

A comparison of the loop-current effect of silicon phthalocyanine and silicon naphthalocyanine rings on their axial ligands

Toshiki Koyama, Takahiko Suzuki, Kenji Hanabusa and Hirofusa Shirai*

Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda 386 (Japan)

Nagao Kobayashi

Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980 (Japan)

(Received October 18, 1993)

Abstract

Silicon phthalocyanine (SiPc) and naphthalocyanine (SiNc) containing two *n*-dodecyloxy axial ligands were synthesized and their NMR spectra were recorded. The effect of the Pc or Nc ring current on their axial ligands was compared between the two systems by using chemical shifts. The ring current effect was larger for Pc in the close vicinity of the molecular center, but at a higher point (about 10 or more carbon atoms) that by the Nc ring becomes stronger. The effect was calculated by computer on the basis of the loop-current effect of π -electrons. Thus, a five- or nine-loop model was used for the Pc or Nc ring, respectively. In close accord with the above experimental results, calculations indicate that the loop-current effect of Pc is larger in the close vicinity of the molecular center but at a distance of more than *c.* 5 Å from the molecular center that of the Nc ring becomes larger.

Key words: Silicon complexes; Phthalocyanine complexes; Loop-current effect

Introduction

The application of axially substituted silicon phthalocyanines and silicon naphthalocyanines as optical materials of the high density digital recording media is studied. For this application of the complexes, thin film formation is very important and depends on their chemical properties, for example, solubility, affinity for the substrates, and self-aggregation. Phthalocyanines have a large molecular plane which induces self-aggregation [1]. Determination of the electromagnetic environment above the phthalocyanine plane can be used to investigate the thin solid films of the complexes. Dichloro(phthalocyaninato)silicon (SiCl₂Pc) and dichloro(naphthalocyaninato)silicon (SiCl₂Nc) are able to substitute alkyl, alkoxy, etc. at their axial position without difficulty [2]. The axial ligands are affected by the environment above the molecular plane, therefore measurements of the axial ligands should give information about the environment.

Phthalocyanines (Pcs) [3] and porphyrins [3c,f, 4] have been known to show a large shielding or anti-shielding effect on their NMR chemical shift. Classically, this phenomenon has been explained as the loop-current effect of π -electrons. This effect moves the NMR chemical shift to a higher magnetic field in the region above the molecular plane (shielding effect) or to a lower field in the peripheral region of the molecular plane. For the Pc molecule, two types of calculation models, named the magnetic dipole approximation and the current loop approximation, have been proposed to date. As has been adopted by several authors [3, 4], we feel the latter approximation to be superior, because it has two adjustable parameters, 'current intensity' and 'ring radius', compared to one in the former. Although the loop-current calculation for silicon phthalocyanine (SiPc) derivatives was once reported by Kenney and co-workers [3d], no comparison has been made between the loop-current effect on Pc and naphthalocyanine (Nc) rings. In this paper, we compare the shielding effects on axial ligands by calculation and from experimental ¹³C NMR data of the dodecyloxy derivatives;

*Author to whom correspondence should be addressed

bis(dodecyloxy)phthalocyaninosilicon and bis(dodecyloxy)naphthalocyaninosilicon.

2. Experimental

2.1. Measurements and calculations

^{13}C and ^1H NMR spectra were recorded on a Bruker AC-250 superconducting Fourier spectrometer, while IR spectra were measured with a Jasco A-302 infrared spectrophotometer. Numerical calculations were performed on a Hitachi H-260 computer system using the FORTRAN 77 program.

