

---

## Regiospecific *ortho*-Lithiation of Phthalocyanines: a Route for One-step Synthesis of Highly Soluble Trimethylsilyl Substituted Phthalocyanines

M. J. Chen,\* C. M. Fendrick, R. A. Watson,† K. S. Kinter,† and J. W. Rathke\*  
Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL, 60439

---

*In situ* trapping of lithiated phthalocyanines by chlorotrimethylsilane produces highly soluble phthalocyanines; the reaction is regiospecific and yields non-peripherally (1, 4, 8, 11, 15, 18, 22, and 25 positions) substituted phthalocyanines,  $H_2Pc(SiMe_3)_x$  where  $x = 4, 3,$  and  $2$ .

---

Low solubility in common organic solvents is a characteristic of phthalocyanines (**1**) that has hampered the development of their solution chemistry. Most of the effort to solubilize phthalocyanines has been directed towards synthesis of peripherally (2,

3, 9, 10, 16, 17, 23, and 24 positions) substituted derivatives.<sup>1-5</sup> A recent paper describes octa-alkylphthalocyanines with substitution at non-peripheral (1, 4, 8, 11, 15, 18, 22, and 25) positions.<sup>6</sup> All of these phthalocyanines were prepared by condensation of precursors, *e.g.*, substituted phthalonitriles and phthalimides, preparations of which are often laborious. We report here a one-step synthesis that converts preformed phthalocyanines into highly soluble non-peripherally substituted phthalocyanines.

---

† Work supported by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, under contract No. W-31-109-ENG-38.

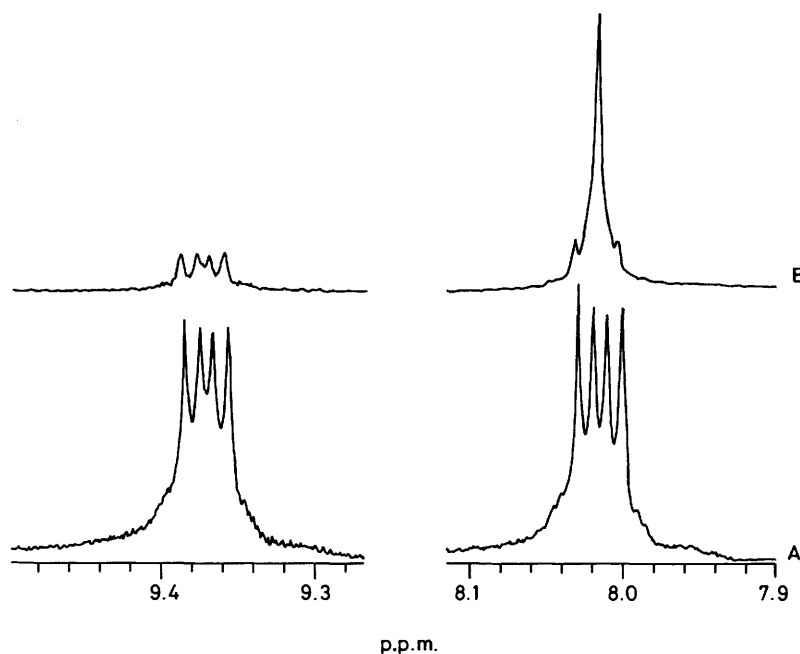
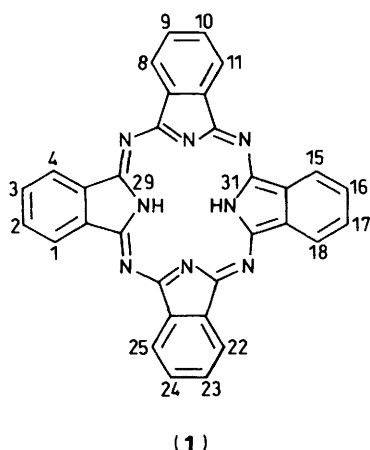


Figure 1.  $^1\text{H}$  N.m.r. spectra (300 MHz) of (A)  $\text{Li}_2\text{Pc}$  and (B) deuteriated  $\text{Li}_2\text{Pc}$  in  $[\text{}^2\text{H}_6]$ -acetone

