that of benzene throughout the spectrum.

Figure 10 displays the ORD and CD curves obtained for (+)-(*neo*-pentyl)(Ph)(Me)Si*H. The compound displays very weak multiple Cotton effects in the α (^1L_b) absorption region. Following these weak Cotton effects, the ORD curve rises. Unfortunately, a cutoff point at 224 mμ was required due to an unfavorable [ϕ]/ε ratio. Down to 224 mμ, CD measurements show no incipient major Cotton effect. Presumably the ORD curve eventually leads into a positive Cotton effect associated with the ^1L_a absorption band near 213–217 mμ. This Cotton effect behavior of (+)-(*neo*-pentyl)(Ph)(Me)Si*H is quite similar to that of simple molecules bearing a phenyl group bonded to asymmetric carbon, *e.g.*, optically active methylphenylcarbinol.[22,23]

Discussion of Results and Conclusions. Interpretation of the ORD and CD behavior of R_3Si^*X compounds is rendered difficult by the involvement of aromatic chromophores in conformationally flexible structures. In a recent review,[24] Crabbé and Klyne have pointed out the present inadequate knowledge pertaining to optically active aromatic chromophores in general, and the present work comprises an attempt to help expand this area of ORD and CD behavior. The following discussion should serve to summarize what has been accomplished as well as to reflect the complexities involved in reaching definite conclusions.

A first approximation might picture the naphthyl and phenyl groups in R_3Si^*X operating as separate, inherently symmetric, but dissymmetrically perturbed chromophores.[25] Phenyl groups bonded to a common silicon center are known to behave, spectrally, like isolated units,[26] and similar behavior obtains for phenyl groups bonded to a neutral, tetrahedral carbon center.[27] This probably relates to the fact that electronic resonance structures through the central atom are not favored which suggests that the naphthyl and phenyl groups in R_3Si^*X may be operating as essentially separate chromophores.[28]

Thus, it is possible that the naphthyl chromophore activity dominates in the ORD and CD spectra of R_3Si^*X just as it does in the absorption spectra. The observed

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(22) L. Verbit, *J. Amer. Chem. Soc.*, **87**, 1617 (1965).

(23) L. Verbit, S. Mitsui, and Y. Senda, *Tetrahedron*, **22**, 753 (1966).

(24) P. Crabbé and W. Klyne, *ibid.*, **23**, 3449 (1967).

(25) A. Moscowitz, *ibid.*, **13**, 48 (1961).

(26) (a) H. Gilman and G. E. Dunn, *J. Amer. Chem. Soc.*, **72**, 2178 (1950); (b) L. D. Freedman and G. O. Doak, *J. Org. Chem.*, **21**, 811 (1956).

(27) A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," Edward Arnold, Ltd., London, 1958, pp 134–135.

(28) We do not wish to exclude the possibility that the naphthyl and phenyl groups in R_3Si^*X operate as coupled oscillators.[24] However, the degree of importance of such interactions to the spectra of flexible molecules of the type included in the present study is not yet known.