2.2. Materials

2.2.1. Synthesis of bis(dodecyloxy)phthalocyaninosilicon ($\text{Si}(\text{OC}_{12}\text{H}_{25})_2\text{Pc}$)

Dichlorophthalocyaninosilicon (1.88 g, 3.1 mmol) was refluxed with dry 1-dodecanol (7 ml, 32 mmol), sodium borohydride (1.21 g, 32 mmol) and dry benzene (50 ml) for 2.5 h. The reaction suspension was cooled, filtered off, and the filtrate was concentrated under reduced pressure. The next day, a dark purple crystalline substance was collected by filtration, washed, and vacuum dried, yield 0.02 g, 0.7%. IR (KBr): 2930, 2850, 1521, 1428, 1338, 1291, 1164, 1122, 1082, 910, 760, 733, 573 cm^{-1} . ^1H NMR (250 MHz, CDCl_3) δ : 9.64 (m, 3,6-Pc), 8.33 (m, 4,5-Pc), 1.5 to -2.2 (m, alkyl-H). Anal. Calc. for $\text{C}_{56}\text{H}_{66}\text{N}_8\text{O}_2\text{Si}$: C, 73.81; H, 7.30; N, 12.30. Found: C, 73.73; H, 7.32; N, 12.49%.

2.2.2. Synthesis of bis(dodecyloxy)naphthalocyaninosilicon ($\text{Si}(\text{OC}_{12}\text{H}_{25})_2\text{Nc}$)

This compound was obtained in 16% yield by the method reported in ref. 5. IR (KBr): 2940, 2860, 1380, 1355, 1267, 1090, 765, 722, 502, 472 cm^{-1} . ^1H NMR, δ : 10.06 (s, 1,4-Nc), 8.62 (m, 5,8-Nc), 7.91 (m, 6,7-Nc), 1.8 to -2.2 (m, alkyl-H). Anal. Calc. for $\text{C}_{72}\text{H}_{74}\text{N}_8\text{O}_2\text{Si}$: C, 77.80; H, 6.71; N, 10.08. Found: C, 77.17; H, 6.95; N, 9.88%.

3. Results and discussion

3.1. Models and calculations

Structural parameters used for five-loop-pair (Fig. 1(a)) or nine-loop-pair (Fig. 1(b)) calculations are shown in Fig. 2(a). These parameters were obtained from X-ray data of Pc [6] and naphthalene [7] molecules. The separation of loops from the Pc and Nc plane was fixed at 0.64 Å in accordance with the five-loop-pair calculation of an SiPc by Kenney and co-workers [3d]. The spatial positions of flexible axial chains are difficult to estimate. However, in order to evaluate the ring current effect on them, their positions have to be

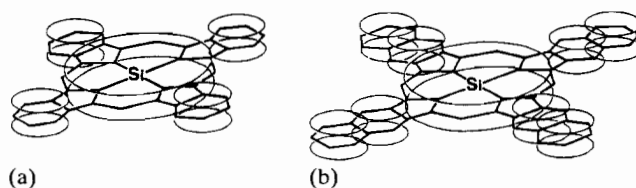


Fig. 1. (a) Five-loop-pair model for Pc and (b) nine-loop-pair model for Nc.

