

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY, SCHENECTADY, N. Y.]

Intramolecular Interactions between Nonbonded Chromophores. The Spectra of Some Phenylsilanes and Siloxanes

BY JOHN F. BROWN, JR., AND PAUL I. PRESCOTT

RECEIVED MAY 23, 1963

The ultraviolet spectra of the polyphenylated silanes and siloxanes, like those of the polyphenylated paraffins and the paracyclophanes, show considerable variations in the appearance of the 250–270 $m\mu$ band, particularly as regards the absolute and relative intensities of the different peaks in the vibrational structure. These variations were studied in detail, with particular emphasis on those in the spectra of the polycyclic phenylsilanes-quinoxanes, where the relative orientations of the benzenoid chromophores could be specified quite precisely. It was found that all the observed variations in peak heights could be related to variations in the absolute and relative intensities of the two overlapping systems which make up the observable 1L_b absorption. In the polyphenylsilanes-quinoxanes, these intensity variations in turn could be accounted for quantitatively in terms of two types of intramolecular electrostatic interactions, namely, induced dipole-dipole (or polarizability) interactions, which affect both the vibrationally induced and the substituent-induced components of intensity, and static dipole-induced dipole interactions (field effects), which affect only the substituent-induced component. The spectra of the diphenylsiloxanes were found to differ somewhat from those silanes and siloxanes carrying only one phenyl group per silicon, apparently as a result of weak bonding interactions between the two phenyls attached to the same silicon. Within the series of diphenylsiloxanes, however, the intensity variations were similar to those in the phenylsilanes-quinoxanes and could be related qualitatively to the same two types of intramolecular interactions between nonbonded phenyl chromophores.

Introduction

The near-ultraviolet spectra of the polyphenylated silanes and siloxanes show noticeable variations from each other and from the analogous monophenylated species, particularly as regards the absolute and relative intensities of the vibrational peaks in the 250–270 $m\mu$ region.^{1–5} Similar variations have long been known in the spectra of polyphenylated paraffins,^{6–8} polyphenylated ethers,⁸ and the higher paracyclophanes^{8,9} and have usually been ascribed qualitatively to the existence of weak bonding interactions between the phenyl rings.^{8,10}

The present study was undertaken in order to obtain more detailed characterization of these spectral variations, and to attempt their interpretation.

At the outset, we recognized that part of the spectral variations must arise from induced dipole-dipole, or polarizability, interactions between proximate but nonbonded chromophores in the same molecule. These are the interactions that may cause wave length shifts (bathochromism or hypsochromism) in dye aggregates and molecular crystals^{11,12} and intensity changes (hypochromism or hyperchromism) in these species, in double chain polynucleotides,¹³ and in helical polypeptides.¹⁴ Detailed expressions for calculating these interactions have recently been reported.¹³ Accordingly, we decided to carry out such calculations on our polyphenylated species in order to find out what portion of the observed spectral variations they could account for.

(1) C. A. Burkhard and E. H. Winslow, *J. Am. Chem. Soc.*, **72**, 3276 (1950).

(2) H. Gilman and G. E. Dunn, *ibid.*, **72**, 2178 (1950).

(3) E. A. Braude, *J. Chem. Soc.*, 1068 (1952).

(4) M. Horák, B. Schneider, and V. Bažant, *Collection Czech. Chem. Commun.*, **24**, 3381 (1959).

(5) T. Uriu and T. Hakamada, *Kogyo Kagaku Zasshi*, **62**, 1421 (1959).

(6) W. R. Orndorff, R. C. Gibbs, S. A. McNulty, and C. V. Shapiro, *J. Am. Chem. Soc.*, **49**, 1541 (1927).

(7) A. E. Gillam and D. H. Hey, *J. Chem. Soc.*, 1170 (1939).

(8) D. J. Cram, N. L. Allinger, and H. Steinberg, *J. Am. Chem. Soc.*, **76**, 6132 (1954).

(9) D. J. Cram and M. F. Antar, *ibid.*, **80**, 3103 (1958).

(10) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy," Edward Arnold, Ltd., London, 1954, p. 120.

(11) D. P. Craig, *J. Chem. Soc.*, 2302 (1955).

(12) M. Kasha, *Rev. Mod. Phys.*, **31**, 162 (1959).

(13) I. Tinoco, *J. Am. Chem. Soc.*, **82**, 4785 (1960), and correction, *ibid.*, **83**, 5047 (1961). Corrected equation independently derived by W. Rhodes, *ibid.*, **83**, 3609 (1961).

(14) I. Tinoco, A. Halpern, and W. T. Simpson, "Polyamino Acids, Polypeptides, and Proteins," M. A. Stehman, Ed., University of Wisconsin Press, Madison, Wis., 1962, p. 147.

The calculation of polarizability interactions requires that the system be specified in detail as to the relative positions and orientations of the interacting chromophores and also as to the wave lengths, intensities, and transition vector orientations of all bands near to that being observed.¹³ This requirement indicated that the calculations would be most meaningful in the case of the polyphenylsilsequioxanes.¹⁵ In these molecules the relatively rigid fused ring structures allow the mean relative positions of the phenyl chromophores to be estimated fairly precisely, steric compressions and conformation-sensitive hyperconjugative effects which might distort the spectral characteristics of the individual chromophores are absent, and the chromophores belong to a group (monosubstituted benzenes) for which reliable spectral data and interpretations exist over a wide range of wave lengths.

There remains, however, one peculiarity of the 250–280 $m\mu$ band system in C_6H_5X species which must be dealt with before quantitative interpretations of intensity variations can be made. This is the long-known fact that the observed absorption arises from two different series of bands.^{16,17} These are the vibrationally-induced band series, having frequencies $\nu_0 + \nu_{e2g} + n\nu_{vib}$, and the substituent-induced series, having frequencies $\nu_0 + n\nu_{vib}$. The reasons for the two series are that the 1L_b benzenoid transition at ν_0 is symmetry forbidden, becoming active only as the 6-fold symmetry of the ring orbitals is distorted, and that suitable distortions are produced both by e_{2g} ring vibrations and also by ring substitution. Thus, any observed absorption in the system, *e.g.*, the total integrated absorption intensity indicated by the oscillator strength, f , must be regarded as made up of two components: a vibrationally induced intensity component (*e.g.*, f_v) and a substituent-induced component (*e.g.*, f_q). Since these two intensity components respond in different ways to structural variations, they must be separated and dealt with individually in our interpretations.

In the past, the procedure for resolving a C_6H_5X f value into f_v and f_q has been to interpolate between the f values of C_6H_6 and *sym*- $C_6H_3X_3$ (in both of which f_q is zero) in order to estimate the f_v and then to subtract this from the f to obtain f_q .¹⁷ This procedure is inherently inapplicable to species of the type $(C_6H_5X)_x$. The alternative procedure used in the present study (*vide infra*) was based upon an analysis of the intensity distributions within individual spectra. This not only overcame the limitations of the older procedure, but also, at least in the case of the monomeric and polymeric monophenylsilicon compounds, provided considerably more precise values of f_v and f_q as well.

