Determination of the Si_{Pc}–O–Si_{Me} Bond Angle Common to the Shift Reagent Compounds $(CH_3)_3SiO(PcSiO)_xSi(CH_3)_3$ ($x = 1–5$) by an Induced Shift Technique and Determination of the Structure of $PcSi[OSi(CH_3)_3]_2$ by X-Ray Crystallography[1]

J. Robert Mooney,[2a] Clement K. Choy,[2a] Kerro Knox,[2b] and Malcolm E. Kenney*[2a]

Contribution from the Chemistry Department, Case Western Reserve University, Cleveland, Ohio 44106, and the Chemistry Department, The Cleveland State University, Cleveland, Ohio 44115. *Received January 18, 1974*

Abstract: Induced shift calculations designed to give quantitative structural information are described. The shift compounds dealt with are the five compounds $(CH_3)_3SiO(PcSiO)_xSi(CH_3)_3$ ($x = 1–5$). A basic assumption made is that the structural parameters associated with the siloxy groups in the five compounds are the same. The structural information sought is the value of the Si_{Pc}–O–Si_{Me} angle. Considerable emphasis is given to the computational techniques used. The angle obtained from following through the steps for a calculation believed free of major pitfalls is 162 (3)°. An X-ray crystal structure study of the simplest of the five compounds, *i.e.*, $PcSi[OSiCH_3)_3]$, is also described. This compound as crystallized from toluene is monoclinic, space group $P2_1/c$. The lattice constants are $a = 18.7610$ (9) Å, $b = 9.8385$ (4) Å, $c = 19.531$ (1) Å and $\beta = 89.6427$ (8)°, and the number of molecules per cell is four. Refined atom coordinates for the 51 nonhydrogen atoms in the asymmetric unit are calculated using as input data 4893 observed reflections. The final R_2 value corresponding to these coordinates is 9.5%. For the central silicon atom the coordination arrangement is verified as being approximately octahedral. The two symmetry independent Si_{Pc}–O–Si_{Me} bond angles are 157.8 (1) and 156.6 (1)°.

In the past several years a considerable amount of work aimed at getting quantitative structural information from the dipolar induced shifts associated with compounds formed by lanthanide shift reagents and various substrates has been described.[3,5] Also described has been a small amount of essentially parallel work using the ring-current induced shifts of an iron(II) phthalocyanine shift reagent complex.[6]

The approaches used in this quantitative shift reagent work are attractive in spite of the problems associated with them[7] because they appear to be capable of giving valuable quantitative structural information about various kinds of groups in solution. In addition they depend on a type of nmr data which generally can be acquired without great difficulty, and (in contrast to the approaches of X-ray crystallography) they yield results unencumbered by associated unneeded results.

In this paper further work using induced shift approaches is described. The shift reagent compounds studied are the five ring-current shift compounds, $(CH_3)_3SiO(PcSiO)_xSi(CH_3)_3$ ($x = 1–5$), and, with the assumption that the structural parameters associated with the siloxy groups in all five compounds are the same, the structural information sought is the value of the Si_{Pc}–O–Si_{Me} angle.

Also described in the paper is a crystallographic study of the simplest of these compounds, *i.e.*, $PcSi[OSi(CH_3)_3]_2$. The results from this study are used to provide a basis for making estimates of some of the parameters needed in the shift reagent structural work, and in addition to provide a basis, when taken in conjunction with other pertinent data, for judging the reasonableness of the shift reagent results.

Experimental Section

Syntheses. $PcSi[OSi(CH_3)_3]_2$.[9] A mixture of $PcSi(OH)_2$[10] (500 mg) and pyridine (~65 ml) was brought to reflux, and a portion of the pyridine (~10 ml) was distilled off. To the remainder was added *N,O*-bis(trimethylsilyl)acetamide (0.5 ml). The resultant was refluxed for 2 hr, and the product was cooled slowly and filtered. The solid thus isolated was washed and dried (198 mg).

$HO(PcSiO)_xH$. In dry apparatus and under dry nitrogen, a mixture of $PcSiCl_2$ (1.00 g), and a solution of potassium *tert*-butoxide (6.0 g) in toluene (300 ml) was refluxed with stirring for 15 hr. The resultant was cooled and evaporated to dryness under reduced pressure. The residue was washed with water and dried (0.91 g). A mixture of a portion of this (0.25 g), sodium methoxide (1.25 g), and 90% ethanol (155 ml) was refluxed for 3 hr. The solid in the suspension thus obtained, after the suspension had been cooled, was filtered off, washed with water and acetone, and dried (0.22 g).

$(CH_3)_3SiO(PcSiO)_xSi(CH_3)_3$. A mixture of $HO(PcSiO)_xH$ (0.2 g), dry pyridine (40 ml), and *N,O*-bis(trimethylsilyl)acetamide (0.6 ml) was refluxed for 2.5 hr and the resultant was evaporated to dryness under reduced pressure. The product, a blue solid, was washed copiously with a 9:1 water–acetone mixture and dried.

Instrumentation and Programing. A Varian XL-100-V15 spectrometer (equipped with a Varian 620 L (16 K) computer) and a Picker four-angle automatic diffractometer were used in making the main experimental observations. The induced shift calculations were carried out in Fortran V using a Univac 1108 computer.

Nmr Data Collection. The solution used for making the nmr measurements was prepared by mixing a portion of the shift compound mixture with appropriate amounts of hexamethyldisiloxane and deuteriochloroform and then filtering the resultant. Spectra of this solution were taken with the instrument operating in Fourier transform mode under conditions such that the accuracy of the resonance positions of the siloxy protons relative to each other was thought to be 0.5 Hz or better. The phthalocyanine content of this solution was estimated to be about 50% monomer shift compound, 44% dimer compound, 4% trimer compound, 0.8% tetramer compound, and 0.2% pentamer compound. No evidence of significant amounts of impurities other than a small amount of hexane-like hydrocarbon was detected in the solution. Separate work with pure samples of the monomer, dimer, and trimer shift compounds indicated, as expected, that the siloxy resonance positions of these compounds as determined from solutions of the pure compound and from mixtures of them are the same.

