creases nonlinearly with decreasing values of $D$ as expected.

In order to include the contribution of magnetic field mixing the entire expressions for $\mu_{\mathrm{eff}}^2$ and $M$ must be reformulated and a calculation made of the magnetic field energy of each contributing state which is not necessarily linear with field. These theoretical refinements would incorporate the additional field dependency in the susceptibilities and should describe the tma data more satisfactorily.[22]

Magnetic susceptibility measurements on the compound which has been formulated to date as TPPFeOH were also made. These as well as Mössbauer[23] and proton magnetic resonance measurements[24] performed in this laboratory have shown "TPPFeOH" to have distinctly different properties from those of the other TPPFeX compounds. Between 2.2 and 20°K this compound exhibited no measureable paramagnetism. Solution susceptibility using nmr techniques at 310°K[24] has shown, however, that $\mu_{\mathrm{eff}} \simeq 1.7$ BM, which is still below the expected 2.2–2.5 BM for low-spin iron(III). These data strongly suggest dimerization with a bridging oxygen to permit superexchange between iron ions.[25]

**Acknowledgment.** The authors wish to thank Professor W. E. Wallace for allowing the use of the instrumental facilities and the U. S. Atomic Energy Commission, Division of Biology and Medicine, for financial support through Contract AT(30-1)3859.

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[22] Such calculations were suggested by one of the referees.

[23] C. Maricondi, D. K. Straub, and L. M. Epstein, manuscript in preparation.

[24] C. Maricondi, D. Davis, and D. K. Straub, manuscript in preparation.

[25] The X-ray crystal structure of this complex is presently being determined by J. L. Hoard at Cornell University.[26]

[26] Note Added in Proof. Fleischer has now reported the dimeric structure [E. B. Fleischer and T. S. Srivastava, *J. Am. Chem. Soc.*, **91**, 2403 (1969)].

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# The Ring-Current Effect of the Phthalocyanine Ring[1,2]

**Thomas R. Janson, Alexander R. Kane, John F. Sullivan, Kerro Knox, and Malcolm E. Kenney**

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**Abstract:** Some simple classical current loop calculations have been carried out on the phthalocyanine ring. Data for the calculations have been supplied by some single-ring and multi-ring silicon and germanium phthalocyanines. Possible structural uses are forseen for the results.

In 1959 and 1960 Bradley and Becker[3] and Ellis, Jackson, Kenner, and Lee[4] reported observing ring-current effects in the nmr spectra of porphyrins. Since then the nmr ring-current effects of these systems and the ring-current effects subsequently found in similar systems have attracted attention both because of their size and because of the importance of the macrocycles supporting them.

Several attempts have been made to develop quantitative descriptions applicable to these effects. Two were described by Bradley and Becker in their 1959 paper.[3] One was based on a model in which the magnetic effect of the ring was approximated by a magnetic dipole. The other was based on a model in which the magnetic effect was approximated by the magnetic effect of a pair of current loops.

Another attempt to describe the ring-current effects of such systems was made by Jackson, Ellis, Kenner, and Lee in their 1960 paper.[4] In this attempt a current-loop approach was also used. Abraham,[5] in much more detailed work, applied both the current-loop and magnetic dipole approaches. Extensions of this work were made by Abraham, Burbidge, Jackson, and Macdonald,[6] and further similar work was carried out by Katz, Strain, Leussing, and Dougherty.[7]

All of this work was patterned after similar work on benzene and related aromatic systems which was carried out by Pople,[8] Waugh and Fessenden,[9] and Johnson and Bovey.[10] Pople's work furnished the basis for the magnetic dipole calculations while that of the others provided the basis for the current-loop calculations.

In this paper the problem of a quantitative treatment of the ring-current effect in the porphyrin-like phthalocyanine ring is taken up. As in most of the previous related ring-current effect work, the current-loop approach is used.

The data on which the work is based come from some single-ring silicon and germanium siloxy compounds previously described and from some newly synthesized multi-ring compounds. Taken together the single-ring

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[1] This paper is based in part on the Ph.D. Thesis of A. R. Kane. The work was supported by the National Science Foundation under Grants GP 1702 and GP 8368, by the National Aeronautics and Space Administration under its Fellowship Program, and by the Office of Naval Research.