Experimental and Calculations

Measurements.—All spectra were measured with a Cary Model 14-MS recording spectrometer in a room held at $25 \pm 0.5^\circ$. It was established that the response of this instrument varied linearly with phenylsilsequioxane concentration, and thenceforth all spectra were measured on solutions containing 2×10^{-3} equiv. per l. of phenyl groups. Except as noted, all spectra were measured 3–6 times on individually prepared solutions in order to make certain that the recorded extinction coefficients could be duplicated to $\pm 0.5\%$. No attempt was made to obtain wave length measurements

of comparable precision; however, the data recorded are all believed to be reliable to 0.5 $m\mu$.

The compounds studied in this investigation were mostly crystalline solids; these were purified by recrystallization before use. The liquid species were purified by vapor phase chromatography. The solvent used in all the work reported was spectrograde chloroform, which contains a trace of ethanol as a preservative. The use of pure (ethanol-free) chloroform and of tetrahydrofuran was examined briefly and then abandoned because of the peroxidation problem. However, no indications were found that the spectra determined in these solvents differed from those determined in spectrograde chloroform; the small shifts in wavelength and relative peak heights recorded below for the compounds $(PhSiO_{3/2})_8$, $(PhSiO_{3/2})_{12}$, and $(PhSiO_{3/2})_{1300}$ were all observed in tetrahydrofuran solutions as well.

The data recorded below are λ_0 , the wave length in $m\mu$ of the O–O transition in the 1L_b system; ϵ -values, the molar extinction coefficients ($M^{-1} \text{ cm}^{-1}$) per phenyl group at λ_0 and at the next three prominent maxima, which are displaced about 6, 11, and 17 $m\mu$ from λ_0 ¹⁸; and f , the total oscillator strength of the 1L_b transition. This last was calculated from the usual formula^{11,14}

$$f = \frac{2303mc^2}{\pi e^2 N} \int \epsilon d\nu = 4.32 \times 10^{-9} \int \epsilon d\nu \quad (1)$$

where ν is the frequency in cm^{-1} . The problem of overlap between the 270 $m\mu$ (1L_b) system and the 210 $m\mu$ (1L_a) system was dealt with by arbitrarily assuming that the portion of the 270 $m\mu$ system that lay below the wave length of minimum total absorption was equal to the portion of the 210 $m\mu$ system that lay above it; *i.e.*, the limit of integration on the short wave length end of the 1L_b system was taken as the absorption minimum. This assumption may conceivably have introduced 1–2% errors in the recorded f values, particularly those for the Ph_2SiX_2 compounds, but probably did not alter the relative values of f within either the $PhSiX_3$ or the Ph_2SiX_2 series.

The data recorded were: Phenyltrimethylsilane: λ_0 , 269.5; ϵ -values, 115, 195, 227, 163; f , 28.5×10^{-4} . 1,1,1,3,5,5,5-Heptamethyl-3-phenyltrisiloxane: λ_0 , 270.0; ϵ -values, 193, 274, 267, 184; f , 36.5×10^{-4} . Octaphenylpentacyclo[9.5.1.1^{3,9}.1^{5,17}.1^{7,13}]-octasiloxane ("phenyl- T_8 , m. 500⁰"); λ_0 , 269.5; ϵ -values, 335, 423, 336, 216; f , 50.3×10^{-4} . Decaphenylhexacyclo[9.9.1.1^{3,9}.1^{5,17}.1^{7,15}.1^{13,19}]-decasiloxane ("phenyl- T_{10} , m. 418⁰"); λ_0 , 269.7; ϵ -values, 325, 412, 333, 213; f , 49.2×10^{-4} . Non-crystalline isomer of phenyl- T_{12} ,¹⁵ presumably largely dodecaphenylheptacyclo[11.11.1.1^{3,11}.1^{5,21}.1^{7,19}.1^{9,17}.1^{17,23}]-dodecasiloxane: λ_0 , 270.0; ϵ -values, 305, 388, 316, 207; f , 47.7×10^{-4} . Dodecaphenylheptacyclo[13.9.1.1^{3,13}.1^{5,11}.1^{7,21}.1^{9,19}.1^{17,23}]-dodecasiloxane ("phenyl- T_{12} , m. 385⁰"); λ_0 , 270.0; ϵ -values, 301, 385, 317, 206; f , 46.7×10^{-4} . Phenylsilsequioxane "prepolymer" fraction,¹⁵ \bar{P}_n 24, approximately (Ma)₂ according to the proposed scheme¹⁹ for describing partially ordered network polymers: λ_0 , 270.0; ϵ -values, 324, 407, 327, 209; f , 48.3×10^{-4} . Phenylsilsequioxane "prepolymer" fraction,¹⁵ \bar{P}_n 84, approximately MaDa₃₀Ma in network polymer description: λ_0 , 270.0; ϵ -values, 329, 409, 323, 205; f , 48.6×10^{-4} . Phenylsilsequioxane high polymer,^{19,20} $[\eta]$ 3.25 dl./g., \bar{P}_n 1300, approximately Ma₃TaDa₆₀ in network polymer description: λ_0 , 270.0; ϵ -values, 337, 415, 323, 204; f , 49.3×10^{-4} . 5-Phenyltriptych-silazolidine²¹: λ_0 , 269.0; ϵ -values, 126, 214, 245, 176; f , 31.3×10^{-4} . 3,3-Diphenyl-1,1,1,5,5,5-hexamethyltrisiloxane: λ_0 , 270.0; ϵ -values, 234, 321, 303, 212; f , 42.5×10^{-4} . 1,1,1,7,7,7-Hexamethyl-3,3,5,5-tetraphenyltetrasiloxane: λ_0 , 270.0; ϵ -values, 242, 325, 304, 212; f , 42.9×10^{-4} . 1,1,1,9,9,9-Hexamethyl-3,3,5,5,7,7-hexaphenylpentasiloxane: λ_0 , 270.0; ϵ -values, 258, 340, 310, 213; f , 44.0×10^{-4} . Linear high copolymers of diphenylsiloxane and dimethylsiloxane units containing 67–75

(18) Our resolutions of f values into f_v values and f_q values required sets of ϵ -values measured at fixed frequency displacements from ν_0 . In principle, ϵ_{\max} values need not represent such sets. We found, however, that the tops of the four peaks from which our ϵ_{\max} values were taken were wider than the variations in the displacements of any of the last three from the first. This meant that our ϵ_{\max} values were within experimental error of being equivalent to fixed displacement sets. Since ϵ_{\max} values are both more easily measured and also more commonly used in other connections, it seemed convenient to use them exclusively in this study.