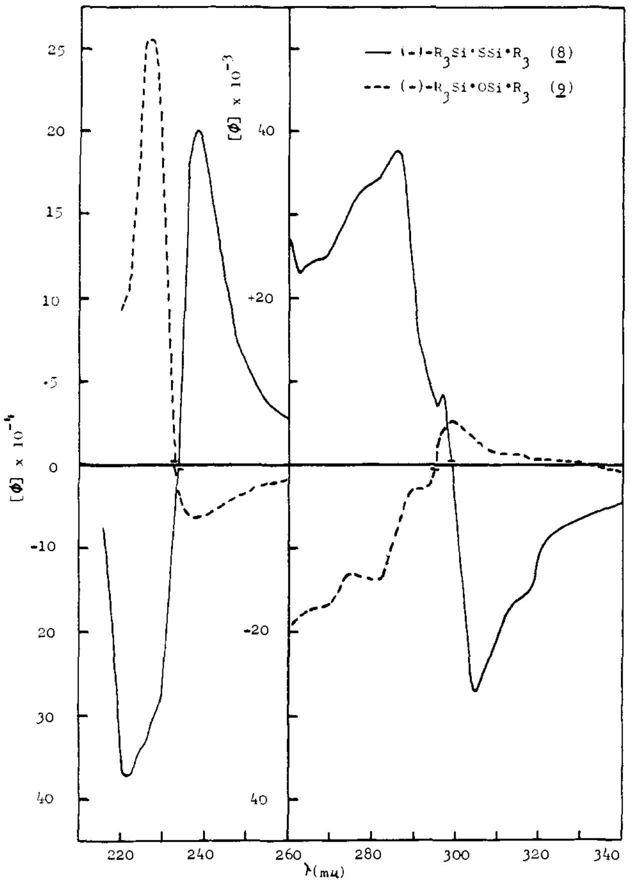

Figure 8. Optical rotatory dispersion curves of (−)-$R_3Si^*SSi^*R_3$ and (−)-$R_3Si^*OSi^*R_3$. These compounds have been assigned opposite configurations based on previous evidence.

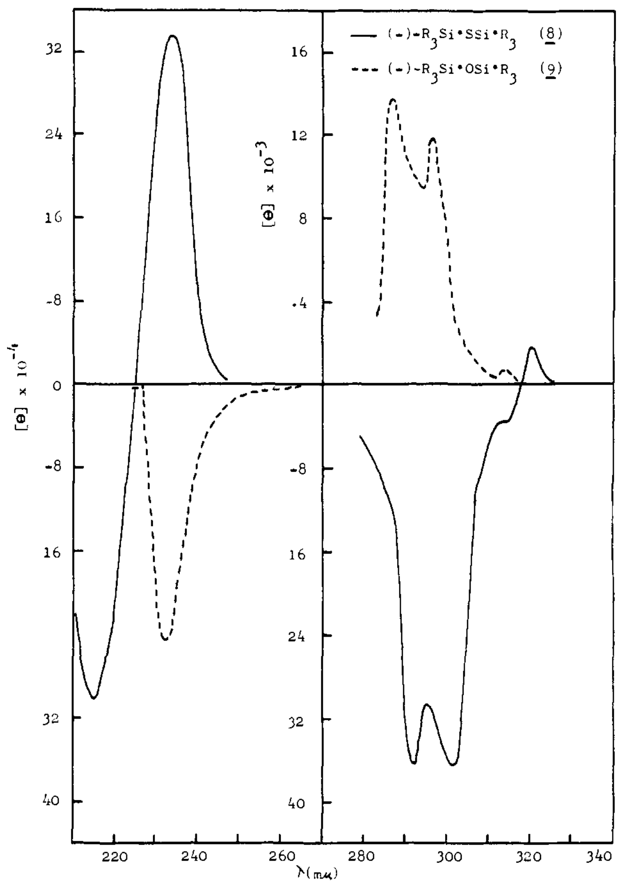

Figure 9. Circular dichroism curves of (−)-$R_3Si^*SSi^*R_3$ and (−)-$R_3Si^*OSi^*R_3$. These compounds have been assigned opposite configurations based on previous evidence.

very weak Cotton effect activity of (+)-(*neo*-pentyl)(Ph)-(Me)Si*H (Figure 10) down to at least 224 mμ supports (but does not rigorously prove) this view. By the time 224 mμ is reached in the spectrum, the naphthyl group is undergoing its very intense primary absorption (λ_{max} 223–225 mμ), and that the considerably weaker primary absorption of the phenyl group does not maximize until *ca.* 213 mμ. Although the observed primary Cotton effects of R_3Si^*X are considered to relate to the primary naphthyl absorption, the contribution which a primary phenyl Cotton effect might make to the background rotation in the short-wavelength range, especially below 225 mμ, is not known. In the spectra of (+)-R_3Si^*H in Figures 2 and 3, if there is a Cotton effect due to the primary phenyl band, it is apparently masked by the primary Cotton curves (ORD and CD) which correlate with the primary naphthyl band.