X-Ray Data Collection. By means of recrystallization from toluene, a batch of crystals of the monomer shift compound containing crystals of proper size and suitable perfection for crystallography was obtained. From this batch a crystal with dimensions of 0.13 ×

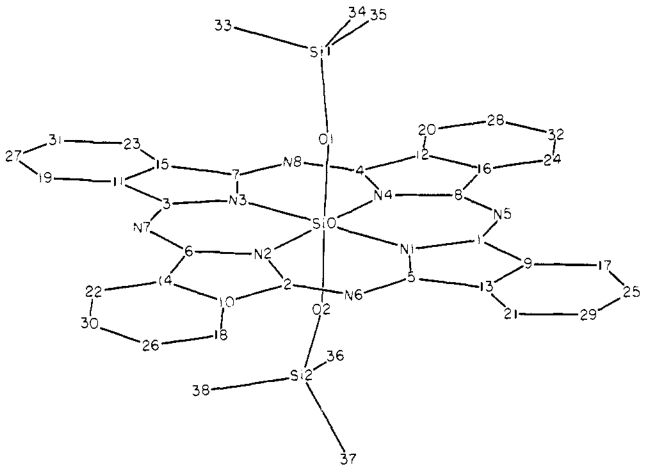

Figure 1. Atom numbering system used for the asymmetric unit of the unit cell of PcSi[OSi(CH$_3$)$_3$]$_2$.

0.28 × 0.40 mm was selected, and a series of Ni-filtered Cu Kα Weissenberg photographs of it were taken. These showed that the unit cell had a mirror plane and a pseudo-mirror plane.

Also taken of this crystal were unfiltered Mo Kα radiation b^* and c^* axis precession photographs. These showed that the crystal systematically failed to yield $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$, reflections and thus that its space group was $P2_1/c$.

Accurate values for the χ, ϕ, and 2θ angles of 28 selected reflections were then obtained using as a starting point values of these angles deduced from the Weissenberg photographs. For this step the diffractometer set for Ni-filtered radiation and for manual mode operation was employed.

These accurate χ, ϕ, and 2θ values were used to secure (by a least-squares procedure) precision lattice constants. The constants thus obtained and the observed flotation density of the compound (1.33 g/cm^3) were, in turn, used to obtain the number of molecules per unit cell. The values found were a = 18.7610 (9) Å, b = 9.8385 (4) Å, c = 19.531 (1) Å, β = 89.6427 (8)°,[11] and Z = 4 (calculated density 1.325 g/cm^3).

The same χ, ϕ, and 2θ values were also utilized for the generation of a full set of angle data for $2\theta \leq 132°$. A complete set of reflection intensity data was then obtained. In this step the automatic diffractometer set for θ–2θ mode operation, for a scanning rate of 2°/min, and for collection of 10-sec background counts for each reflection was employed.No evidence of the occurrence of crystal decomposition or of crystal misalignment during data acquisition was found.

Of the 6291 space group allowed reflections collected, 4893 were considered to be observed above background. These were corrected for Lorentz and polarization effects but not for extinction or absorption effects.

X-Ray Structure Determination. Using the data thus accumulated, a Patterson map with the origin peak removed was constructed.[12] This map, with assignment of its strongest peak to the molecule–molecule vector, suggested the approximate coordinates of the central silicon atom of the asymmetric unit.

A sharpened Patterson map with the origin peak removed was next constructed. This, with group assignment of a portion of its many approximately x-direction peaks to ring-atom to ring-atom vectors, suggested the approximate ring-plane orientation of the unit.

With this tentative information and with data about appropriate ring-atom to ring-atom relationships derived from previous work with metal-free phthalocyanine,[15] trial positions for the ring-carbon, ring-nitrogen, and ring-silicon atoms were chosen. These were then modified, using a rigid-body rotation technique, so as to lead to the best agreement between 200 selected observed structure factors and the corresponding calculated structure factors (only rotations of the ring-atom group about its normal vector were used in this step).

Next a three-dimensional Fourier map was constructed using as a basis the positions thus developed for the ring atoms (including the central silicon atom) and appropriate positions for the trans oxygen atoms. This yielded improved positions for these atoms and revealed the approximate positions of the siloxy silicon atoms. Using these atom positions another map was constructed. This gave generally improved positions for the main ring atoms, the oxygen atoms, and the siloxy silicon atoms, and revealed the approximate positions of the siloxy carbon atoms. Finally, a map based on these positions was constructed. From this, generally improved positions for all the atoms whose positions had been used as input were obtained.

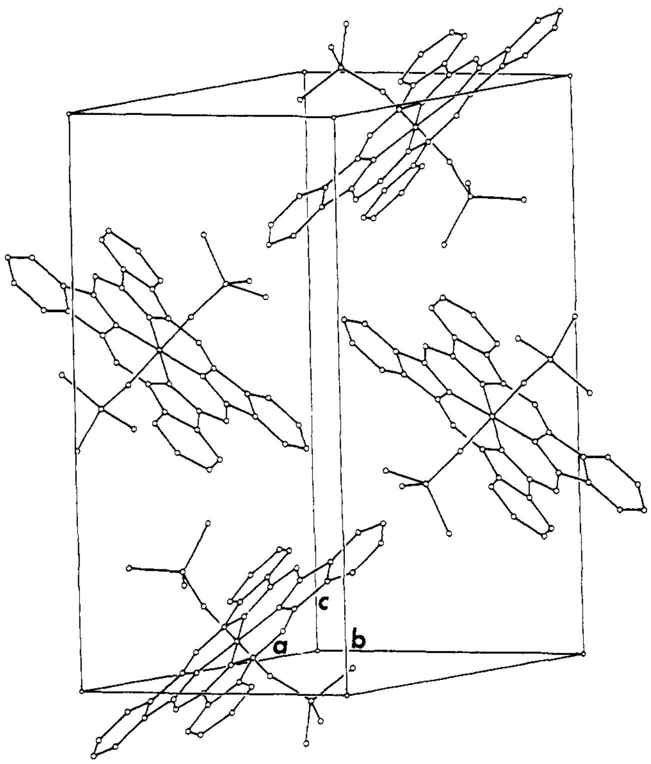

Figure 2. Packing of molecules in unit cell of PcSi[OSi(CH$_3$)$_3$]$_2$.