(19) J. F. Brown, Jr., *J. Polymer Sci.*, **1C**, 83 (1963).

(20) J. F. Brown, Jr., L. H. Vogt, Jr., A. Katchman, J. W. Eustance, K. M. Kiser, and K. W. Krantz, *J. Am. Chem. Soc.*, **82**, 6194 (1960).

(21) C. L. Frye, G. E. Vogel, and J. A. Hall, *ibid.*, **83**, 996 (1961).

(15) J. F. Brown, Jr., L. H. Vogt, Jr., and P. I. Prescott, *J. Am. Chem. Soc.*, **86**, 1120 (1964).

(16) A. L. Sklar, *J. Chem. Phys.*, **10**, 135 (1942).

(17) J. Petruska, *ibid.*, **34**, 1120 (1961).

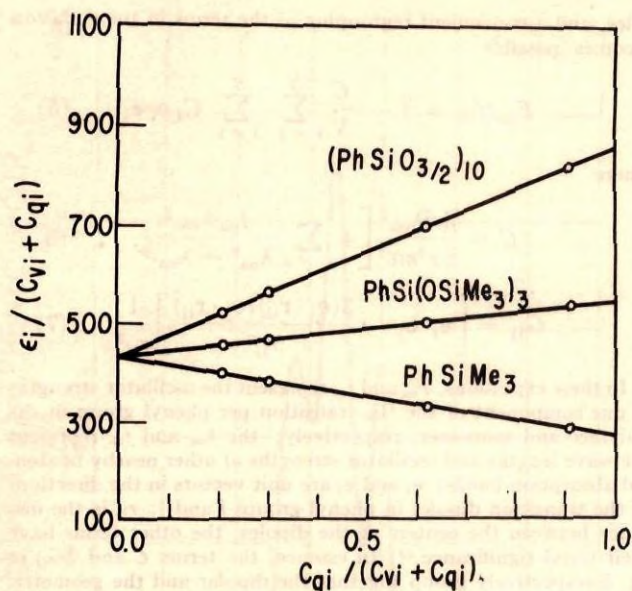


Fig. 1.—Plots of relative intensity, $\epsilon_i/(C_{vi} + C_{qi})$, vs. relative contribution of substituent-induced intensity, $C_{qi}/(C_{vi} + C_{qi})$, for some monophenylsilicon compounds.

mole % diphenylsiloxane (average of three closely agreeing sets of data): λ_0 , 270.0; ϵ -values, 280, 361, 316, 213; f , 46.1×10^{-4} . 2,2-Dimethyl-4,4,6,6-tetraphenylcyclotrisiloxane: λ_0 , 270.5; ϵ -values, 309, 401, 348, 240; f , 51.2×10^{-4} . Hexaphenylcyclotrisiloxane: λ_0 , 271.0; ϵ -values, 316, 404, 344, 235; f , 51.4×10^{-4} . 2,2-Dimethyl-4,4,6,6,8,8-hexaphenyl-cyclotetrasiloxane: λ_0 , 270.5; ϵ -values, 275, 364, 325, 223; f , 46.4×10^{-4} . Octaphenylcyclotetrasiloxane: λ_0 , 271.0; ϵ -values, 282, 368, 326, 224; f , 47.9×10^{-4} . 2,2,4,4,6,6-Hexaphenyl-8,8,10,10-tetramethylcyclopentasiloxane: λ_0 , 270.5; ϵ -values, 254, 335, 306, 210; f , 42.7×10^{-4} . 2,2,4,4,8,8,10,10-Octaphenyl-6,6,12,12-tetramethylcyclohexasiloxane: λ_0 , 271.0; ϵ -values, 260, 343, 309, 213; f , 44.5×10^{-4} .

Resolution of f_v and f_q .—The procedure for resolving f into f_v and f_q was based upon the premise that within a series of closely related C_6H_5X species the distributions of intensity among the different vibrational levels should remain constant within either the vibrationally induced or the substituent-induced systems. Thus, the observed intensity at any point in the spectrum should always be the sum of a fixed proportion of the total vibrationally induced intensity and another fixed proportion of the total substituent-induced intensity, and these two intensity components should be calculable from observations of relative intensities at different points in the spectrum.¹⁸

In making such calculations of f_v and f_q from the ϵ 's and f 's, it was found convenient to introduce the quantities V and Q to represent the total contributions of vibrationally induced and substituent-induced intensity to the measured ϵ -values (*i.e.*, for the spectrum of compound j measured at points i , $V_i + Q_i = \sum \epsilon_{ij}$); and also the coefficients C_{vi} and C_{qi} representing the fraction of the total V or Q operating at point i . Thus, our basic premise was that relations

$$\epsilon_{ij} = C_{vi}V_j + C_{qi}Q_j \quad (2)$$

where all the C_{vi} and C_{qi} values are constants, should describe all of the observed extinction coefficients.

In order to solve eq. 2 for the C_{vi} and C_{qi} values, which is necessary in order to determine the V and Q values, and thence the f_v and f_q values, it was necessary to have two more pieces of information than could be provided by measurements of ϵ_{ij} . Those used were: First, C_v (270 $m\mu$) was assumed to be 0.17 C_v (265). The basis for this was that the vibrationally induced component of intensity is known to be inactive in the O—O transition itself,¹⁷ and hence the only intensity observable in this component at λ_0 must be that resulting from the edge of the first allowed transition 4 $m\mu$ away. Examination of the band contours in several benzenoid spectra showed that the intensity at a point 4 $m\mu$ above the first allowed band was generally quite close to 0.17 of that band intensity. The precision of this figure is not very critical, since C_v (270 $m\mu$) is only about 0.03. Second, it was as-

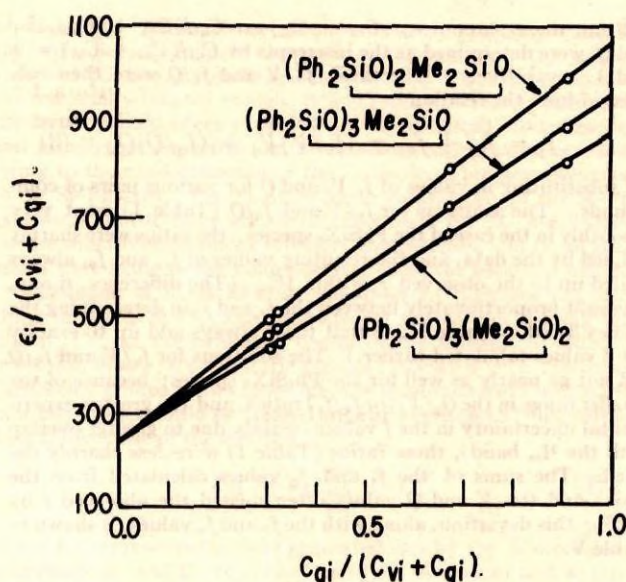


Fig. 2.—Plots of relative intensity, $\epsilon_i/(C_{vi} + C_{qi})$, vs. relative contribution of substituent-induced intensity, $C_{qi}/(C_{vi} + C_{qi})$, for some diphenylsilicon compounds.

sumed that the V_j values were approximately equal in certain compounds where there was no reason to expect variations due to hypochromism or change in the substituent type. The bases for this assumption were, first, that normally there is very little total variation in f_v anyway, and, second, that examination of the data showed groups of compounds in both the $PhSiX_3$ and Ph_2SiX_2 series that had the same V within experimental error; *i.e.*, by subtracting the ϵ -values of one compound from the corresponding ones of another (thus eliminating the $C_{vi}V$ terms in eq. 2) sets of C_{qi} values resulted which were the same for all pairs in the group.