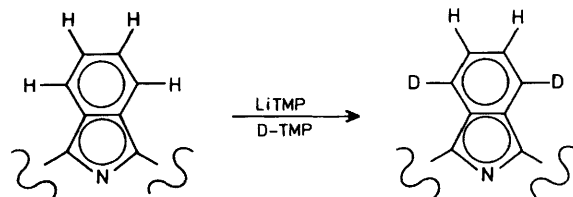


Addition of lithium 2,2,6,6-tetramethylpiperidide (Li-TMP; 7.8 mmol) to a solution of 29*H*, 31*H*-phthalocyanine ( $\text{H}_2\text{Pc}$ , 1.0 mmol) and chlorotrimethylsilane (8.7 mmol) in tetrahydrofuran at  $-78^\circ\text{C}$ , followed by slow warming to ambient temperature, and acidification, produced a mixture of trimethylsilyl-substituted phthalocyanines,  $\text{H}_2\text{Pc}(\text{SiMe}_3)_x$ . The product mixture, separated *via* column chromatography, gave isolated yields of 13, 18, and 3% for  $x = 4, 3$ , and  $2$ , respectively.\* No  $\text{H}_2\text{Pc}(\text{SiMe}_3)_x$  with  $x > 4$  was obtained even for a reaction with a ratio of  $\text{Li-TMP}/\text{H}_2\text{Pc} = 32$ ; under these conditions, the yield of  $x = 4$  product was increased. In this reaction, the sterically hindered Li-TMP, instead of attacking  $\text{Me}_3\text{SiCl}$ , *ortho*-lithiates  $\text{H}_2\text{Pc}$ , which is then trapped by  $\text{Me}_3\text{SiCl}$  to afford the

\* All these products were isolated as isomeric mixtures from which some pure isomers may be isolated. The analytical data for  $\text{H}_2\text{Pc}(\text{SiMe}_3)_x$  fractions are presented below. (1) For  $x = 4$ , Found: C, 65.8; H, 6.35; N, 14.05; Si, 13.4. Calc. for: C, 65.8; H, 6.25; N, 13.95; Si, 14.00%. (2) For  $x = 3$ , Found: C, 67.25; H, 5.9; N, 15.6; Si, 11.51. Calc. for: C, 67.35; H, 5.8; N, 15.35; Si 11.55%. (3) For  $x = 2$ , Found: C, 69.2; H, 5.2; N, 16.95; Si, 8.65. Calc. for: C, 69.25; H, 5.20; N, 17.0; Si, 8.55%.

products.<sup>7</sup> The product mixture is very soluble in nonpolar organic solvents. For example, the solubility in  $\text{CH}_2\text{Cl}_2$  is 0.07M at  $25^\circ\text{C}$ .

The  $^1\text{H}$  n.m.r. spectra of the aromatic protons of  $\text{Li}_2\text{Pc}(\text{SiMe}_3)_4$  show that there are only half as many non-peripheral protons ( $\delta = 9.34\text{--}9.41$  p.p.m.) as the peripheral protons ( $\delta = 7.98\text{--}8.05$  p.p.m.), indicating that the lithiation and, therefore, the silylation are directed very selectively, if not entirely, to the non-peripheral positions. Such heteroatom directed *ortho*-lithiations are well known in aromatic and heteroaromatic systems.<sup>8</sup> In support of this conclusion, a Li-TMP catalyzed H-D exchange reaction at  $-23^\circ\text{C}$  between  $\text{Li}_2\text{Pc}$  and  $[\text{}^2\text{H}]$ -2,2,6,6-tetramethylpiperidine, leads to selective replacement of the non-peripheral hydrogens. As expected, the  $^1\text{H}$  n.m.r. spectra of the deuteriated  $\text{Li}_2\text{Pc}$  (Figure 1) shows a singlet at  $\delta 8.02$  p.p.m. for the peripheral protons, because their couplings to the non-peripheral protons vanish; the multiplet at  $\delta 9.37$  p.p.m. for the residual non-peripheral protons is relatively weak. The  $^2\text{H}$  n.m.r. spectra of the deuteriated  $\text{Li}_2\text{Pc}$  show a strong singlet at  $\delta 9.38$  p.p.m. for the non-peripheral deuteriums while the expected singlet at  $\delta 8.02$  p.p.m. for the peripheral