With the thus derived main-atom positons and with estimated benzo hydrogen atom positions based on these,[16] a final least-squares structure was worked out (the methyl hydrogen atoms were not included in this structure). The parameters refined in this step were the overall temperature factor, the nonhydrogen atom positions, and the anisotropic temperature factors of the nonhydrogen atoms. The weighted R_2 value ultimately obtained was 9.5%.

Using the numbering scheme of Figure 1, the results of this work are summarized in Tables I–IV and Figures 2 and 3.[17] Some important averaged bond parameters are shown in Figure 4.

Nmr Approaches and Results

Siloxy Parameter Equality Assumption. Just before the beginning of this work a crystallographic study of [(CH$_3$)$_3$SiO]$_2$CH$_3$SiO(PcSiO)$_3$Si(CH$_3$)[OSi(CH$_3$)$_3$]$_2$, an analog of the trimer shift compound, was completed. This showed that the backbone of the ring stack in this compound is linear, that the rings of its stack are nearly planar, and that they are perpendicular to the backbone.[18]

With this in mind it is reasonable to assume that in the four multiring shift compounds of this study the ring-stack backbones are linear and that the rings are nearly planar and are perpendicular to the backbones. Accordingly, it can be concluded that the geometrical environments of the siloxy groups in the five shift compounds are essentially the same, and that the electronic effects operating on them, except for ring-current effects, are quite similar. This leads to the conclusion that the assumption of equality among the structural parameters associated with them, which is key to this work, is reasonable.

Determination of the Si$_{Pc}$–O–Si$_{Me}$ Bond Angle.[19] Among

Table I. Atomic Coordinates in Unit Cell of $PcSi[OSi(CH_3)_3]_2$[a]

Atom type	x	y	z
SiO	0.23226 (5)	0.11643 (9)	0.42518 (4)
Si1	0.25863 (6)	−0.13242 (11)	0.52940 (5)
Si2	0.26155 (5)	0.34377 (10)	0.31014 (5)
O1	0.23088 (12)	−0.00492 (23)	0.48553 (11)
O2	0.22997 (12)	0.24014 (24)	0.36600 (11)
N1	0.30666 (14)	0.20932 (28)	0.47377 (14)
N2	0.30293 (14)	0.01835 (28)	0.37341 (14)
N3	0.15854 (14)	0.02159 (27)	0.37714 (13)
N4	0.16167 (14)	0.21328 (27)	0.47700 (14)
N5	0.23665 (17)	0.35758 (29)	0.54652 (15)
N6	0.41176 (15)	0.10466 (31)	0.42403 (16)
N7	0.22808 (16)	−0.11693 (29)	0.29883 (15)
N8	0.05355 (15)	0.11395 (30)	0.43266 (15)
C1	0.29721 (19)	0.30768 (35)	0.52272 (17)
C2	0.37600 (17)	0.02651 (34)	0.38111 (18)
C3	0.16769 (18)	−0.07330 (34)	0.32587 (17)
C4	0.08929 (18)	0.19850 (34)	0.47245 (17)
C5	0.37867 (18)	0.18933 (34)	0.46598 (18)
C6	0.29070 (18)	−0.07443 (34)	0.32213 (17)
C7	0.08643 (17)	0.03262 (34)	0.38909 (17)
C8	0.17465 (19)	0.31175 (34)	0.52540 (17)
C9	0.36647 (20)	0.35217 (36)	0.54741 (19)
C10	0.41102 (19)	−0.06608 (37)	0.33416 (19)
C11	0.09892 (18)	−0.12428 (34)	0.30450 (18)
C12	0.05384 (19)	0.29132 (37)	0.51893 (18)
C13	0.41696 (19)	0.27762 (36)	0.51200 (19)
C14	0.35748 (19)	−0.12760 (35)	0.29625 (18)
C15	0.04802 (18)	−0.05941 (34)	0.34449 (18)
C16	0.10734 (20)	0.36218 (37)	0.55239 (18)
C17	0.38639 (23)	0.44700 (41)	0.59677 (20)
C18	0.48268 (20)	−0.09856 (40)	0.32402 (22)
C19	0.07972 (22)	−0.22088 (38)	0.25613 (20)
C20	−0.01772 (22)	0.31389 (46)	0.53312 (21)
C21	0.48936 (22)	0.29450 (43)	0.52424 (22)
C22	0.37266 (23)	−0.22350 (42)	0.24594 (21)
C23	−0.02445 (20)	−0.08758 (40)	0.33861 (22)
C24	0.09103 (23)	0.46071 (42)	0.60117 (21)
C25	0.45789 (26)	0.46397 (48)	0.60785 (23)
C26	0.49778 (24)	−0.19492 (46)	0.27412 (24)
C27	0.00787 (23)	−0.24873 (41)	0.24969 (24)
C28	−0.03309 (24)	0.41289 (53)	0.58154 (23)
C29	0.50831 (23)	0.38890 (50)	0.57280 (24)
C30	0.44349 (24)	−0.25509 (46)	0.23543 (24)
C31	−0.04241 (22)	−0.18415 (42)	0.29034 (25)
C32	0.02005 (27)	0.48297 (49)	0.61442 (23)
C33	0.34600 (28)	−0.08993 (75)	0.57100 (31)
C34	0.19366 (30)	−0.16956 (63)	0.59890 (26)
C35	0.26721 (55)	−0.28477 (59)	0.47205 (34)
C36	0.27426 (36)	0.25207 (64)	0.22694 (23)
C37	0.19845 (26)	0.48892 (46)	0.30038 (28)
C38	0.34872 (23)	0.41573 (50)	0.33943 (26)
H17	0.3496	0.5006	0.6226
H18	0.5194	−0.0554	0.3509
H19	0.1157	−0.2668	0.2278
H20	−0.5446	0.2632	0.5084
H21	0.5255	0.2406	0.4984
H22	0.3345	−0.2693	0.2182
H23	−0.0610	−0.0443	0.3663
H24	0.1286	0.5116	0.6252
H25	0.4720	0.5310	0.6425
H26	0.5472	−0.2211	0.2656
H27	−0.0051	−0.3184	0.2156
H28	−0.0841	0.4293	0.5914
H29	0.5587	0.4054	0.5819
H30	0.4563	−0.3209	0.2006
H31	−0.0939	−0.2060	0.2852
H32	0.0068	0.5490	0.6499