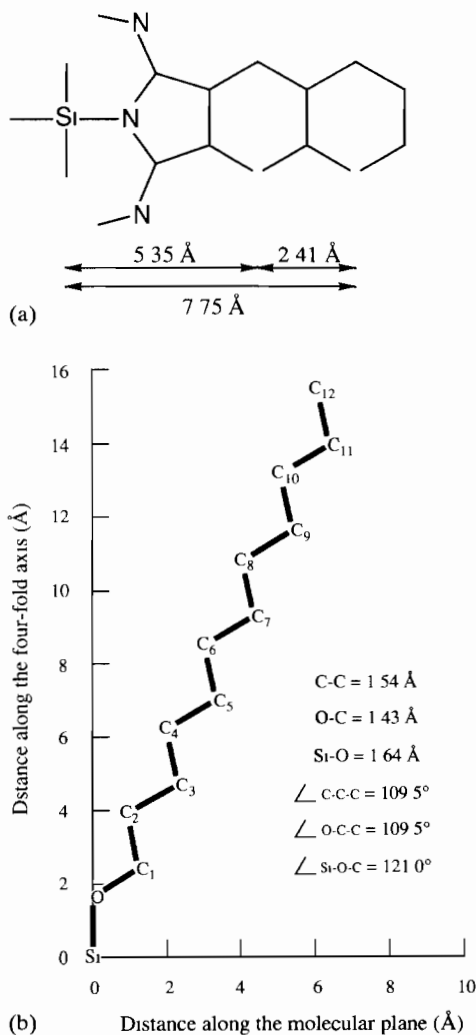
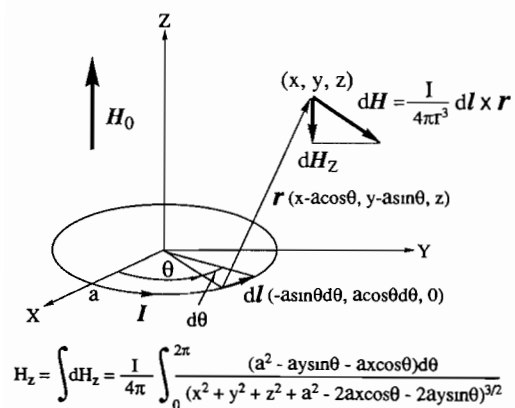


Fig. 2. Structural parameters used for $\text{Si}(\text{OC}_{12}\text{H}_{25})_2\text{Pc}$ and $\text{Si}(\text{OC}_{12}\text{H}_{25})_2\text{Nc}$. (a) Pc or Nc ring and (b) the axial ligand

postulated. Since they are anticipated to be moving above the molecular plane in solution, the fundamental values for distances and angles observed in normal organic compounds were adopted as the average spatial positions (Fig. 2(b)) [8]. The magnetic field strength (H) and the shielding shift ($\Delta\delta$) generated by a current-loop were calculated using the equations based on the Biot-Savart law as shown in Fig. 3.



$$10^{-6} \times \Delta\delta_{\text{eff}} (\text{ppm}) = \frac{H_{\text{eff}}}{H_0} = \frac{H_z}{3H_0}$$

Fig. 3. Calculations for the magnetic field strength (H_z) and the shielding shift ($\Delta\delta_{\text{eff}}$) generated by a current-loop of an aromatic ring.

3.2. Isoshielding lines

Figure 4(a) and (b) shows the calculated average isoshielding lines of the Pc and Nc rings, respectively. Although, there are no large differences between the isoshielding lines in Fig. 4(a) and (b), the isoshielding intensity for the Nc around the molecular center is smaller than for the Pc. However, at a distance of more than *c.* 5 Å along the four-fold axis, the shielding intensity of the Nc ring becomes larger than that of

the Pc. These are induced by the outer four benzo loops on the Nc molecule.

3.3. NMR measurements

Figure 5(a) and (b) are the observed ^{13}C NMR spectra of the Pc and Nc in the axial ligand region. In the spectrum of the Pc, 12 sharp signals from the 12 axial carbons are observed, but in the Nc the signals are broader and not as well resolved as in the Pc. Since it is difficult to assign the closely located signals to the individual axial carbons, they were assigned by comparing them with the chemical shift reported for 1-dodecanol [9] on the assumption that the shielding effect may be simply decreased with increasing distance from the molecular plane, i.e. in the order of the number of the axial carbons shown in Fig. 2(b).

The shielding intensity, $\Delta\delta_{\text{Pc or Nc}}$, is defined by

$$-\Delta\delta_{\text{Pc or Nc}} = \delta_{\text{Pc or Nc}} - \delta_{\text{OH}}$$

where $\delta_{\text{Pc or Nc}}$ is the observed chemical shift for the axial carbon of the Pc or the Nc and δ_{OH} is the chemical shift of ^{13}C NMR reported for 1-dodecanol. The shielding intensity determined by the above equation was compared with the calculated data, and plotted in Fig. 6(a) and (b). In both the Pc and Nc systems, the observed shielding intensity almost agrees with that calculated from our models, and decrease, of course, with the distance from the molecular center of the Pc and Nc. The shielding intensity, $\Delta\delta_{\text{Pc or Nc}}$ values, from