The solutions for the C_{vi} and C_{qi} values calculated from the measured extinction coefficients and from these two assumptions are shown in Table I.

TABLE I
DISTRIBUTIONS OF INTENSITY WITHIN THE VIBRATIONALLY- AND SUBSTITUENT-INDUCED COMPONENTS OF THE 1L_b TRANSITION IN PHENYLSILICON COMPOUNDS

Point of measurement (peak), $m\mu$	PhSiX ₃ species		Ph ₂ SiX ₂ species	
	C_v	C_q	C_v	C_q
270	0.038	0.363	0.027	0.286
264	.226	.369	.160	.343
259	.412	.182	.493	.217
253	.324	.086	.320	.154
Total	1.000 V	1.000 Q	1.000 V	1.000 Q
Ratio f_v/V	4.39×10^{-6}		4.2×10^{-6}	
Ratio f_q/Q	3.555×10^{-6}		3.85×10^{-6}	

The validity of these values, and of the basic premise that a single set of intensity distribution coefficients could relate all of the variations in the ϵ 's to variations in V and Q , was checked by plotting relative intensities, $\epsilon_{ij}/(C_{vi} + C_{qi})$, against relative contributions of substituent-induced intensity, $(C_{qi}/C_{vi} + C_{qi})$. Examples of such plots are shown in Fig. 1 and 2. The expected linearity was obtained in almost all cases. The exceptions were, first, one sample of phenylsilsesquioxane high polymer where the deviation was eventually traced to the presence of traces of bi-phenyl-type impurities and, second, the diphenyltrisiloxane, $Me_3SiO(Ph_2SiO)_3SiMe_3$, where the curvature was sufficient to indicate that the C_{vi} and C_{qi} values were appreciably different from those in the other diphenylsiloxanes. The linear pentasiloxane $Me_3SiO(Ph_2SiO)_5SiMe_3$ gave a normal fit, but the tetrasiloxane $Me_3SiO(Ph_2SiO)_4SiMe_3$ was intermediate between the clearly deviant trisiloxane and the pentasiloxane. It was not possible to solve for the C_{vi} and C_{qi} values in these two deviant diphenylsiloxanes; however, the values of V determined from the best lines through the points were the same as those for most of the other diphenylsiloxanes, indicating that the f_v values were probably unaffected.

From these plots of $\epsilon_{ij}/(C_{vi} + C_{qi})$ vs. $C_{qi}/(C_{vi} + C_{qi})$, V_i and Q_i were determined as the intercepts at $C_{qi}/(C_{vi} + C_{qi}) = 0$ and 1, respectively. The ratios f_v/V and f_q/Q were then calculated from the relation

$$f_j = f_{vj} + f_{qj} = (f_v/V)V_j + (f_q/Q)Q_j \quad (3)$$

by substituting in values of f , V , and Q for various pairs of compounds. The solutions for f_v/V and f_q/Q (Table I) went very smoothly in the case of the PhSiX_3 species; the ratios were sharply defined by the data, and the resulting values of f_{vj} and f_{qj} always added up to the observed f_j within 1%. (The difference, if any, was split proportionately between the f_v and f_q in determining the values listed in Table II, so that these always add up to exactly the f values tabulated earlier.) The solutions for f_v/V and f_q/Q did not go nearly as well for the Ph_2SiX_2 species; because of the smaller range in the Q_i/V_i (or f_{qj}/f_{vj}) ratios, and the greater experimental uncertainty in the f values (mainly due to greater overlap with the $^1\text{L}_a$ band), these ratios (Table I) were less sharply defined. The sums of the f_v and f_q values calculated from the ratios and the V and Q values often missed the observed f by 1–2%; this deviation, along with the f_v and f_q values, is shown in Table V.

TABLE II

WAVE LENGTHS AND INTENSITIES (PER PHENYL GROUP) OF $^1\text{L}_b$ TRANSITIONS IN MONOPHENYLSILANES AND SILOXANES IN CHLOROFORM AT 25°

Compound	λ_0 , m μ	$f_v \times 10^4$	$f_q \times 10^4$
PhSiMe_3	269.5	18.9	9.6
$\text{PhSiMe}(\text{OSiMe}_3)_2$	270.0	19.3	17.2
$\text{PhSi}(\text{OSiMe}_3)_3$	269.5	18.9	19.3
$(\text{PhSiO}_{1/2})_8$, m. 500°	269.5	19.0	31.2
$(\text{PhSiO}_{1/2})_{10}$, m. 418°	269.7 ^d	18.9	30.3
$(\text{PhSiO}_{1/2})_{12}$, noncryst. ^a	270.0	18.8	28.5
$(\text{PhSiO}_{1/2})_{12}$, m. 385°	270.0	18.7	28.0
$(\text{PhSiO}_{1/2})_n$, $\bar{n} = 24^b$	270.0	18.4	29.9
$(\text{PhSiO}_{1/2})_n$, $\bar{n} = 84^b$	270.0	17.8	30.8
$(\text{PhSiO}_{1/2})_n$, $\bar{n} = 1300^c$	270.0	17.4	31.9
$\text{PhSi}(\text{OCH}_2\text{CH}_2)_3\text{N}^a$	269.0	20.6	10.7

^a Single value determination. ^b "Prepolymer" fraction, further identified in Experimental section. ^c Double chain ("ladder") polymer. ^d Value left unrounded in order to avoid indicating a discontinuity in the wave length progression along the series.