[a] The hydrogen atoms were assigned a B parameter (isotropic thermal parameter) of 5.79 $Å^2$.

the procedures which can be envisioned for obtaining the desired Si_{Pc}-O-Si_{Me} bond angle, several have features making them of particular interest. One of these is one in which the Si_{Pc}-O-Si_{Me} angles for each of the five compounds giving calculated induced shifts in as good agreement as possible with the observed induced shifts are obtained and then averaged. Another is one in which the single angle simultaneously giving calculated induced shifts for each of the multiring compounds in as good agreement as possible with the observed induced shifts is obtained.

For carrying out calculations appropriate to these two procedures, it is helpful to assume that the Si_{Pc}-O bonds in the five compounds are perpendicular to the phthalocyanine rings. It is also helpful to assume that all possible microconformers for the Si_{Pc}-O, O-Si_{Me}, and Si_{Me}-C bonds are populated and that all are equally populated. It is then necessary to assume, in light of the experimental data, that rapid interconversion between conformers occurs.

Individual Angle Approach. One of the ways of carrying out a calculation appropriate to the individual angle procedure and the assumptions outlined begins with the selection of a reasonable trial value for the Si_{Pc}-O-Si_{Me} bond angle. Then the positions of one of the siloxy protons of the monomer for a series of incremental rotations about the Si_{Pc}-O, O-Si_{Me}, and Si_{Me}-C axes are determined[21] (using bond parameters set on the basis of the crystallographic data for the monomer, data for ordinary methyl groups,[22] and the assumption of a symmetrical distribution for the four bonds about the methyl carbons). Following this the induced shifts corresponding to these positions are obtained by means of a Johnson-Bovey type equation[23] for the phthalocyanine ring,[24] and an appropriate average of the induced shifts is obtained. An incremental adjustment of the angle is then made and the calculation repeated. Selection of new trial angles and repetition of the process are continued until a calculated induced shift in as good agreement as possible with that obtained by taking the difference between the siloxy proton shifts for the monomer and for hexamethyldisiloxane is secured.[27]

Next a parallel calculation for the most distant ring of the dimer is carried through (using bond parameters for the ring-stack set on the basis of those for the trimer analog). However, in this calculation the trial angle is refined by a least-squares linear-Taylor differential-correction technique (as it simplifies for one observation).

Following this, similar calculations for the most-distant-ring induced shifts are carried out for the next two oligomers. Finally a calculation of the type used for the monomer is carried out for the pentamer. The five angles thus obtained are then averaged.

The results of numerically carrying through the steps for calculations of this type are presented in Table V. As can be seen, the angle obtained is quite poorly defined.[28]

One of the factors obviously leading to this problem is the unsuitability of hexamethyldisiloxane as a reference compound for the monomer. Another is the small size of the magnetic field gradients provided by the most distant rings of the pentamer and tetramer.

Single Angle Approach. A way of carrying out a calculation appropriate to the single angle procedure also starts with the selection of an appropriate trial angle. Then using the observed induced shifts for the dimer through the pentamer and the corresponding calculated induced shifts (obtained essentially as before), the trial angle is refined by least-squares.

As close inspection reveals, a calculation of this type is superior to a calculation of the previous type because it substantially decreases the importance of the pentamer-tetramer field gradient size problem. Further, it obviously completely avoids the monomer reference problem.

The results of numerically carrying through the steps appropriate to a calculation of this type are given in Table V.