With respect to the second primary Cotton effects directly observed in some cases and inferred in others from the ORD and CD spectra, these are also considered likely to be related to the naphthyl chromophore. However, it is also possible that they derive from participation of the phenyl chromophore.

If the observed Cotton effects in the ORD and CD spectra of R_3Si^*X are directly related to the naphthyl chromophore, then these Cotton effects may be assigned to corresponding naphthyl transitions. Most clearly, the weak long-wavelength Cotton effects encountered near the first absorption maximum at 318 mμ would relate to the forbidden naphthalene α transition (^1L_b).[11] Cotton effects occurring in the secondary absorption region (compounds **8**, **9**, and **10**) would probably relate to the allowed *para* transition (^1L_a). Finally the primary Cotton effects observed in the region of the primary absorption would probably relate to the intense allowed β transition (^1B_b) of the naphthyl chromophore.

It is interesting to note that the naphthalene α (^1L_b) and β (^1B_b) transitions are both longitudinally (long axis) polarized,[29] while the *para* (^1L_a) transition is transversely (short axis) polarized in the naphthalene nucleus.[11] Thus, there may be an important, fundamental relationship between the weak, long-wavelength (α) Cotton effect and the primary (β) Cotton effect(s) of R_3Si^*X.

As inherently symmetric chromophores, the optical activity of the naphthyl and phenyl groups in R_3Si^*H would depend on their respective dissymmetrically perturbing environments. These in turn would be a function of configuration and conformation. Substituent X in R_3Si^*X could affect the optical activity of the chromo-

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(29) LCAO–MO treatment of naphthalene involving first-order configuration interaction predicts this relationship. First-order configuration interaction of degenerate excited states in naphthalene gives rise to a lower state (α) and a higher state (β). Transition from the ground state to the α state is forbidden, while that to the β state is allowed.[30]

(30) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, Chapter 8.

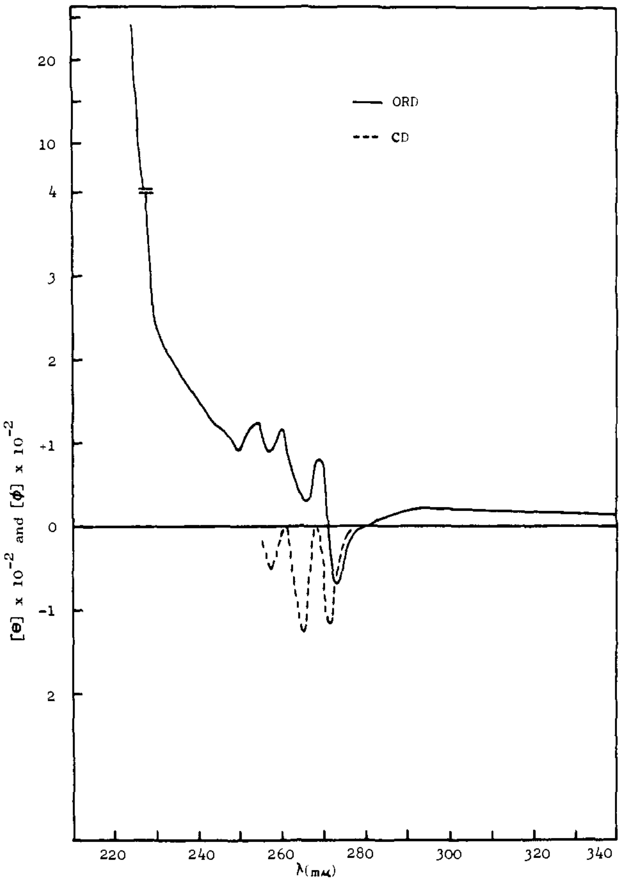

Figure 10. Optical rotatory dispersion curve and circular dichroism curve of (+)-(*neo*-C_5H_{11})(Ph)(Me)Si*H.

phores by (1) electronic interaction with them through the bonding framework, (2) its perturbation of the chromophores as an element of their spatial environments, and (3) its simultaneous conformational effects on the molecule as a whole.