[2] The term ring-current effect is employed solely for convenience and is not to be construed as implying physical reality.

[3] E. D. Becker and R. B. Bradley, *J. Chem. Phys.*, 31, 1413 (1959).

[4] J. Ellis, A. H. Jackson, G. N. Kenner, and J. Lee, *Tetrahedron Letters*, 2, 23 (1960).

[5] R. J. Abraham, *Mol. Phys.*, 4, 145 (1961).

[6] R. J. Abraham, P. A. Burbidge, A. H. Jackson, and D. B. Macdonald, *J. Chem. Soc.*, *B*, 620 (1966).

[7] J. J. Katz, H. H. Strain, D. L. Leussing, and R. C. Dougherty, *J. Am. Chem. Soc.*, **90**, 784 (1968).

[8] J. A. Pople, *J. Chem. Phys.*, 24, 1111 (1956).

[9] J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957).

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

Table I. Nmr Spectra of Oligomers ($\tau$)

| Central element | No. of rings | 3,6 ligand protons<br>Outer ring | <br>Inner ring | 4,5 ligand protons<br>Outer ring | <br>Inner ring | Siloxy methyl protons<br>Outer methyl | <br>Inner methyl |
|---|---|---|---|---|---|---|---|
| Si[a] | 1 | 0.37 | | 1.70 | | 11.22 | 12.90 |
| Si | 2 | 1.00 | | 1.69 | | 11.91 | 14.00 |
| Si | 3 | 1.49 | 1.64 | 1.98 | 1.74 | 12.25 | 14.49 |
| Si | 4 | 1.80 | 2.10 | 2.19 | 1.94 | 12.45 | 14.76 |
| Si | 5 | | | | | 12.56 | 14.90 |
| Ge[b] | 1 | 0.36 | | 1.68 | | 11.23 | 12.85 |
| Ge | 2 | 1.02 | | 1.69 | | 11.85 | 13.81 |

[a] J. N. Esposito, J. E. Lloyd, and M. E. Kenney, *Inorg. Chem.*, **5**, 1979 (1966), but redetermined. [b] A. R. Kane, R. G. Yalman, and M. E. Kenney, *ibid.*, **7**, 2588 (1968).

and multi-ring compounds form two sets of oligomers. As is pointed out later, these two sets of oligomers provide a type of data which is particularly useful for ring-current calculations. One of the silicon oligomers is illustrated in Figure 1.

Throughout the paper the emphasis is not on studying aromaticity but rather on securing an adequate description for the ring-current effect of the phthalocyanine ring.

## Experimental Section

**Silicon Oligomers.** Of the several syntheses of the oligomeric silicon phthalocyanines carried out, the following is typical. A mixture of $PcSi(OH)_2$[11] (785 mg) and $PcSi(OH)(OSi(CH_3)(OSi(CH_3)_3)_2)$[12] (543 mg) was finely ground, heated at approximately 300° under vacuum for 20 hr, and then subjected to a 3-hr carbon tetrachloride extraction (250 ml). The extract was evaporated to dryness and the product chromatographed on Woelm alumina of activity II with petroleum ether and benzene as eluents. This gave fractions containing one-ring oligomer (22 mg), two-ring oligomer (50 mg), three-ring oligomer (25 mg), four-ring oligomer (28 mg), and a fraction containing some five-ring oligomer (10 mg).

Recrystallization of a sample of the one-ring oligomer made up of the products of several syntheses from an ethanol–*n*-hexane solution (2:3) gave pure one-ring oligomer.[12] Red-reflecting, blue-transmitting, nmr-pure crystals of the two-ring oligomer were obtained by an *n*-heptane recrystallization of a composite sample of this oligomer. *Anal.* Calcd for $C_{78}H_{74}N_{16}O_7Si_8$: C, 59.59; H, 4.75; Si, 14.29. Found: C, 59.57; H, 4.67; Si, 15.04, 15.27. Similar appearing nmr-pure crystals of the three-ring oligomer were obtained by a recrystallization of a composite sample of this oligomer from a toluene–*n*-heptane solution (1:4). Red-reflecting, blue-transmitting, nmr-pure crystals of the four-ring oligomer were obtained by solution of a composite sample of this compound in carbon tetrachloride followed by filtration and evaporation. Nmr-pure five-ring oligomer was not obtained. However, chromatographic enrichment of a mixture of fractions containing some of this oligomer followed by filtration of a carbon tetrachloride solution of the resultant gave a fraction containing about 25% of the oligomer (much of the remainder being four-ring oligomer).