Calculation of q .—The transition-moment parameter q , which measures the displacement of charge from the substituent to the ring during the transition, was calculated according to the formula¹⁷

$$q = \left(\frac{3hf_q}{8\pi^2mc\nu_0} \right)^{1/2} = (9.22 \times 10^{-12}f_q\lambda_0)^{1/2} \quad (4)$$

where λ_0 is given in cm. In determining the sign of q for the $-\text{SiMe}_3$ group, use was made of the report that the two strongest bands in anisole are both reduced about 20% upon addition of a p - SiMe_3 substituent.²² Since the q for methoxy is $+21 (\times 10^{10} \text{ cm.})$,¹⁷ this indicated a value of roughly -3 for $-\text{SiMe}_3$, showing that the sign of the more precise value, ± 4.9 , determined from eq. 4 must be negative. Since electron-withdrawing substituents on silicon should make q more negative,¹⁷ it was evident that the signs of the larger q values calculated for the siloxanes should be negative as well. The sign was also presumed to be negative for the triptych-siloxazolidine substituent, since the absolute value of the q was about the same as for $-\text{SiMe}_3$, and the two substituents are known to be the same in ground-state electronegativity.²¹

Calculation of Polarizability Interactions.—The effects of polarizability interactions upon the absorption intensities f_v and f_q were calculated from Tinoco's equation 1.¹³ For $^1\text{L}_b$ bands in $(\text{C}_6\text{H}_5\text{X})_x$ species, these effects are produced by interactions between the dipoles of the $^1\text{L}_b$ system components in one ring and those of $^1\text{L}_a$ and ^1B polarizations in other rings. Since these last are both doubly degenerate in the plane of the ring, they are both related in the same way geometrically to the $^1\text{L}_b$ transition di-

poles, and a convenient regrouping of the terms in the equation becomes possible

$$F_{oa}/f_{oa} = 1 - \frac{C}{N} \sum_{i=j}^N \sum_{j \neq i}^N G_{ij} \mathbf{e}_i \cdot \mathbf{e}_j \quad (5)$$

where

$$C = \frac{3e^2\lambda_{oa}^2}{8\pi^2mc^2} \left[4 \sum_{a' \neq a} \frac{f_{oa'}\lambda_{oa'}^2}{\lambda_{oa}^2 - \lambda_{oa'}^2} \right] \quad (6)$$

$$G_{ij} = \left[\mathbf{e}_i \cdot \mathbf{e}_j - \frac{3(\mathbf{e}_i \cdot \mathbf{r}_{ij})(\mathbf{e}_j \cdot \mathbf{r}_{ij})}{r_{ij}^2} \right] \frac{1}{r_{ij}^3} \quad (7)$$

In these expressions, F_{oa} and f_{oa} represent the oscillator strengths of one component of the $^1\text{L}_b$ transition per phenyl group in the polymer and monomer, respectively; the λ_{oa} and f_{oa} represent the wave lengths and oscillator strengths of other nearby benzenoid absorption bands; \mathbf{e}_i and \mathbf{e}_j are unit vectors in the directions of the transition dipoles in phenyl groups i and j ; r_{ij} is the distance between the centers of the dipoles; the other terms have their usual significance.¹³ In essence, the terms C and $\sum G_{ij}$ in eq. 5 respectively group together the dipolar and the geometric factors that determine the magnitude of the hypochromic interaction.

The numerical values substituted in eq. 6 were: λ_{oa} , the center of the $^1\text{L}_b$ system, 2630 Å.; $\lambda_{oa'}$, the center of the $^1\text{L}_a$ system, 2100 Å.; $\lambda_{oa''}$, the center of the ^1B system, 1900 Å.; $f_{oa'}$, $1/2 \times 0.14$ along each of two mutually perpendicular axes; $f_{oa''}$, $1/2 \times 0.80$ along each of two mutually perpendicular axes. The values of $\lambda_{oa'}$ and $\lambda_{oa''}$ were estimated from their values in benzene²³ and the generalization that frequency shifts for the $^1\text{L}_a$ and ^1B systems in substituted benzenes are normally about three times as large as those in the $^1\text{L}_b$ system; this assumption is supported by observation in the case of the 210 m μ band in PhSiMe_3 .³ The values of $f_{oa'}$ and $f_{oa''}$ represent average values for monosubstituted benzenes; the intensities of these transitions in substituted benzenes are known to vary very little from those in benzene itself.¹⁷ These substitutions allowed C to be calculated as $18.6 \times 10^{-24} \text{ cm.}^3$. This value was used without rounding in the calculations described below; however, the uncertainties in the far-ultraviolet λ and f values probably limit its reliability to $\pm 10\%$. This value of C , incidentally, should be about the same for the polyphenylated hydrocarbons and other $(\text{C}_6\text{H}_5\text{X})_x$ species where X has only a modest conjugative ability.

In calculating the geometrical factors by eq. 7, it was assumed that the transition dipoles for $^1\text{L}_a$, ^1B , and the vibrationally-induced component of $^1\text{L}_b$ were centered at the center of the ring, and that each of these doubly degenerate transitions could be represented by two perpendicular dipoles lying in the plane of the ring. The transition dipole for the substituent-induced component of $^1\text{L}_b$ was assumed to be centered at the ring carbon bearing the silicon and directed along the C-Si axis; the $^1\text{L}_a$ and ^1B dipoles in other rings that interact with this dipole were assumed to lie as nearly parallel with this dipole as the orientation of their rings would allow. In calculating the distances and angles, it was assumed that the polycyclic silsesquioxanes in solution would adopt a conformation in which all \angle s OSiO and OSiC were 109.5° ; all \angle s SiOSi were equal; all phenyl rings were regular plane hexagons; and the interatomic distances were Si-O, 1.62 Å.; Si-C, 1.88 Å.; and C-C, 1.40 Å. Typical geometrical parameters calculated were: $(\text{PhSiO}_{1/2})_8$: silicon atoms arranged as at the vertices of a cube¹⁵ with phenyls projecting out along the diagonals; \angle s SiOSi , 148.5° ; \angle s between neighboring Si-Ph axes, 70.5° ; distance between centers of neighboring Ph's, 6.96 Å. $(\text{PhSiO}_{1/2})_{10}$: Si's arranged as at vertices of a pentagonal prism¹⁵ having squares and regular pentagons as faces; \angle s SiOSi , 154° ; \angle s between neighboring Ph-Si's, 60° (2), 65° (1); distances between centers of nearest phenyls, 6.49 Å. (2), 6.74 Å. (1). $(\text{PhSiO}_{1/2})_{12}$: Si's arranged as at vertices of a hexagonal prism¹⁵ having squares and regular hexagons as faces; \angle s SiOSi , 154° ; \angle s between neighboring Ph-Si's, 50° (2), 65° (1); distances between centers of nearest phenyls, 5.98 Å. (2), 6.74 Å. (1). Phenylsilsesquioxane "ladder" polymer: Si's arranged as in *cis*-syndiotactic double chain,^{18,20} or as in squares joined together at 114° angles; \angle s SiOSi , 154.5° ; \angle s between neighboring Ph-Si's, 115.5° (2), 64.5° (1); distances between centers of phenyls on nearest Si's,

the observed spectra, which generally showed peaks near 270, 264, 259, and 253 $m\mu$, and shoulders near 247.5 and 266 $m\mu$.