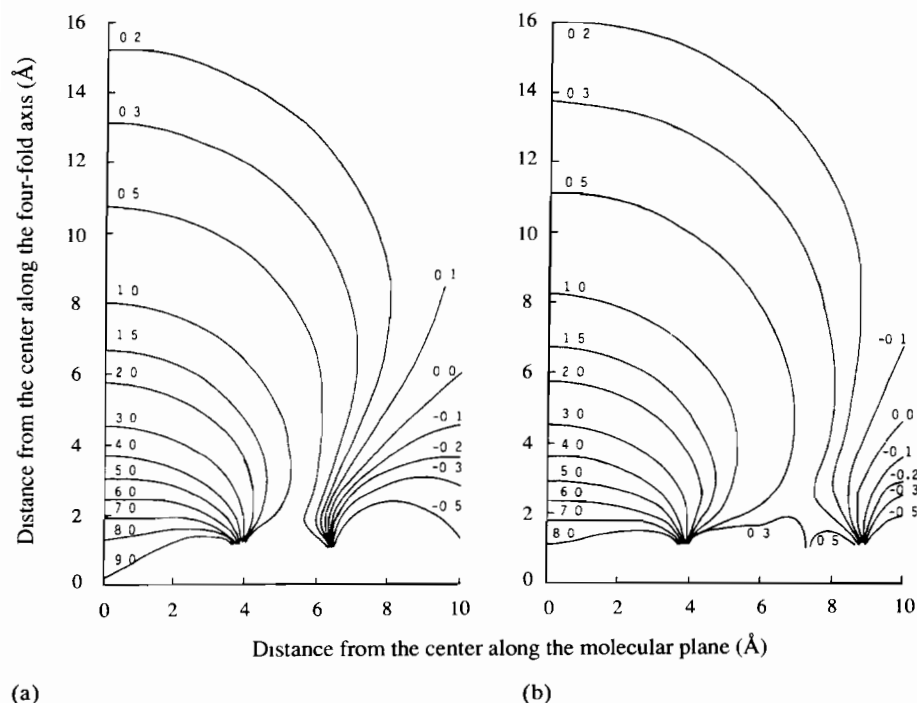


Fig. 4. The average isoshielding lines of (a) the Pc and (b) the Nc rings in ppm as developed for silicon Pc and Nc rings. The plot represents one quadrant of a plane passing through the center of the ring. The ordinate represents the distance from the ring center along the four-fold axis and the abscissa represents the distance from the ring center in the ring plane.

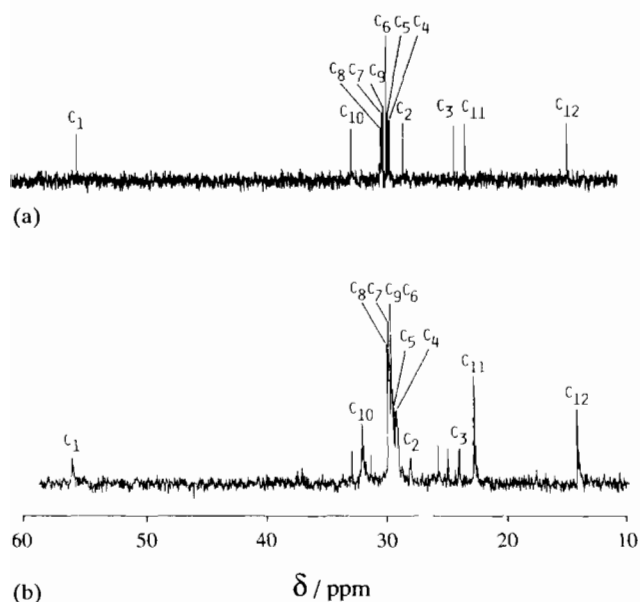


Fig. 5. 250 MHz ^{13}C NMR spectra of (a) $\text{Si}(\text{OC}_{12}\text{H}_{25})_2\text{Pc}$ and (b) $\text{Si}(\text{OC}_{12}\text{H}_{25})_2\text{Nc}$ in CDCl_3 .