On the basis of the several syntheses carried out, it was concluded that higher ratios of $PcSi(OH)_2$ in the reaction mixtures led to higher ratios of the larger oligomers but at the expense of lower over-all yields of soluble products. The presence of one-ring oligomer in the product mixture was noteworthy since carefully purified $PcSi(OH)(OSi(CH_3)(OSi(CH_3)_3)_2)$ was used as a reactant. Apparently it was formed by the migration of entire siloxy end groups during the reaction.

Solutions of the three-ring and four-ring oligomers were found to be prone to the formation of insoluble decomposition products. It was concluded that these products were probably multi-ring species that had lost end groups.

**Germanium Two-Ring Oligomer.** A mixture of $PcGe(OH)_2$ (385 mg), $PcGe(OSi(CH_3)(OSi(CH_3)_3)_2)_2$[13] (658 mg), and diphenyl ether (20 ml) was refluxed for 2 hr, filtered, and evaporated to dryness. The product was extracted with carbon tetrachloride (30 ml) and the extract evaporated to dryness. The resultant was chromatographed on a 3:1 mixture of Celite 545 and Sea Sorb 43[14] using benzene and petroleum ether as eluents. This gave the two-ring oligomer as red-reflecting, blue-transmitting crystals.[15]

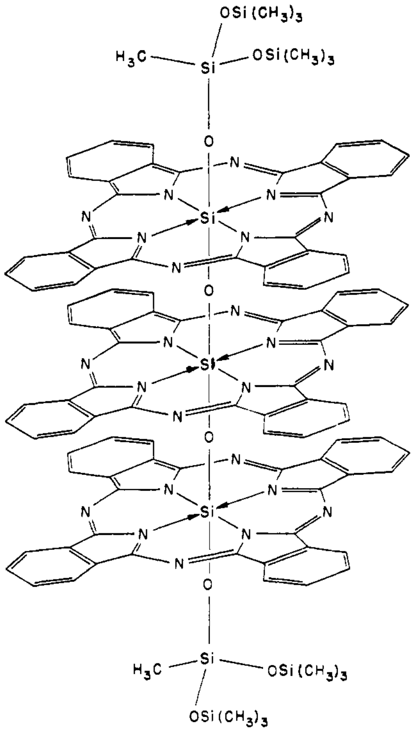

Figure 1. The three-ring silicon phthalocyanine oligomer.

**Instrumental.** A Varian HA-100 spectrometer operating at approximately 30° was used in determining line positions. Carbon tetrachloride was used as a solvent and tetramethylsilane as an internal reference.

A Varian A-60A spectrometer was used for the temperature dependence measurements.

The calculations were carried out in ALGOL.

## Results and Discussion

**Analysis of Nmr Spectra.** In Table I the resonance positions and assignments for the oligomers used in this study are given. The resonance positions for the germanium one-ring oligomer have been published previously; the rest of the positions are newly listed or are from earlier work but redetermined, all as noted. The assignments for the methyl and ring protons of the one-

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[11] Pc is used for the phthalocyanine ligand, $C_{32}H_{16}N_8$.

[12] J. N. Esposito, J. E. Lloyd, and M. E. Kenney, *Inorg. Chem.*, **5**, 1979 (1966).

[13] A. R. Kane, R. G. Yalman, and M. E. Kenney, *ibid.*, **7**, 2588 (1968).

[14] Fisher Scientific Co., Pittsburgh, Pa.

[15] Three-ring oligomer was also a product of this synthesis.