The resolution of the total integrated absorption intensity into the components f_v and f_q , accomplished by analysis of the relative peak heights, gave the results shown in Table II. The practicability of such a resolution (Fig. 1, 2) indicated that all of the observed variations in the absolute and relative heights of the peaks at 270, 259, and 253 $m\mu$ could be attributed to variations in the absolute and relative values of f_v and f_q .

The calculated effects of polarizability interactions on f_v and f_q are shown in Table III. These showed

TABLE III
CALCULATED PER CENT HYPOCHROMISM^a IN 1L_b TRANSITION
COMPONENTS OF PHENYLSILSESQUIOXANES

Compound	Assumed structure	Component	
		f_v	f_q
(PhSiO _{3/2}) ₈	Cube	0	-0.8
(PhSiO _{3/2}) ₁₀	Pentagonal prism	1	2.3
(PhSiO _{3/2}) ₁₂	Hexagonal prism	2	4.7
(PhSiO _{3/2}) _n	"Ladder"	9	9.0

^a Reduction in absorption intensity of polymer relative to that of monomer (e.g., isolated PhSiO_{3/2} unit).

that the effect of such interactions was hypochromic in all cases except for the f_q component of (C₆H₅SiO_{3/2})₈, where a weak hyperchromism was indicated. The values of phenylsilsesquioxane f_v and f_q corrected for hypochromism or hyperchromism are given in Table IV, along with the values of the substituent constant q^{17} and comparative values of f_v , f_q , and q for some other phenylsilanes and nonsilicon¹⁷ C₆H₅X species.

TABLE IV
CORRECTED^a VALUES FOR 1L_b INTENSITY PARAMETERS IN PHENYLSILANES, PHENYLSILOXANES, AND OTHER MONOSUBSTITUTED BENZENES

Compound	$f_v \times 10^4$	$f_q \times 10^4$	q (cm. $\times 10^{10}$)
A. Tetracoordinated silicon compounds			
PhSiMe ₃	18.9	9.6	-4.9
PhSiMe(OSiMe ₃) ₂	19.3	17.2	-6.5
PhSi(OSiMe ₃) ₃	18.9	19.3	-6.9
(PhSiO _{3/2}) ₈ , m. 500°	19.1	31.0	-8.8
(PhSiO _{3/2}) ₁₀ , m. 418°	19.1	31.0	-8.8
(PhSiO _{3/2}) ₁₂ , m. 385°	19.0	29.9	-8.6
(PhSiO _{3/2}) _n , "ladder"	19	35.1	-9.4
B. Pentacoordinated silicon compounds			
PhSi(OCH ₂ CH ₂) ₃ N	20.6	10.7	-5.2
C. Other C ₆ H ₅ X's ¹⁷			
PhOH	(20) ^b	154	+20
PhF	17	70	+12.5
PhCl	18	12	+6.0
PhMe	21	10	+5.0
PhH	16.4	0.0	0.0
PhNC	(20) ^b	15	-6
PhCF ₃	20	33	-9
PhCN	(20) ^b	52	-11

^a For hypochromism due to polarizability interactions between different phenyl groups in the same molecule. ^b Assumed value used in estimating f_q .

The f_v values listed in Table IV show that ordinary, tetracoordinated monophenylsilanes and siloxanes have f_v values of $19.1 \pm 0.2 \times 10^{-4}$. This value is in the middle of the range $17-21 \times 10^{-4}$ which has been observed for other C₆H₅X species. Turning to Table II

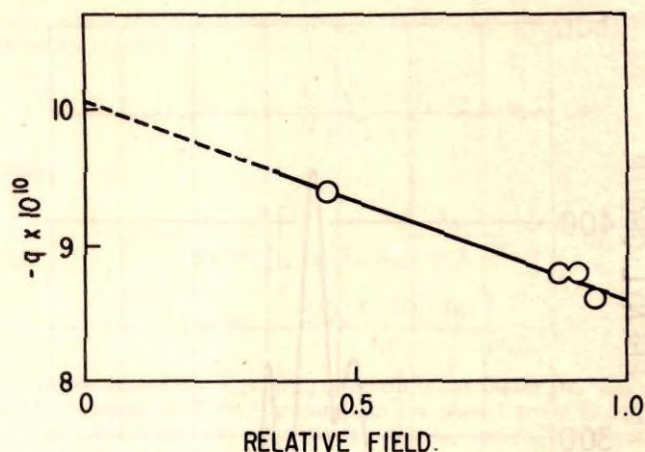


Fig. 4.—Plot of the transition moment parameter q against relative values of intramolecular electrostatic field for four phenylsilsesquioxanes. The relative field is expressed as calculated ΣG_{ij} values in units of 10^{23} cm.⁻³.

with this figure, we find an increasing hypochromism in f_v as we descend the series from (PhSiO_{3/2})₈ to (PhSiO_{3/2})₁₂ to the "prepolymers" to the phenylsilsesquioxane "ladder" high polymer. In the last case, the decline in f_v to 17.4×10^{-4} corresponds to a hypochromism of 9%, which agrees with that calculated and listed in Table III.

Examination of the f_q and q values listed in Table IV shows that silicon always behaves as an electron-withdrawing substituent on benzene undergoing transition to the 1L_b state. Presumably, this occurs because of increased $d\pi-p\pi$ bonding between the aromatic ring and the silicon in the 1L_b state. As expected, the electron-withdrawing power of the silicon substituents increases as the alkyl groups are replaced by siloxys. The -SiO_{3/2} substituent in phenylsilsesquioxanes has an electron-withdrawing power comparable to -CF₃ when measured by the q -value for the 1L_b transition. This electron-withdrawing power is also reflected in its effects on ground-state benzene. We have observed that the phenylsilsesquioxanes are completely resistant to the Ph-Si bond cleavages by halogens and strong acids which are characteristic of the phenyltrialkylsilanes; instead, they undergo slow m -substitution when treated with HNO₃-H₂SO₄ mixtures.

The variations in f_q and q among the phenylsilsesquioxanes are of some interest, particularly in the group (PhSiO_{3/2})₁₀, (PhSiO_{3/2})₁₂, and (PhSiO_{3/2})_x "ladder" polymer. Here, the calculated bond angles and the conformation angles within PhSi(OSi)₃ units are almost identical (with the values for "ladder" falling between those of the decamer and dodecamer) so that it is not possible to invoke alleged differences in the $d\pi-p\pi$ bonding pattern within the siloxane backbone as bases for the variations in q . Instead, it appears that the fields generated by the dipoles of the other PhSiO_{3/2} units in the molecules are responsible. Qualitatively, such field effects would be expected to be similar in nature and magnitude to those produced by varying the substituents on the silicon. We were not able to calculate the absolute magnitude of such field effects upon q ; however, it was possible to calculate the relative fields expected in the different silsesquioxane structures, and to make the comparison of these with q shown in Fig. 4. This shows that q does decline in proportion to the calculated field, and also that the -SiO_{3/2} should