the measurement for the carbons near the molecular center are larger than those from the calculation. It must be remembered that the measured $\Delta\delta_{\text{Pc or Nc}}$ values for the axial carbons contain not only the shielding effects of the loop currents but also the structural difference between the dodecyloxy groups bonded with Si and H, because we have used 1-dodecanol as the reference compound in order to determine the shielding intensity, $\Delta\delta_{\text{Pc or Nc}}$. This deviation is negligible and the measured $\Delta\delta_{\text{Pc or Nc}}$ values indicate the shielding effects for more than the 3rd carbons in the axial ligands. In that region in Fig. 6(b) the calculated shielding intensity for the Nc using our nine-loop pair model agreed very

closely with the observed result. In comparison with the calculated values for the Pc and the Nc systems, only a slight difference was obtained, whereas there was a difference between the observed data for the two molecules. In order to show the difference in the shielding effect between the Pc and the Nc systems more explicitly, the difference in the chemical shifts, $\Delta\delta_{\text{Pc-Nc}}$, between δ_{Pc} and δ_{Nc} is shown in Fig. 6(c). In a wide range of distances from the molecular center, the shielding effect of Pc is larger than that of Nc. The shielding effect of the Nc ring becomes stronger than that of Pc only at a distance of more than the 10th carbon in the axial group, although this distance was estimated to be from the 3rd carbon in the calculation (Fig. 4). The divergence between the practical system and calculation may be ascribable to the limits of approximation of the nine-loop pair model which was constructed by simply extending the five-loop pair model.

In conclusion, the loop-current effect of SiPc and SiNc rings on their axial ligand was compared by the observed chemical shifts for the carbons in their axial alkyl groups as well as from calculations using model systems. The results indicate that the shielding effect of the Pc ring is larger in the neighborhood of the molecular center than that of the Nc ring, but that it becomes relatively smaller with increasing distance from the molecular center. It was also demonstrated that the loop-current calculation for the SiNc ring is useful for predicting the spatial configuration of the alkyl carbons in the magnetic environment on the molecular plane in solution.