With reference to the conformation of R_3Si^*X, it is relevant to note that accurately scaled molecular models indicate that a leading factor is "crowding" incurred between the hydrogen atom located in the *peri* position (relative to the silicon atom) on the naphthalene nucleus and the other groups bonded to the silicon center. Maximum freedom of intramolecular motions is attained when the *peri* hydrogen is flanked by the two groups of the remaining three that have the smallest steric requirements.[5] Thus, it is expected that for R_3Si^*X compounds where the functional group X is smaller than the methyl group, approximately the same conformational distributions will obtain.

X-Ray structural studies[13] on (+)-R_3Si^*H (**1**) and (+)-R_3Si^*F (**2**) indeed indicate intramolecular crowding involving the *peri* hydrogen. From the observed structures, it is apparent that the *peri* hydrogen tries to turn away from the methyl group and comes closest to the smallest substituent on silicon, *i.e.*, the hydrogen or the fluorine atom. However, this conformation apparently does not completely solve the problem of crowding, since the naphthalene group is seen to be somewhat "buckled" out of planarity, apparently due to the crowding of the *peri* hydrogen.[13] The deviations from planarity are larger when X is fluorine than when it is hydrogen, in apparent accord with the larger size of the fluorine atom.[31]

Returning to the spectral results of the present study, it was found that (+)-R_3Si^*H (**1**) displays a positive long-wavelength (α) Cotton effect and a positive, single primary (β) Cotton effect. Holding configuration constant, replacement of H in (+)-R_3Si^*H by groups F, Cl, OH, OCH_3 in turn causes no essential changes in long-wavelength behavior, *i.e.*, positive ORD background curves with superimposed positive Cotton effects still obtain (in the case of (−)-R_3Si^*Cl (**3**), the long-wavelength plain curve remains positive, although the rotational sign is negative at wavelengths longer than 370 mμ). However, in each case double primary Cotton effects are engendered, with the first (and *positive*) Cotton effect apparently red shifted with respect to the primary absorption curve by adjacency to a second, oppositely signed primary Cotton effect. In effect, replacement of H in (+)-R_3Si^*H with the other groups introduces a second important optically active primary transition, unresolved in the absorption curve. The cause of this is not clear. It could be due to a structural effect, relating to the larger size of the new substituents relative to hydrogen, *e.g.*, perhaps a new vibronic state is introduced. On the other hand, the change could be caused by inherent electronic factors, perhaps relating to the fact that these new substituents contain, in contrast to hydrogen, nonbonding electrons. It is reasonable to expect that the optical activity of aromatic π–π* transitions is affected by mixing with n–π* transitions or transitions involving d orbitals.[32]

It is interesting to note that the Cotton effect behavior of R_3Si^*X is quite similar for X = F, Cl, OH, and OCH_3. The net effect of electronic and structural changes on Cotton effect behavior within that variance of X appears small. This result appears consistent with the suggestion that these compounds have similar conformational distributions by reason of the X groups being smaller than the methyl group (see above).

On proceeding to the simple sulfur substituents (X = SH, SCH_3), considerable deviance from the pattern set by the halogen and oxygen substituents is incurred. While the long-wavelength (α) Cotton effects remain positive for the (+)-R_3Si^*H configuration, these are superimposed on negative ORD background curves. For (−)-R_3Si^*SH, the ORD background curve apparently derives from the dominating negative second primary Cotton effect. The positive first primary Cotton effect of this compound, which apparently relates to its (+)-R_3Si^*H configuration, is largely masked in the ORD spectrum, but it is clearly observable in the CD spectrum. The reason for the incursion of this dominating second primary Cotton effect is not known. It appears that (−)-$R_3Si^*SCH_3$ displays similar behavior, except that a positive first primary Cotton effect is not observable, as mentioned above.