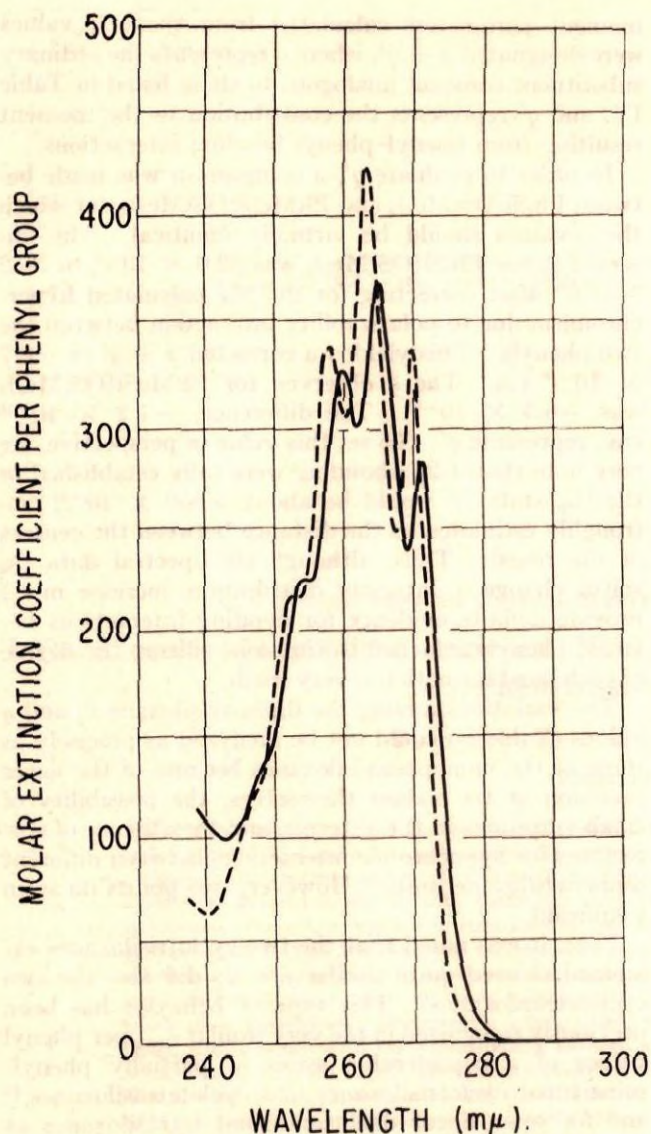


Fig. 5.—Ultraviolet spectra of $(\text{Ph}_2\text{SiO})_4$, solid curve, and $(\text{PhSiO}_{3/2})_8$, dotted curve.

behave as an even more electronegative substituent on ${}^1\text{L}_b$ benzene if a structure could be devised where the adverse field effects of adjacent siloxane units were absent.

The λ_0 values listed in Table II show that only barely measurable variations exist among the different monophenylsilicon compounds. These variations could not be ascribed to induced dipole-dipole interactions. Calculations made with Tinoco's equation A15¹³ showed that the hypsochromism arising from such interactions should be immeasurably small. Nor could any obvious relation between λ_0 and q be found. It was noted, however, that the species in which the C_6H_5 chromophores were more crowded by each other or by other siloxane groups tended to show λ_0 at slightly longer wave lengths than those in which the C_6H_5 's were freely exposed to the medium. The shifts observed were comparable to those produced by changing from one hydrocarbon solvent to another,²⁵ and it seems likely that they resulted simply from variations in the dispersion forces exerted on the chromophores by their local environments.²⁶

Our conclusion from the foregoing data and analysis

- (25) N. D. Coggeshall and A. Pozefsky, *J. Chem. Phys.*, **19**, 980 (1951).
 (26) H. C. Longuet-Higgins and J. A. Pople, *ibid.*, **27**, 192 (1957).

is that in molecular systems containing two or more proximate but nonbonded phenyl chromophores—e.g., in polyphenylated siloxanes, alkanes, ethers, etc., having at least two saturated atoms between the phenyls—the spectral variations in wave length are insignificant, but the variations in peak intensity and intensity distribution are sizable, are capable of characterization in terms of the physical constants f_v and f_q , and are susceptible to detailed interpretation in terms of intramolecular polarizability and polarization effects. One implication of this conclusion is that the ${}^1\text{L}_b$ ultraviolet spectra of such polyphenylated species should be of considerable utility in defining their molecular configurations. Thus, for any proposed configuration, it should be possible to estimate the magnitude of the polarizability and polarization effects according to eq. 5–8, and then to check such estimates against the observed departures of f_v and f_q from their values in structural analogs having isolated phenyl groups.

Diphenylsilicon Compounds.—The 200–300 $\text{m}\mu$ ultraviolet spectra of silanes and siloxanes carrying two phenyl groups per silicon were found to be very similar to those of diphenylmethane⁷ and the higher $[1.n]$ -paracyclophanes⁹; i.e., they showed to a small degree the effects which become marked in the lower $[1.n]$ -paracyclophanes and which are believed to arise from $2p\sigma$ -bonding between the two benzene rings.^{8,27} A typical spectrum is shown in Fig. 5; spectra of some Ph_2SiX species, which are very similar, are given in ref. 2 and 4.

As illustrated in Fig. 5, the appearance of the spectra differs from those of the monophenylsilicon compounds in four respects. First, the ${}^1\text{L}_b$ λ_0 is shifted to longer wave lengths by about 1 $\text{m}\mu$. Second, the edge of the ${}^1\text{L}_a$ rise is shifted to longer wave lengths by about 3 $\text{m}\mu$, thus moving the absorption minimum from 239–240 to 242–243 $\text{m}\mu$. Third, the over-all intensity is increased; e.g., the whole spectrum of $\text{Ph}_2\text{Si}(\text{OSiMe}_3)_2$ is stronger than that of $\text{PhSiMe}(\text{OSiMe}_3)_2$, even making allowance for the presence of two phenyl groups rather than one. Fourth, the distribution of intensity is altered, becoming stronger at the short wave length end of the system and weaker near λ_0 . This change in intensity distribution occurs in both the substituent-induced and the vibrationally induced intensity components (Table I). This indicates that the excited state carbon-carbon distances are slightly greater in the diphenylsilane derivatives than in the monophenylsilicon species. All four of these visible changes represent the expected consequences of $2p\sigma$ (or other) bonding interactions between the rings.

The resolution of the observed oscillator strengths into the components f_v and f_q could not be carried out with as high precision as with the monophenylsilicon compounds, probably because of the effects of the configuration-sensitive bonding interactions upon the f -values and the intensity distributions. However, the values obtained and listed in Table I are still believed to be reliable to 2–3% in most cases.