deuteriums is barely discernible. At higher reaction temperatures, the selectivity is poorer. The fact that all eight non-peripheral protons of  $\text{Li}_2\text{Pc}$  are replaced in the H-D exchange experiment but only a maximum of four trimethylsilyl groups may be put on these positions suggests that only one trimethylsilyl group may occupy each of the pockets between two adjacent isoindole moieties, presumably due to the bulkiness of the group. With this constraint, there are four isomers for  $\text{H}_2\text{Pc}(\text{SiMe}_3)_4$  which have a statistical distribution

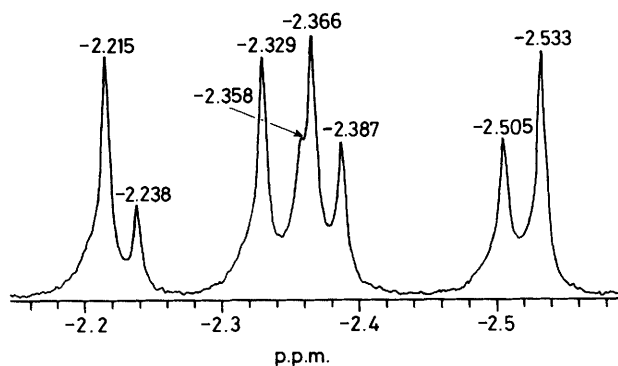


Figure 2.  $^{29}\text{Si}\{^1\text{H}\}$  N.m.r. spectrum (60 MHz; TMS at  $\delta = 0$ ) of  $\text{H}_2\text{Pc}(\text{SiMe}_3)_4$  in  $\text{CDCl}_3$

of 1:1:2:4. An isomeric mixture of this distribution would have eight  $^{29}\text{Si}$  resonances of equal intensity for the eight magnetically distinct  $\text{SiMe}_3$  groups. Consistent with this, the  $^{29}\text{Si}$  n.m.r. spectrum of  $\text{H}_2\text{Pc}(\text{SiMe}_3)_4$  (Figure 2) shows 8 resonances at  $-2.515 \geq \delta \geq -2.533$  p.p.m. (in reference to TMS in  $\text{CDCl}_3$  at  $\delta = 0$ ). The distribution of isomers appears to be close to statistical (within a factor of 3). For the purpose of comparison, one of the four isomers, 1,8,15,22-tetrakis-(trimethylsilyl)phthalocyanine, has been prepared by a more

laborious synthetic route.\* This isomer gives a single  $^{29}\text{Si}$  resonance at  $\delta -2.366$  p.p.m..

\* Synthesis of this compound will be reported separately.

#### Acknowledgements

We thank Professor J. Halpern and Dr. D. W. Slocum for helpful discussion.

#### References

- 1 J. Metz, O. Schneider, and M. Hanack, *Inorg. Chem.*, 1984, **23**, 1065.
- 2 A. W. Snow and N. L. Jarvis, *J. Am. Chem. Soc.*, 1984, **106**, 4706.
- 3 A. R. Koray, V. Ahsen, and Ö. Bekâoğlu, *J. Chem. Soc., Chem. Commun.*, 1986, 932.
- 4 N. Kobayashi and Y. Nishiyama, *J. Chem. Soc., Chem. Commun.*, 1986, 1462.
- 5 C. C. Leznoff, S. Greenberg, B. Khouw, and A. B. P. Lever, *Can. J. Chem.*, 1987, **65**, 1705.
- 6 M. J. Cook, M. F. Daniel, K. J. Harrison, N. B. McKeown, and A. J. Thomson, *J. Chem. Soc., Chem. Commun.*, 1987, 1086.
- 7 T. D. Krizan and J. C. Martin, *J. Am. Chem. Soc.*, 1983, **105**, 6155.
- 8 H. W. Gschwend and H. R. Rodriguez, *Org. React.*, 1979, **26**, 1; P. Beak and V. Snieckus, *Acc. Chem. Res.*, 1982, **15**, 306.

Received 26th October 1988 (Accepted 12th January 1989);  
Paper 9/00224C