This change in primary Cotton effect behavior of R_3Si^*SH and $R_3Si^*SCH_3$, relative to the other R_3Si^*X compounds studied, may result from structural changes owing to the size of the sulfur atom, which is slightly larger

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(31) The fact of a "buckled" naphthalene in the crystal lattice does not, of course, necessarily apply to the molecule in solution. However, the concept furnishes a graphic example of possible perturbation of the naphthalene chromophore.

(32) A. Moscowitz, A. Rosenberg, and A. E. Hansen, *J. Amer. Chem. Soc.*, **87**, 1813 (1965).

than the chlorine atom, and nearly the same size as the methyl group. Or, it could also be the result of the electronic nature of the sulfur substituent. In this connection it is pertinent to note that uv studies[33] of simple silicon–sulfur compounds reveal that the compound Me_3SiSMe has a uv maximum at 224.5 mμ (log ε 2.15) which is believed to be due to promotion of a nonbonding sulfur electron into a bonding molecular orbital formed by combination of 3d orbitals of sulfur and silicon. Presumably this chromophore could conjugate with the aryl groups on silicon in a fashion paralleling the conjugated Si–Si chromophore in aryldisilanes.[34,35] The observed dominating negative primary Cotton effects of $(-)$-R_3Si^*SH and $(-)$-$R_3Si^*SCH_3$ could relate to such a chromophore.

In contrast to $(-)$-R_3Si^*SH and $(-)$-$R_3Si^*SCH_3$, disilthiane $(-)$-$R_3Si^*SSi^*R_3$ displays a dominant positive first primary Cotton effect paralleling that of the halogen and oxygen compounds. The basis of this behavioral difference within the same configuration Si–S family is not understood.[36]

The basis of the intensified Cotton effect activity of disilthiane, $(-)$-$R_3Si^*SSi^*R_3$, and disiloxane, $(-)$-$R_3Si^*OSi^*R_3$, relative to the monosilanes, is not clear at present. However, as indicated above, further studies show that Cotton effect activity is intensified by replacement of OCH_3 in $(+)$-$R_3Si^*OCH_3$ by $OC(CH_3)_3$,[20] and so it is possible that steric effects are, at least in part, involved. Restriction of conformational freedom would appear to be a reasonable cause for Cotton effect intensification. However, the disilazane, $(-)$-$R_3Si^*NHSi^*R_3$, displays Cotton effects considerably weaker than the disiloxane and the disilthiane.

Clearly, further work and greater knowledge of the structural and electronic nature of R_3Si^*X molecules are needed to provide a completely satisfactory framework of interpretation of the ORD and CD behavior of R_3Si^*X.

As the present results demonstrate, positive first primary Cotton effects, positive long-wavelength Cotton effects, as well as positive long-wavelength plain dispersion curves (at >320 mμ) normally relate to the $(+)$-R_3Si^*H configuration. However, for certain compounds, the weak positive long-wavelength Cotton effect may be superimposed on a *negative* ORD background curve due to either intermediate *negative* secondary Cotton effects (*e.g.*, $(-)$-$R_3Si^*SSi^*R_3$) or to *negative* primary Cotton effects which dominate the spectrum (*e.g.*, $(-)$-R_3Si^*SH, $(-)$-$R_3Si^*SCH_3$). Thus, special caution must be exercised when X is large and/or different in electronic nature relative to that in reference R_3Si^*X compounds.