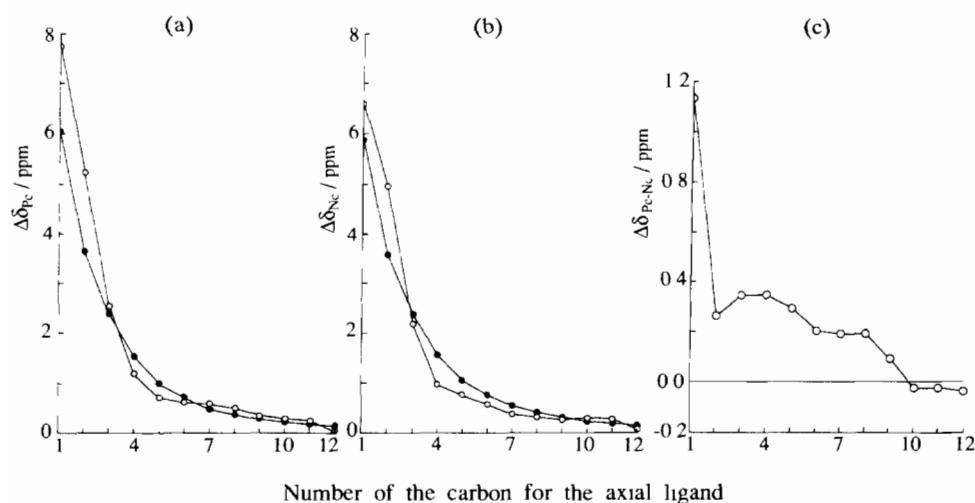


Fig. 6. Observed (O) and calculated (●) chemical shift, $\Delta\delta$, for the axial ligand of (a) $\text{Si}(\text{OC}_{12}\text{H}_{25})_2\text{Pc}$ and (b) $\text{Si}(\text{OC}_{12}\text{H}_{25})_2\text{Nc}$ in CDCl_3 . In (c) is plotted the difference of the observed chemical shift for the axial carbons between $\text{Si}(\text{OC}_{12}\text{H}_{25})_2\text{Pc}$ and $\text{Si}(\text{OC}_{12}\text{H}_{25})_2\text{Nc}$. Values for $\text{Si}(\text{OC}_{12}\text{H}_{25})_2\text{Nc}$ were subtracted from those for $\text{Si}(\text{OC}_{12}\text{H}_{25})_2\text{Pc}$.

References

- 1 (a) H. Sigel, P. Waldmeier and B. Pijls, *Inorg. Nucl. Chem. Lett.*, **7** (1971) 161; (b) E.W. Abel, J.M. Pratt and R. Whelan, *J. Chem. Soc., Dalton Trans.*, **6** (1976) 509.
- 2 F.H. Moser and A.L. Thomas, *The Phthalocyanines*, Vol. 2, CRC Press, Boca Raton, FL, 1983, p. 4.
- 3 (a) J.N. Esposito, L.E. Sutton and M.E. Kenney, *Inorg. Chem.*, **6** (1967) 1116; (b) L.E. Sutton and M.E. Kenney, *Inorg. Chem.*, **6** (1967) 1869; (c) A.R. Kane, R.G. Yalman and M.E. Kenney, *Inorg. Chem.*, **7** (1968) 2588; (d) T.R. Janson, A.R. Kane, J.F. Sullivan, K. Knox and M.E. Kenney, *J. Am. Chem. Soc.*, **91** (1969) 5210; (e) J.E. Maskasky, J.R. Mooney and M.E. Kenney, *J. Am. Chem. Soc.*, **94** (1972) 2132; (f) J.E. Maskasky and M.E. Kenney, *J. Am. Chem. Soc.*, **95** (1973) 1443.
- 4 (a) E.D. Becker and R.B. Bradley, *J. Chem. Phys.*, **31** (1959) 1413; (b) J. Ellis, A.H. Jackson, G.N. Kenner and J. Lee, *Tetrahedron Lett.*, **2** (1960) 23, (c) R.J. Abraham, *Mol. Phys.*, **4** (1961) 145, (d) R.J. Abraham, P.A. Burbidge, A.H. Jackson and D.B. MacDnald, *J. Chem. Soc. B*, (1966) 620; (e) J.J. Kattz, H.H. Strain, D.L. Leussing and R.C. Dougherty, *J. Am. Chem. Soc.*, **90** (1968) 784.
- 5 B.L. Wheeler, G. Nagasubramanian, A.J. Bard, L.A. Schechtman, D.R. Dinny and M.E. Kenney, *J. Am. Chem. Soc.*, **106** (1984) 7404
- 6 A.B.P. Lever, *Adv. Inorg. Chem. Radiochem.*, **7** (1965) 27
- 7 H.O. House, D.G. Koespell and W.J. Cambell, *J. Org. Chem.*, **37** (1972) 1003.
- 8 (a) S.H. Pine, *Organic Chemistry (Japanese Edn.)*, Hirokawa, Tokyo, 1989, p. 130; (b) W.S. Sheldrick, in S. Patai and Z. Rapport (eds.), *The Chemistry of Organic Silicon Compounds*, Part 1, Wiley, Jerusalem, 1989, p. 262.
- 9 Texas A&M University, *Selected ¹³C NMR Nuclear Magnetic Resonance Spectral Data*, Vol. 1, American Petroleum Institute, TX, 1975, Serial No. 111.