**Table II.** Additional Nmr Spectra ($\tau$)

| | Ligand protons | | Siloxy methyl protons | | Siloxy ethyl protons | | Central methyl protons |
|---|---|---|---|---|---|---|---|
| | 3,6 | 4,5 | Outer | Inner | Outer | Inner | |
| $PcSi(CH_3)(OSi(CH_3)(OSi(CH_3)_3)_2)$[a] | 0.40 | 1.73 | 11.26 | 12.99 | | | 16.31 |
| $PcSi(OSi(C_2H_5)_3)_2$[b] | 0.32 | 1.65 | | | 11.25 | 12.48 | |
| $PcGe(OSi(C_2H_5)_3)_2$[b] | 0.30 | 1.62 | | | 11.24 | 12.42 | |
| $HOSi(C_2H_5)_3$[c] | | | | | 9.05 | 9.46 | |
| $HOSi(CH_3)(OSi(CH_3)_3)_2$[c,d] | | | 9.89 | 9.97 | | | |

[a] J. N. Esposito, J. E. Lloyd, and M. E. Kenney, *Inorg. Chem.*, **5**, 1979 (1966), but redetermined. [b] L. E. Sutton and M. E. Kenney, *ibid.*, **6**, 1869 (1967). [c] A. R. Kane, R. G. Yalman, and M. E. Kenney, *ibid.*, **7**, 2588 (1968). [d] Values mistakenly inverted in original reference.

ring silicon and germanium oligomers are from the literature cited. Simple inspection was used to obtain assignments for the rest of the methyl protons. The assignments for the ring protons of the two-ring silicon and germanium oligomers were obtained by analogy with the assignments made previously for a similar silicon oligomer.[12]

Less straightforward was the development of assignments for the ring protons of the three-ring and four-ring silicon oligomers since the spectra of both compounds showed complex patterns of lines. In each, however, a pair of symmetrical AA′XX′ multiplets was discernible. Assignment of the low-field multiplets of these pairs to the 3,6 protons of the outer rings and assignment of the high-field multiplets to the 4,5 protons of the outer rings were made.

The remaining aromatic resonances were then compared to a series of computer-plotted[16] AA′BB′ spectra having coupling constants appropriate for the silicon phthalocyanine ring[17] and the best matches chosen. The positions of the two kinds of ring protons of the inner rings were taken as the centers of the experimental resonance patterns plus and minus one-half the chemical shifts of the matching computer-plotted spectra.

Finally, the resonance positions of the inner 3,6 and 4,5 protons of the three-ring and four-ring compounds were estimated from the data on the positions of the 3,6 and 4,5 protons of the outer rings of the one-ring, two-ring, and three-ring compounds,[18] and the positions obtained by the computer-plotting procedure assigned to the inner 3,6 and 4,5 protons on the basis of these estimates.[19] An interesting feature of the resulting assignments is that for the four-ring oligomer the high-field position is associated with the 3,6 protons.

The data given in Table II on the single-ring phthalocyanines and the related silanols are from the literature as indicated.

**Structural Parameters.** Since structural data on the phthalocyanines used in this study are lacking,[20] it was necessary to make some structural assumptions in order to carry out the calculations. Five basic ones were made. The first of these was that the macrocylic rings of the compounds were planar. Supporting this assumption were the results of structural work on $PcH_2$,[21] PcCu,[22] PcNi,[23] PcPt,[24,25] and $(PcMn)_2O \cdot 2py$.[26]

The second assumption was that the bond angles and bond lengths listed for the macrocyclic rings of $(PcMn)_2O \cdot 2py$ could be used for the rings of the silicon and germanium compounds. This assumption was supported by the similarity of the data reported for PcCu, PcPt, and $(PcMn)_2O \cdot 2py$.

In addition it was assumed that the rings of the multi-ring compounds were stacked on lines running through the metal atoms and perpendicularly to the ring planes. Furnishing support for this assumption were the data on the backbone–ring relationships in $(PcMn)_2O \cdot 2py$.

Finally it was assumed that the ring–ring separation in the multi-ring silicon compounds was 3.32 Å and that the same separation in the two-ring germanium compound was 3.50 Å. These last two assumptions were based on work done on $(PcSiO)_x$ and $(PcGeO)_x$.[27]

**Ring Rotation.** In some of the calculations a factor of importance was the degree of ring–ring rotation about the central backbone of the multi-ring compounds. Accordingly, the 3,6 and 4,5 multiplets of the two-ring silicon oligomer were examined in carbon tetrachloride solution from −20 to 40° and in decahydronaphthalene solution from 40 to 150°. No evidence for alteration of the multiplets was found.

An examination of the 3,6 and 4,5 multiplets of the two-ring germanium oligomer was also made. These were found to be very similar to those associated with the more closely spaced rings of the silicon oligomer.