For variance of X beyond that involved in the present study, further deviations from the general behavioral pattern set by X = H, F, Cl, OH, and OCH_3 may be engendered. Due to the possibility of weak Cotton effects superimposed on oppositely signed rotational background curves, and due to the usual multiplicity of secondary and primary Cotton effects, *CD spectra seem virtually essential for clear identification of Cotton effects of R_3Si^*X and similar structures.*

Experimental Section

ORD, CD, and uv absorption spectra were determined on a Durrum-JASCO Model ORD/UV/CD-5 instrument, using a 450-W xenon lamp. The optical system, employing a double-prism monochromator, was continuously flushed with nitrogen. The temperature of the sample compartment was 29 ± 1° during operation. Slit width over the entire wavelength range used (700–200 mμ) was varied according to an instrumental program, and it together with the photomultiplier voltage were recorded simultaneously with the spectral measurements. The photomultiplier voltage served to monitor the adequacy of light transmittance for optical rotation and differential absorption measurements. Fused silica cells with 5- and 1-mm path lengths were used. Spectroquality cyclohexane (Matheson Coleman and Bell) was used as solvent for all runs, with sample concentration ranges for ORD and CD spectra given in Table II. For uv absorption curves down to 210 mμ using a 1-mm path length, concentrations ranged down to *ca.* 10^{-4} *M*.

Normal operating procedure was comprised of long-wavelength (700 to *ca.* 330 mμ) scans using the initial sample concentration and the 5-mm cell, and subsequent scans penetrating into the absorption region of the spectrum using the 1-mm cell and successively diluted solutions. In the absorption region, a chart wavelength scale of 2 mμ/cm was usually used with slow scanning speeds. The limit of each progressive scan was determined by its particular absorbance, the normal maximum allowed being *ca.* 2. Successive dilutions were usually by a factor of 0.5 (checked by absorbance), and ORD, CD, and absorption curves of each sample were determined. Intermediate and final concentrations were checked, by their absorbances, against independently prepared standard solutions. Each scan was set up to overlap with a significant portion of the preceding scan. This procedure and/or replicate runs served to check for the reproducibility of the curves. The normal instrumental settings for scans in the absorption region were: $(\pm)20° \times 10^{-3}$/full scale for ORD, and $(\pm)0.002\ \Delta A$/full scale for CD. All measurements were subjected to blank corrections, and the reported curves are composites of the data afforded by the partial scans and processed according to standard equations.

Molecular rotations were calculated using the equation

$$[\phi]_\lambda = \frac{\alpha_\lambda M}{cl}$$

where α_λ is the observed rotation (degrees) at wavelength λ, *M* is the molecular weight of the compound, *c* is the concentration in grams/100 ml, and *l* is the cell path length in decimeters. Molecular absorptivities were calculated using the equation

$$\varepsilon = \frac{A}{c'l'}$$

where *A* is the absorbance, *c′* is the molar concentration, and *l′* is the cell path length in centimeters.

Molecular ellipticities, $[\theta]_\lambda$, were calculated using the relationship

$$[\theta]_\lambda = 2.303\,\frac{4500}{\pi}\,\Delta\varepsilon_\lambda$$

where

$$\Delta\varepsilon_\lambda = \frac{\Delta A_\lambda}{c'l'}$$

in which ΔA_λ is the observed difference in absorbance between left and right circularly polarized light, *i.e.*, $(A_L - A_R)$ at wavelength λ, *c′* is the molar concentration, and *l′* is the path length in centimeters.

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(33) C. W. N. Cumper, A. Melnikoff, and A. I. Vogel, *J. Chem. Soc., A*, 242 (1966).

(34) H. Gilman, W. H. Atwell, and G. L. Schwebke, *J. Organometal. Chem.*, **2**, 369 (1964).

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

(36) It should be noted that the uv data given for Si–S compounds in ref 33 indicate that, in contrast to Me_3SiSMe, the corresponding disilthiane, $Me_3SiSSiMe_3$, does not display a uv maximum near 224 mμ, but evidently only a normal independent sulfur transition at 202.5 mμ (log ε 3.46). The absence of such an Si–S chromophore in optically active $R_3Si^*SSi^*R_3$ could account for its differing primary Cotton effect behavior relative to R_3Si^*SH and $R_3Si^*SCH_3$, which may bear that chromophore. A further possible basis for difference may be the fact that $R_3Si^*SSi^*R_3$ contains *two* naphthyl groups which may be operating as degenerate coupled oscillators.