Table II. Thermal Parameters of the Atoms in $PcSi[OSi(CH_3)_3]_2$

Atom type	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
SiO	0.00194 (2)	0.00683 (9)	0.00195 (2)	−0.00017 (4)	−0.00021 (2)	0.00003 (4)
Si1	0.00363 (4)	0.00885 (11)	0.00227 (3)	0.00067 (5)	0.00001 (2)	0.00102 (4)
Si2	0.00233 (3)	0.00812 (10)	0.00197 (2)	−0.00012 (4)	0.00010 (2)	0.00033 (4)
O1	0.00278 (7)	0.00783 (25)	0.00235 (7)	−0.00001 (11)	−0.00025 (6)	0.00058 (10)
O2	0.00265 (7)	0.00845 (26)	0.00240 (7)	−0.00066 (11)	−0.00027 (6)	0.00074 (11)
N1	0.00246 (8)	0.00766 (30)	0.00215 (7)	−0.00044 (13)	−0.00030 (6)	0.00000 (12)
N2	0.00220 (8)	0.00814 (30)	0.00235 (8)	−0.00000 (12)	−0.00010 (6)	−0.00034 (12)
N3	0.00223 (8)	0.00736 (28)	0.00209 (7)	−0.00011 (12)	−0.00013 (6)	0.00000 (12)
N4	0.00230 (8)	0.00714 (28)	0.00226 (8)	0.00005 (12)	−0.00004 (6)	−0.00011 (12)
N5	0.00323 (10)	0.00821 (31)	0.00229 (8)	−0.00047 (14)	−0.00013 (7)	−0.00062 (13)
N6	0.00238 (9)	0.01010 (35)	0.00285 (9)	−0.00034 (14)	−0.00036 (7)	0.00013 (14)
N7	0.00281 (9)	0.00860 (32)	0.00239 (8)	−0.00018 (14)	−0.00015 (7)	−0.00060 (13)
N8	0.00210 (8)	0.00993 (34)	0.00277 (9)	0.00011 (13)	−0.00020 (7)	0.00007 (14)
C1	0.00282 (11)	0.00830 (37)	0.00234 (9)	−0.00076 (16)	−0.00033 (8)	0.00015 (15)
C2	0.00224 (10)	0.00856 (37)	0.00256 (10)	−0.00015 (15)	−0.00006 (8)	0.00029 (15)
C3	0.00258 (10)	0.00812 (35)	0.00221 (9)	−0.00030 (15)	−0.00032 (7)	−0.00027 (15)
C4	0.00246 (10)	0.00808 (35)	0.00240 (9)	0.00022 (15)	0.00002 (8)	0.00043 (15)
C5	0.00243 (10)	0.00819 (37)	0.00252 (9)	−0.00030 (15)	−0.00041 (8)	0.00041 (15)
C6	0.00247 (10)	0.00801 (35)	0.00246 (9)	0.00012 (15)	−0.00004 (8)	−0.00014 (15)
C7	0.00221 (9)	0.00819 (35)	0.00251 (9)	−0.00032 (15)	−0.00028 (7)	0.00085 (15)
C8	0.00295 (11)	0.00761 (35)	0.00217 (9)	−0.00000 (15)	−0.00002 (8)	0.00016 (14)
C9	0.00326 (12)	0.00848 (38)	0.00256 (10)	−0.00082 (17)	−0.00064 (9)	0.00012 (16)
C10	0.00274 (11)	0.00835 (37)	0.00291 (10)	0.00026 (16)	0.00033 (9)	0.00041 (16)
C11	0.00264 (10)	0.00794 (36)	0.00251 (10)	−0.00067 (15)	−0.00056 (8)	0.00038 (15)
C12	0.00297 (11)	0.00895 (39)	0.00259 (10)	0.00047 (17)	0.00034 (8)	0.00037 (16)
C13	0.00280 (11)	0.00884 (38)	0.00274 (10)	−0.00086 (16)	−0.00073 (9)	0.00024 (16)
C14	0.00292 (11)	0.00864 (38)	0.00245 (10)	−0.00012 (16)	0.00032 (8)	0.00009 (15)
C15	0.00267 (10)	0.10741 (35)	0.00280 (10)	−0.00042 (15)	−0.00060 (8)	0.00055 (15)
C16	0.00323 (12)	0.00901 (39)	0.00246 (10)	0.00047 (17)	0.00021 (9)	0.00024 (16)
C17	0.00413 (15)	0.01023 (44)	0.00277 (11)	−0.00126 (21)	−0.00046 (10)	−0.00020 (18)
C18	0.00259 (11)	0.01115 (45)	0.00358 (13)	0.00041 (18)	0.00031 (10)	0.00093 (20)
C19	0.00381 (13)	0.00880 (40)	0.00300 (11)	−0.00051 (19)	−0.00100 (10)	−0.00059 (17)
C20	0.00309 (13)	0.01426 (54)	0.00320 (12)	0.00096 (21)	0.00028 (10)	0.00036 (21)
C21	0.00308 (13)	0.01174 (48)	0.00384 (14)	−0.00084 (20)	−0.00103 (11)	0.00025 (21)
C22	0.00389 (14)	0.01094 (46)	0.00306 (12)	0.00056 (21)	0.00049 (10)	−0.00072 (19)
C23	0.00254 (11)	0.01006 (42)	0.00397 (13)	−0.00059 (17)	−0.00081 (10)	0.00064 (20)
C24	0.00393 (14)	0.01141 (47)	0.00283 (11)	0.00080 (21)	0.00042 (10)	−0.00045 (19)
C25	0.00481 (17)	0.01344 (55)	0.00350 (14)	−0.00237 (25)	−0.00153 (13)	−0.00055 (22)
C26	0.00347 (14)	0.01232 (52)	0.00416 (15)	0.00147 (21)	0.00095 (12)	0.00107 (23)
C27	0.00367 (14)	0.00966 (45)	0.00423 (14)	−0.00104 (20)	−0.00159 (12)	−0.00065 (21)
C28	0.00365 (15)	0.01668 (62)	0.00355 (14)	0.00201 (25)	0.00070 (12)	−0.00015 (24)
C29	0.00329 (14)	0.01619 (63)	0.00392 (15)	−0.00169 (23)	−0.00121 (12)	−0.00041 (24)
C30	0.00389 (15)	0.01228 (52)	0.00383 (14)	0.00074 (22)	0.00107 (12)	−0.00075 (22)
C31	0.00299 (13)	0.01067 (46)	0.00503 (17)	−0.00124 (20)	−0.00173 (12)	0.00132 (23)
C32	0.00487 (18)	0.01408 (58)	0.00343 (14)	0.00194 (26)	0.00103 (13)	−0.00139 (23)
C33	0.00380 (17)	0.03008 (112)	0.00492 (20)	0.00057 (36)	−0.00080 (15)	0.00517 (40)
C34	0.00519 (21)	0.02049 (81)	0.00379 (16)	−0.00179 (33)	0.00068 (14)	0.00294 (30)
C35	0.01513 (57)	0.01058 (64)	0.00515 (23)	0.00465 (49)	0.00077 (29)	−0.00074 (31)
C36	0.00742 (27)	0.02189 (88)	0.00245 (13)	−0.00044 (39)	0.00109 (15)	−0.00168 (27)
C37	0.00387 (16)	0.01139 (51)	0.00536 (19)	0.00130 (23)	−0.00034 (13)	0.00180 (26)
C38	0.00139 (14)	0.01515 (58)	0.00437 (16)	−0.00246 (23)	−0.00246 (12)	0.00171 (25)