Examination of the f_v values listed in Table V immediately reveals a drop to about half the value per phenyl ring for the monophenylsilicon species. In other words, the f_v per monomer unit is about the same in the diphenylsiloxanes as in the monophenylsiloxanes,

- (27) P. D. Bartlett and E. S. Lewis, *J. Am. Chem. Soc.*, **72**, 1005 (1950).

despite the presence of two benzene rings rather than one. We offer no explanation for this observation.

The variations among the f_v 's listed in Table V are probably not outside the range of experimental uncertainty except in the case of the linear diphenylsiloxane copolymers, where the low value, indicative of an 8–10% hypochromism in f_v , was confirmed repeatedly. Presumably, even more hypochromism should be present in linear polydiphenylsiloxane itself; however, that material is a highly crystalline, insoluble polymer which cannot be put into solution for study.

TABLE V
WAVE LENGTHS AND INTENSITIES (PER PHENYL GROUP) OF
 1L_b TRANSITIONS IN DIPHENYLSILOXANES IN CHLOROFORM AT
25°

Compound ^a	λ_0 , m μ	f_v $\times 10^4$	f_q $\times 10^4$	Devn. ^b $\times 10^4$	$q + q'$ (cm. $\times 10^{10}$)
Me ₃ SiO(Ph ₂ SiO)SiMe ₃	270.0	10.1	32.0	+0.4	-8.9
Me ₃ SiO(Ph ₂ SiO) ₂ SiMe ₃	270.0	10.1	32.5	+ .3	-9.0
Me ₃ SiO(Ph ₂ SiO) ₃ SiMe ₃	270.0	10.1	33.9	.0	-9.2
(Ph ₂ SiO) ₂ , (Me ₂ SiO) _n , $\bar{n} > 500^c$	271.0	9.1	36.7 ^d	+ .3	-9.6 ^d
(Ph ₂ SiO) ₂ (Me ₂ SiO)	270.5	10.1	40.6	+ .5	-10.0
(Ph ₂ SiO) ₃	271.0	9.3	41.5	+ .6	-10.2
(Ph ₂ SiO) ₄ (Me ₂ SiO)	270.5	10.2	36.4	- .2	-9.5
(Ph ₂ SiO) ₄	271.0	9.9	37.1	+ .9	-9.6
(Ph ₂ SiO) ₃ (Me ₂ SiO) ₂	270.5	10.1	33.3	- .7	-9.1
(Ph ₂ SiO) ₄ (Me ₂ SiO) ₂	271.0	9.9	34.2	+ .4	-9.2

^a Compounds further identified in Experimental section.

^b Deviation of observed value of f from calculated $f_v + f_q$.

^c Linear high copolymers containing 67–75 mole % Ph₂SiO.

^d If corrected for hypochromism due to interactions between phenyls of different Ph₂SiO units, f_q and $q + q'$ would rise to 40.3×10^{-4} and 10.0×10^{-10} cm., respectively, assuming hypochromism in f_q to be same as that in f_v . Hypochromic correction would probably be very small for the other f_q values tabulated.

The observation of hypochromism in these linear polymers indicates considerable nonrandomness in the local spatial interrelationships among the chromophoric groups. This was confirmed by studies of the siloxane chain vibrations. The coupled ν_a SiOSi (SiOSi asymmetric stretching) chain vibrational bands in the spectra of the diphenylsiloxane copolymers in solution were as sharp as those in crystalline polydiphenylsiloxane, and their positions suggested an extended simple helix having 2–3 siloxane units per turn rather than the less orderly mean configuration indicated for polydimethylsiloxane.²⁸ The basis for this configurational order in linear polydiphenylsiloxanes is believed to be steric hindrance. The bulky phenyl groups are densely spaced along the chain and must greatly restrict the opportunities for configurational randomization.

Examination of the diphenylsiloxane f_q values (Table V) shows that they are generally larger than those of the monophenylsilicon compounds (Tables II and IV). It is believed that this is the result of the bonding interaction between phenyls. Accordingly, the transition

moment parameters calculated from these f_q values were designated $q + q'$, where q represents the ordinary substituent constant analogous to those listed in Table IV, and q' represents the contribution to the moment resulting from phenyl–phenyl bonding interactions.

In order to evaluate q' , a comparison was made between Ph₂Si(OSiMe₃)₂ and PhMeSi(OSiMe₃)₂, for which the q -values should be virtually identical. The observed f_q for Ph₂Si(OSiMe₃)₂ was 32.0×10^{-4} , or 30.2×10^{-4} after correcting for the 6% calculated hyperchromism due to polarizability interaction between the two phenyls. This yielded a corrected $q + q'$ of -8.7×10^{-10} cm. The q observed for PhMeSi(OSiMe₃)₂ was -6.5×10^{-10} . The difference, -1.2×10^{-10} cm., represents q' . To set this value in perspective, we may note that if 2p σ -bonding were fully established in the 1L_b state, q' would be about $\pm 500 \times 10^{-10}$ cm. (roughly estimated as the distance between the centers of the rings). Thus, although the spectral data (λ_0 shifts, change in intensity distribution, increase in f_q) provide definite evidence for bonding interactions between phenyls attached to the same silicon, the degree of such bond formation is very small.

The variations among the diphenylsiloxane f_q and q values (Table V) could not be analyzed as precisely as those of the monophenylsiloxanes because of the lower precision of the values themselves, the possibility of small variations in the q' terms, and the absence of corrections for hypochromic interactions between different diphenylsiloxane units. However, two points do seem significant.

First, it was noted that the two cyclotrisiloxanes examined showed quite similar f_q 's, as did also the two cyclotetrasiloxanes. This type of behavior has been previously recognized in the very similar ϵ_{\max} per phenyl values of a considerable series of partially phenyl-substituted cyclotrisiloxanes and cyclotetrasiloxanes,²⁹ and for some linear disiloxanes and tetrasiloxanes as well.⁴ Evidently, the major factor determining f_q and q is something associated with the structure of the siloxane skeleton itself rather than an interaction between the phenyl chromophores.

Second, the uncorrected f_q 's for monocyclics having 3, 4, 5, 6, and ∞ units per ring were noted to be about 41, 37, 33, 34, and 37×10^{-4} , respectively. (Correction for hypochromism would probably do little more than to raise the last value 3–4 units relative to the others.) This variation in f_q seems to parallel the probable variation in mean angles between the twofold symmetry axes of adjacent Ph₂SiO₂ units, which must at first decrease with increasing ring size and then increase as greater puckering becomes possible.³⁰ Since the electrostatic fields produced at the chromophores by the diphenylsiloxane or dialkylsiloxane units should vary approximately as the angles between these axes, it is probable that a field effect is again responsible for the variations in f_q and q .

(28) J. F. Brown, Jr., American Chemical Society Division of Polymer Chemistry Preprints, Vol. 2, 1961, No. 2, p. 112.

(29) C. R. Sporck and A. Coleman, to be published.

(30) L. K. Frevel and M. J. Hunter, *J. Am. Chem. Soc.*, **67**, 2275 (1945).