On the basis of these results, it was concluded that the rings of the multi-ring compounds probably rotate freely on an nmr time scale when in solution.

**Single-Loop-Pair Calculations.** For these calculations it was assumed that the incremental shift associated with the 3,6 and 4,5 protons of an oligomer, Table III, represented the influence of the ring at one end of the oligomer on the ring protons at the other end of it. It was also assumed that 6.30 ppm, approximately the difference between the resonance position of the methyl protons in tetramethylsilane and the resonance position of the central methyl protons in $PcSi(CH_3)(OSi(CH_3)(OSi(CH_3)_3)_2)$, represented the influence of the ring on the central methyl.[28,29]

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(16) LAOCN3 program of A. A. Bothner-By and S. Castellano.

(17) A. R. Kane, Ph.D. Thesis, Case Western Reserve University, 1969, p 37, and later work.

(18) For example, the position of the 3,6 protons of the inner ring of the three-ring oligomer was calculated to be 0.37 + 2 × 0.63 or $\tau$ 1.63, that is, the position of the unperturbed 3,6 protons plus twice the shielding increment provided by an adjacent ring.

(19) Any uncertainties in assigning these inner ring protons do not affect the ring-current calculations since these protons were not used in the calculations.

(20) A structural determination of the three-ring oligomer is being done.

(21) J. M. Robertson, *J. Chem. Soc.*, 1195 (1936).

(22) C. J. Brown, *ibid.*, *A*, 2488 (1968).

(23) J. M. Robertson and I. Woodward, *ibid.*, 219 (1937).

(24) J. M. Robertson and I. Woodward, *ibid.*, 36 (1940).

(25) C. J. Brown, *ibid.*, *A*, 2494 (1968).

(26) L. H. Vogt, Jr., A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **6**, 1725 (1967).

(27) W. J. Kroenke, L. E. Sutton, R. D. Joyner, and M. E. Kenney, *ibid.*, **2**, 1064 (1963).

(28) Since the resonance position of the central methyl protons in the methylsilicon phthalocyanines varies by about 0.1 ppm and since tetra-

Table III. Some Incremental Shifts for Oligomers (ppm)

| | | 3,6 outer ligand protons | | | 4,5 outer ligand protons | | | Inner siloxy methyl protons | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Central element | No. of rings | Obsd | 1 loop pair | 5 loop pairs | Obsd | 1 loop pair | 5 loop pairs | Obsd | 1 loop pair | 5 loop pairs |
| Si | 1 | | | | | | | 2.93 | 3.52 | 3.08 |
| Si | 2 | 0.63 | 0.59 | 0.60 | −0.01 | −0.22 | −0.08 | 1.10 | 1.25 | 1.08 |
| Si | 3 | 0.49 | 0.60 | 0.52 | 0.29 | 0.26 | 0.25 | 0.49 | 0.54 | 0.47 |
| Si | 4 | 0.31 | 0.36 | 0.32 | 0.21 | 0.23 | 0.21 | 0.27 | 0.27 | 0.24 |
| Si | 5 | | | | | | | 0.14 | 0.15 | 0.14 |
| Ge | 1 | | | | | | | 2.88 | 3.39 | 2.96 |
| Ge | 2 | 0.66 | | | 0.01 | | | 0.96 | 1.15 | 0.99 |

A simple Johnson–Bovey current-loop calculation[10] was then carried out. For this, pairs of loops having a radius of $a$ and a separation of $p$ from the ring plane and carrying a total current of $2n$ electrons were postulated, Figure 2. With $p$ fixed at 0.64 Å (in accordance with Johnson and Bovey), sets of values for the total incremental shift were obtained for successively adjusted values of $a$ and $n$ until a good fit was obtained between the calculated and observed incremental shift values. A linearized least-squares scheme was used in this minimization.

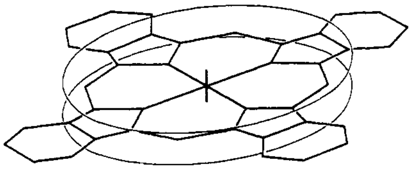

Figure 2. Single-loop-pair model.