[a] The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Selected Bond Lengths (Å)

SiO–N1	1.924 (2)	Si1–C33	1.881 (5)
SiO–N2	1.922 (2)	Si1–C34	1.855 (4)
SiO–N3	1.918 (2)	Si1–C35	1.877 (5)
SiO–N4	1.915 (2)	Si2–C36	1.873 (4)
SiO–O1	1.678 (2)	Si2–C37	1.865 (4)
SiO–O2	1.680 (2)	Si2–C38	1.875 (3)
O1–Si1	1.608 (2)		
O2–Si2	1.603 (2)		

Table IV. Selected Bond Angles (deg)

N1–SiO–O1	89.9 (1)	O1–Si1–C33	110.1 (2)
N2–SiO–O1	91.1 (1)	O1–Si1–C34	109.3 (2)
N3–SiO–O1	89.4 (1)	O1–Si1–C35	109.4 (2)
N4–SiO–O1	88.6 (1)	O2–Si2–C36	109.2 (2)
N1–SiO–O2	91.0 (1)	O2–Si2–C37	108.9 (1)
N2–SiO–O2	91.3 (1)	O2–Si2–C38	109.9 (2)
N3–SiO–O2	89.7 (1)		
N4–SiO–O2	89.0 (1)	C33–Si1–C34	107.3 (2)
		C34–Si1–C35	109.4 (3)
O1–SiO–O2	177.4 (1)	C35–Si1–C33	111.3 (3)
		C36–Si2–C37	111.0 (2)
SiO–O1–Si1	157.8 (1)	C37–Si2–C38	107.3 (2)
SiO–O2–Si2	156.6 (1)	C38–Si2–C36	110.0 (2)

The angle obtained is, as is seen from the size of its standard deviation, well defined. Also, as judged in the light of the average of the symmetry independent but statistically equivalent (at the 99% confidence level) solid state Si_{Pc}–O–Si_{Me} angles in the monomer (157.2 (8)°), the single solid state Si_{Pc}–O–Si_{siloxy} angle in the trimer analog[18] (154.7 (3)°), and the solid state Si_{Pc}–O–Si_{Et} angle in $PcSi(CH_3)(OSi(C_2H_5)_3)\cdot 0.5\ C_6H_{12}$ (169.1(2)°),[29] the angle appears to be reasonable.[30] These observations suggest (although they do not prove) that this latter general procedure and the specific calculation described are sound.[31]

Alternative Single Angle Approach. A reasonable alternative to this single angle approach type of calculation is one which is the same in all respects except that it is assumed

Table V. Ring-Current Calculation Results

	Induced shifts (ppm)					Angles (deg)	
	Monomer	Dimer	Trimer	Tetramer	Pentamer	Individual	Final
Observed	2.87	1.06	0.48	0.25	0.13		
Individual angle	2.90					180	
		1.06				163	
			0.48			157	
				0.25		148	
					0.13	180	
							166 (14)
Single angle							
Multiple conformer		1.06	0.47	0.24	0.14		162 (3)
Three conformer		1.06	0.47	0.24	0.14		162 (3)

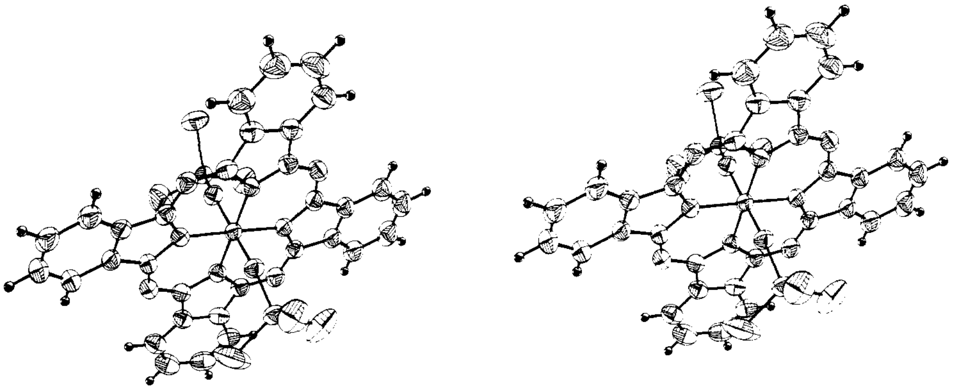

Figure 3. Ellipsoids of apparent thermal motions of the carbon, silicon, nitrogen, and oxygen atoms in $PcSi[OSi(CH_3)_3]_2$. Spheres shown for hydrogen atoms are arbitrary.

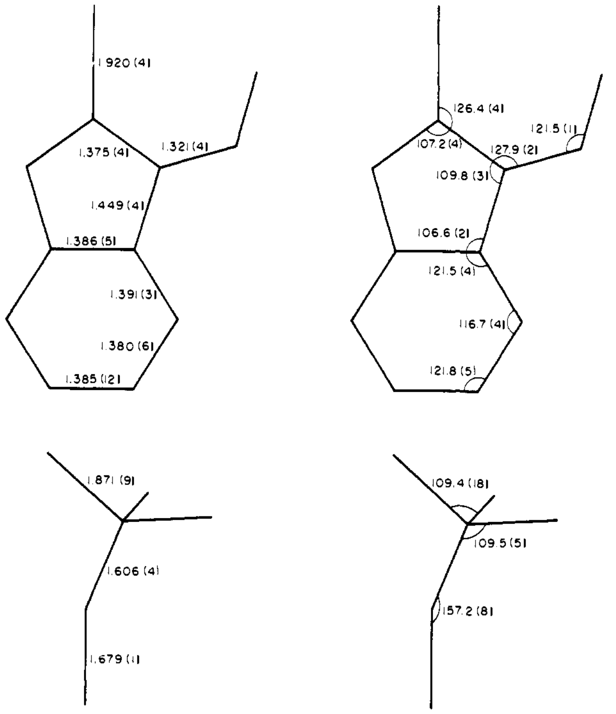

Figure 4. Average bond lenths and bond angles in the ring and siloxy side chains of $PcSi[OSi(CH_3)_3]_2$.

that only the three equivalent O-Si_{Me} conformers of the type illustrated in Figure 5 are populated and that each of these is equally populated (interconversion between the conformers being assumed to be rapid, of course). The results obtained from carrying through the steps appropriate to this calculation are, Table V, the same as those obtained from carrying through steps appropriate to its multiple conformer analog.