The final values obtained for $a$, $2n$, and the incremental shift of the central methyl protons were, respectively, 4.78 Å, 8.62 ppm, and 6.28 ppm. The final values obtained for the incremental shifts of the ring protons are listed in Table III.

A test of the parameters thus developed was carried out using the data available on the incremental shifts associated with the inner methyl groups of the silicon oligomer siloxy side chains[32] (the compound $HOSi(CH)_3(OSi(CH_3)_3)_2$ being used as a reference in determining the observed incremental shift for the one-ring oligomer). A bond length of 3.30 Å and a bond angle of 180° were taken for the Si–O–Si bond. Rotation about the Si–O and Si–C bonds was taken to be free. The incremental shifts for the methyl protons of each oligomer were then calculated for a series of closely spaced configurations of the side chain, and the final incremental shift was obtained by averaging.[33] The results are shown in Table III. As a further test similar calculations were carried out for the inner methyls of the germanium oligomers (using an Si–O–Ge bond length of 3.41 Å). These results are also shown in Table III.[34]

**Five-Loop-Pair Calculations.** This calculation was carried out in essentially the same fashion as the one just outlined except that it was based on the five-loop-pair model illustrated in Figure 3. The $a$, $p$, and $n$ parameters worked out for benzene by Johnson and Bovey[10] were taken for the four benzo loop pairs of each ring. A calculation was then made of the incremental shifts which such benzo loop pairs would cause for the outer 3,6 and 4,5 protons of the two-, three-, and four-ring oligomers if the rings were assumed to be rotating freely (again using a series of configurations). A calculation was also made of the incremental shift which would be associated with the central methyl group. The differences between these calculated increments and the observed increments (again taking 6.30 ppm as the observed increment for the central methyl) were then assumed to be the increments attributable to the single central loop pair.

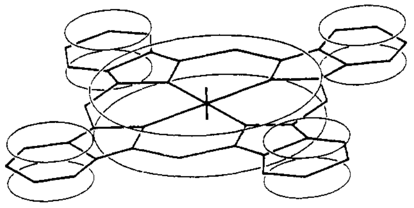

Figure 3. Five-loop-pair model.

Next, following the same procedure as in the single-loop-pair calculation, calculated shifts were fitted to these central-loop-pair increments holding $p$ at 0.64 Å and adjusting $a$ and $n$ to give the best fit. The final value obtained for $a$ was 3.90 Å and for $2n$ was 8.43. The final total calculated incremental shifts obtained for the ring protons are given in Table III. A final value of 6.30 ppm was obtained for the incremental shift of the central methyl protons.

The parameters developed in this calculation were tested, as were the single-loop-pair parameters, by calculating increments for the inner methyl protons of the

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methylsilane is not the ideal reference compound, some uncertainty attaches to the use of 6.30 ppm as the incremental shift.

(29) The assumption made for the central methyl protons is similar to that made by Johnson and Bovey in their benzene calculations; *i.e.*, the effect of the ring on the probe proton is given by the difference between the position of the probe proton and the position of a similar probe proton supported by an analogous but nonaromatic system. The assumption made in the case of the ring protons is different, because for them it is assumed that the effect of the ring on the probe protons is given by the difference between the position of the probe proton in the presence of the ring and the position of essentially the same proton in the absence of the ring. A complication with this approach is that the rings clearly interact with each other to some extent, marked blue shifts in the electronic spectra of the oligomers with increasing chain length (interpretable in terms of exciton theory[30]) being observed.[31]

(30) M. Kasha, *Radiation Res.*, **20**, 55 (1963).

(31) A. R. Kane, Ph.D. Thesis, Case Western Reserve University, 1969, p 78, to be discussed in detail elsewhere.

(32) A complication in using the incremental shifts of the side-chain protons in this and following calculations is that the increments all must be somewhat temperature dependent because of chain motions.

(33) The incremental shift for the average position of a moving proton is not the same, in general, as its average incremental shift.

(34) It should be noted that because of the use of circular current loops centered on the macrocyclic rings, the question of free rotation of the rings does not arise in this one-loop-pair calculation.

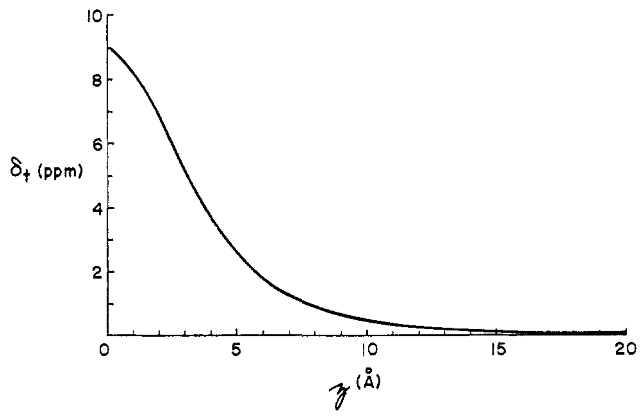

Figure 4. Graph of incremental chemical shift *vs.* distance along the fourfold axis of the phthalocyanine ring as determined from the five-loop-pair calculations.

side groups of the silicon and germanium oligomers. Table III gives the results.

As is seen, the fit for the values from this calculation is significantly better than the fit for the values from the previous calculation. This result is not surprising, because bond length data on the phthalocyanines suggest that the outer benzo rings are quite benzene-like in character and that the bonds attaching them to the inner great ring have substantial single-bond character.[22]

Calculations for the five-loop-pair models were also carried out for frozen configurations of the rings. A fit nearly as good as that obtained for free rotation of the rings was obtained with full staggering of the rings. A somewhat poorer fit was obtained with full eclipsing of the rings.

If it is assumed that the $\pi$ electrons of the nitrogen atoms are essentially localized, the final values obtained for $a$ and $2n$ in the freely rotating five-loop-pair calculations appear reasonable. Little emphasis is placed on this result as a description of physical reality, however, since the model is a simple classical one. What is more important is that a relatively good fit between observed and calculated increments has been achieved with satisfactory internal consistency.

**Additional Calculations.** Examination of the structure of $PcSi(OSi(C_2H_5)_3)_2$ shows that the methylene groups of the triethylsiloxy groups are in positions comparable to those occupied by the inner methyl groups of $PcSi(OSi(CH_3)(OSi(CH_3)_3)_2)_2$. It was accordingly interesting to compare the observed incremental shift for these methylene groups (taking triethylsilanol as a reference in determining the incremental shift) with that calculated for the inner methyl groups of $PcSi(OSi(CH_3)(OSi(CH_3)_3)_2)_2$. As is seen, Table IV, the agreement obtained is good even though the model used in getting the calculated incremental shift is probably considerably less valid for this case because of hindrance to rotation about the Si–C bond. Similar agreement was found for analogous data for the germanium compound, Table IV.

**Table IV.** Incremental Shifts for Siloxy Protons of Triethylsiloxyphthalocyanines (ppm)

| | Outer protons | | Inner protons | | |
|---|---|---|---|---|---|
| | Obsd | 5 loop pairs | Obsd | 1 loop pair | 5 loop pairs |
| $PcSi(OSi(C_2H_5)_3)_2$ | 2.20 | 2.89 | 3.02 | 3.52 | 3.08 |
| $PcGe(OSi(C_2H_5)_3)_2$ | 2.19 | 2.78 | 2.96 | 3.39 | 2.96 |

For the terminal methyl groups of the triethylsiloxy compounds, calculations assuming free rotation about the bonds in the side chains were found to be inadequate as the data in Table IV show. Similarly calculations for the outer methyls of the siloxy side chains of the oligomers assuming free rotation in the chains were also found inadequate, Table V.

**Table V.** Incremental Shifts for Outer Methyl Protons of Oligomers (ppm)

| Central element | No. of rings | Obsd | 5 loop pairs |
|---|---|---|---|
| Si | 1 | 1.33 | 2.55 |
| Si | 2 | 0.69 | 0.88 |
| Si | 3 | 0.34 | 0.41 |
| Si | 4 | 0.20 | 0.21 |
| Si | 5 | 0.11 | 0.12 |
| Ge | 1 | 1.34 | 2.36 |
| Ge | 2 | 0.62 | 0.81 |

**Potential Application.** Since the equation developed adequately describes the ring-current effect of the phthalocyanine ring and since the effect extends for a considerable distance from the ring, Figure 4, it may be possible to use the phthalocyanine ring in quantitative structural studies. Work of this type has been done on some chlorophyll complexes.[7]