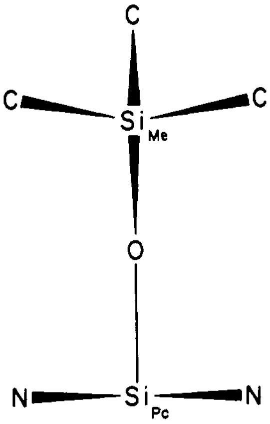

Figure 5. Low energy O-Si_{Me} conformer.

As is evident, the O-Si_{Me} microconformer population arrangement of the three-conformer calculation and the arrangement of the multiple conformer calculation bracket the arrangement which reasonably can be assumed to best approximate the real arrangements (*i.e.*, one in which all possible microconformers are populated with the three like that of Figure 5 being most populated). Since this is the case, it can be concluded that the use of these approximate arrangements probably does not lead to serious error in the results obtained.

Comments. Making the general approach applied in this work attractive are the fixed stoichiometries, nonisomerizable structures, and nonlabile metal-ligand bonds of the shift compounds used. Also making it attractive are the relatively simple field gradients, the very simple field alignments, the very small Si_{Pc}-O axis rotation barriers, and the lack of sources of contact shift effects in the compounds. Further adding to the desirability of the approach is, for the multiring compounds, the immediate availability of suitable reference compounds. Balancing to some extent these favorable features are the relatively small shifts produced in the compounds. Obviously the combination of attractive and unattractive features in this approach is unlike that in the lanthanide approach.[8,33-38]

Three-Parameter Calculations. A procedure for obtaining the Si_{Pc}-O and O-Si_{Me} bond lengths and the Si_{Pc}-O-Si_{Me} bond angle basically similar to the single angle procedure can also be envisioned. However, such a procedure is encumbered with the problem of parameter correlations and currently appears unpromising.

Crystallographic Results

The data on the nearest neighbor arrangement around the silicon in $PcSi[OSi(CH_3)_3]_2$ and in other silicon phthalocyanines[18,29] provide direct proof of the approximately octahedral coordination of the silicon in these compounds. It is accordingly now incontestably clear that the largest known group of octahedral silicon compounds is the phthalocyanine group.[39]

In accord with expectations, the data on the monomer shift compound pertaining to the Si_{Pc}-O and Si_{Pc}-N bond lengths, Table III, show that the Si_{Pc}-O bonds are shorter than the Si_{Pc}-N bonds. Also in accord with expectations the data on the Si_{Me}-O and Si_{Pc}-O bond lengths show that the Si_{Me}-O bonds are shorter than the Si_{Pc}-O bonds.

The essential planarity found for the ring, Figures 2 and 3, is important in view of the nonplanarity of the ring in the closely related compound $PcSnCl_2$. Apparently the silicon atom is small enough to fit into the ring without distorting it.[40]

Similar to that found earlier for other phthalocyanines is the nonequivalence of the six interior angles of the benzo rings.[41] Probably this nonequivalence arises as a result of strain placed on the rings by their fusion with the pyrrole rings.

Supplementary Material Available. A table of $|F_o|$ and F_c (in electrons) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 X 148, 24X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-3033

References and Notes

(1) Support for this work was provided by National Science Foundation Grants, GP-22739 and GP-33528X, and by the Research Initiation Program of The Cleveland State University. The X-ray crystallographic work reported is from the M.S. thesis of C. K. Choy and the nuclear magnetic resonance work is from the Ph.D. thesis of J. R. Mooney. The former was written at The Cleveland State University and the latter at Case Western Reserve University. For the nmr work described, use was made of the Major Analytical Instruments Facility of Case Western Reserve University.

(2) (a) Case Western Reserve University; (b) The Cleveland State University.

(3) See, for example, Roberts[4] paper

(4) G. E. Hawkes, C. Marzin, D. Leibfritz, S. R. Johns, K. Herwig, R. A. Cooper, D. W. Roberts, and J. D. Roberts in "Nuclear Magnetic Shift Reagents," R. E. Sievers, Ed., Academic Press, New York, N.Y., 1973, pp 129–142.

(5) An account of work of essentially the same kind based on a cobalt(II) porphyrin shift reagent complex has recently been given by C. D. Barry, H. O. A. Hill, B. E. Mann, P. J. Sadler, and R. J. P. Williams, *J. Amer. Chem. Soc.*, **95**, 4545 (1973).

(6) J. E. Maskasky, J. R. Mooney, and M. E. Kenney, *J. Amer. Chem. Soc.*, **94**, 2132 (1972).

(7) For one of the problems associated with the lanthanide work see, for example, Horrocks' comments.[8]

(8) W. De W. Horrocks, Jr., and J. P. Sipe, III, *Science*, **177**, 994 (1972).

(9) R. Rafaeloff, F. J. Kohl, P. C. Krueger, and M. E. Kenney, *J. Inorg. Nucl. Chem.*, **28**, 899 (1966).

(10) M. K. Lowery, A. J. Starshak, S. J., J. N. Esposito, P. C. Krueger, and M. E. Kenney, *Inorg. Chem.*, **4**, 128 (1965).

(11) Here and throughout the paper the figure in parentheses following a number is the estimated standard deviation of the number in the least significant figure.

(12) The atomic scattering factors for all atoms except hydrogen were taken from the International Tables for X-Ray Crystallography.[13] The hydrogen scattering factor was taken from the work of Stewart, Davidson, and Simpson.[14]

(13) C. H. MacGillavary, G. D. Rieck, and K. Lonsdale, Ed., "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 201–209.

(14) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(15) E. C. Bissel, Ph.D. Thesis, Case Western Reserve University, Cleveland, Ohio, 1970.

(16) A C–H bond length of 1.00 Å was assumed.

(17) Figures 2 and 3 were prepared with Johnson's program, C. K. Johnson, ORTEP-II, Oak Ridge National Laboratory, Oak Ridge, Tenn., March 15, 1971.

(18) D. R. Swift, Ph.D. Thesis, Case Western Reserve University, Cleveland, Ohio, 1970.

(19) In principle work on another of the siloxy bond parameters could have been done. However, this would have necessitated the setting of a relatively accurate value for the Si_{Pc}–O–Si_{Me} bond angle and this would have been difficult.[20]

(20) The known crystallographic Si_{Pc}–O–Si bond angles cover a range of at least 25° (the smallest known Si_{Pc}–O–Si angle is the Si_{Pc}–O–Si_{siloxy} angle in the trimer analog, 154.7 (3)°, and the largest known Si_{Pc}–O–Si angle is the Si_{Pc}–O–Si_{Pc} angle in the same compound, 179.6 (2)°).

(21) Only an arc of 0–45° is used for the incremental rotations about the Si_{Pc}–O axis since the symmetry of the ring makes the use of a larger arc unnecessary.

(22) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 18**, S18s (1965).

(23) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(24) The equation used is based on a five-loop model and has the form

$$\delta = \frac{e^2}{6\pi c^2 m}\left\{\frac{n_r}{a_r}[(1 + \rho_r)^2 - z^2]^{-1/2}\left[K(k_r) + \frac{1 - \rho_r^2 - z^2}{(1 - \rho_r)^2 + z^2}E(k_r)\right] + \frac{n_b}{a_b}\sum_{i=1}^{4}[(1 + \rho_{b_i})^2 + z^2]^{-1/2}\left[K(k_b) + \frac{1 - \rho_{b_i} - z^2}{(1 - \rho_{b_i})^2 + z^2}E(k_b)\right]\right\}$$

with z, ρ_r, and ρ_{b_i} giving the position of the proton in cylindrcal coordinates with respect to the inner and four benzo loop centers, a_r and a_b the radii of the inner and benzo loops, and n_r and n_b the number of electrons per loop in the inner and benzo loops. $K(k_r)$ and $K(k_b)$ are complete elliptic integrals of the first kind and $E(k_r)$ and $E(k_b)$ are complete elliptic integrals of the second kind, where

$$k_r = \left[\frac{4\rho_r}{(1 + \rho_r)^2 + z^2}\right]^{1/2}$$

$$k_b = \left[\frac{4\rho_{b_i}}{(1 + \rho_{b_i})^2 + z^2}\right]^{1/2}$$

This equation was developed by Janson[25] and is similar to one already described.[26]

(25) T. R. Janson, Ph.D. Thesis, Case Western Reserve University, Cleveland, Ohio, 1971.

(26) T. R. Janson, A. R. Kane, J. F. Sullivan, K. Knox, and M. E. Kenney, *J. Amer. Chem. Soc.*, **91**, 5210 (1969).

(27) Dishing of the rings is ignored in this calculation as it was in the development of the phthalocyanine ring-current equation used.[25]

(28) The differential correction refinement technique cannot be used for obtaining the monomer and pentamer shift compound angles because as the trial angles approach 180° the derivatives approach zero.

(29) A. P. D'Addario, Ph.D. Thesis, Case Western Reserve University, Cleveland, Ohio, 1971.

(30) These comparisons must be made with care, of course, both because the crystallographic and nmr bond angle values pertain to Si_{Pc}–O–Si_{siloxy} systems under very different constraints, and because the known range of crystallographic Si_{Pc}–O–Si bond angles is relatively large.[20]

(31) The result obtained from carrying through the steps appropriate to a single angle multiple conformer procedure in which all five induced shifts are included and in which the angle is refined to a minimum sum of the squares of the residuals by trial and error is an improbable 180°.[32] Of interest in connection with this result is the fact that following through the steps necessary to obtain a calculated monomer induced shift corresponding to an angle of 162° gives a value of 2.99 ppm. This value, since it is larger than the corresponding experimental hexamethyldisiloxane based value, implies that the reason hexamethyldisiloxane is a poor reference compound is that its siloxy protons are too shielded. This, in turn, implies that three methyl groups are less effective in competing for the electrons of a silicon atom bonded to a siloxy group than are a phthalocyanine ring and a siloxy group.

(32) Again the differential correction technique cannot be used.

(33) J. Reuben, *J. Amer. Chem. Soc.*, **95**, 3534 (1973).

(34) R. Porter, T. J. Marks, and D. F. Shriver, *J. Amer. Chem. Soc.*, **95**, 3548 (1973).

(35) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

(36) J. J. Uebel and R. M. Wing, *J. Amer. Chem. Soc.*, **94**, 8910 (1972).

(37) R. E. Cramer and R. Dubois, *J. Amer. Chem. Soc.*, **95**, 3801 (1973).

(38) G. N. LaMar and J. W. Faller, *J. Amer. Chem. Soc.*, **95**, 3817 (1973).

(39) The number of well-characterized silicon phthalocyanines in the literature is over 40.

(40) D. Rogers and R. S. Osborn, *Chem. Commun.*, 840 (1971).

(41) See, for example, L. H. Vogt, Jr., A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **6**, 1725 (1967).