The raw data gathered from a rate determination consisted of a plot of milliliters of standard acid added as a function of time. Over approximately 10% of the reaction this plot was linear after a small induction period, the time necessary for the monomethylamine to reach a steady-state concentration in the reaction vessel. Therefore the rate of reaction was determined using the method of initial rates[2] and the direct determination of d[NH_2CH_3]/dt under initial reaction conditions of reactant concentrations. Initial nucleophile concentrations were varied from 0.025 to 0.40 M.

Product Characterization. The two 2,2-diphenylethylamine-di(para-substituted phenyl)boranes isolated as reaction products in this study were prepared by the following general procedure. Equimolar quantities (2.5 mmol) of the desired methylamine-borane and $(C_6H_5)_2CHCH_2NH_2$ (0.4932 g, 2.33 mmol) were weighed out and placed in the reaction flask of the kinetic apparatus. The saturator was filled with solvent in a nitrogen-filled drybox and fitted to the reaction flask into which the minimum amount of solvent necessary to dissolve the substrate and nucleophile was added. The p-bromo derivative was synthesized using both benzene and diglyme as solvents, while the p-methoxy derivative was synthesized using only diglyme. The kinetic apparatus was assembled as described above and placed in the constant temperature bath overnight. If diglyme was the solvent used, it was removed by vacuum-line techniques, the resulting oil taken up in the minimum amount of benzene, hexane added, and crystallization allowed to proceed at 0°. Otherwise, hexane was added directly to the benzene solution and crystallization allowed to proceed. The compounds were recrystallized twice again from a benzene-hexane solvent mixture. Yields were 70–80% of theory. The physical properties of the compounds follow. Di(p-bromophenyl) derivative, mp 148°. *Anal.* Calcd for $C_{26}H_{24}BNBr_2$: C, 59.91; H, 4.65; B, 2.07; N, 2.69; Br, 30.67. Found: C, 60.28; H, 4.68; B, 2.19; N, 2.56; Br, 30.62. Di-(p-anisyl) derivative, mp 118°. *Anal.* Calcd for $C_{28}H_{30}BNO$: C, 79.41; H, 7.17; B, 2.55; N, 3.31. Found: C, 79.64; H, 7.20; B, 2.41; N, 3.07.

Acknowledgment. This research was generously supported by National Science Foundation Grants No. GP7735 and GP4922, for which the authors express their appreciation.

Dodecamethyldioxa[1.1]di-p-disilinocyclophane. A Novel Organosilicon Cyclophane

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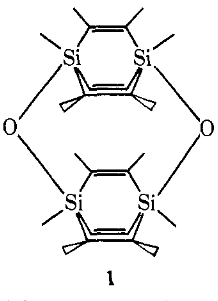
Received October 7, 1970

Abstract: The title compound was prepared *via* high-dilution hydrolysis of 1,4-dichloropermethyl-p-disiline (**2**). This cyclophane exhibits high stability toward electron bombardment as evidenced by its very simple mass spectrum. Reduction of the cyclophane by potassium metal produces an unusual radical anion ($a^{H}_{Si-CH_3} = 1.25$ G, $a^{H}_{C-CH_3} = 2.5$ G, $g = 2.00169$) in which the unpaired electron is delocalized *via* transannular interactions which involve the Si–O–Si moiety only to a minor extent.

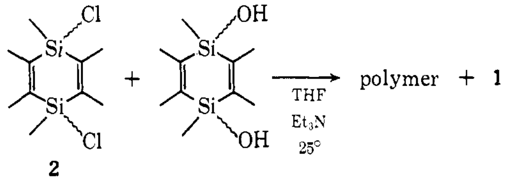
Although paracyclophanes containing silicon atoms at the bridge positions have been known for some time,[1] paracyclophane analogs with bridgehead silicon atoms have not been reported.

We present in this paper the isolation and evidence corroborating the structure determination of a [1.1]paracyclophane analog **1**.



1

In connection with other work we had the occasion to prepare a 1,4-dichloropermethyl-p-disiline[2] (**2**) *via* standard procedures.[3,4] Treatment of **2** with anhydrous hydrazine[5] afforded polymers plus a crystalline solid. The nmr ir, mass, and esr spectra (*vide infra*) of the crystalline compound, produced in 1–5% yield, agree well with structure **1**. Although this was an accidental synthesis, we succeeded in the preparation of **1** by an independent route which, of course, is an additional proof of structure.



2

Compound **1** crystallizes from a dilute ether solution in perfect hexagonal prisms, is thermally stable, and sublimes near 268°. Its thermal stability allows purification *via* gas chromatography (60 × 0.6 cm column, SE-30 on silanized chromosorb W 30–60 mesh; injection, 300°; column, 200°; detection, 300°).

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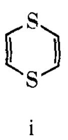
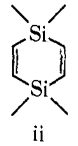
(1) H. Gilman, *Advan. Organometal. Chem.*, 7, 43 (1968).

(2) Heterocycles containing the nucleus i are described as p-dithiines. Because of the similarity between ii and i, we feel justified in calling



i



ii

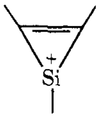
compounds of type ii p-disilines. Application of this nomenclature shortens the name of substituted ii considerably.

(3) W. H. Atwell and D. R. Wyenberg, *J. Amer. Chem. Soc.*, **90**, 3438 (1968).

(4) Dow Corning Corp., British Patent 1,160,661 (1969); *Chem. Abstr.*, 71, 81512j (1969).

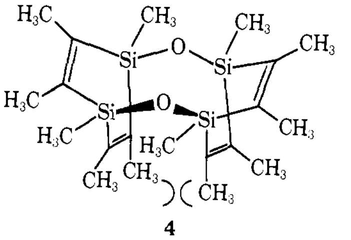
(5) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1967, p 434.

Spectroscopic Properties. The presence of a prominent parent peak in the mass spectrum of **1** (*m/e* 420, 100% relative intensity) establishes the molecular weight of the substance and is indicative of the substance's stability toward electron bombardment. The most efficient fragmentation process is loss of a methyl group (75% relative intensity) presumably from silicon, which is not an unexpected result.[6] An exact mass measurement of the parent peak and consideration of the silicon and carbon isotope peaks established the empirical formula ($C_{20}H_{36}O_2Si_4$) to within 2 ppm. Exact mass measurement of the *m/e* 97 peak revealed that it was due to $[C_5H_9Si]^+$. We are tentatively assigning a silirene structure (**3**) to this fragment. Volpin and coworkers[7] mistakenly[3] believed they had isolated a neutral analog of **3**. It is very possible that the siliconium ion **3** is quite stable in the gas phase. It is formed in 14% relative intensity and, next to loss of a methyl group from the parent, this constitutes the most efficient fragmentation process of **1**.

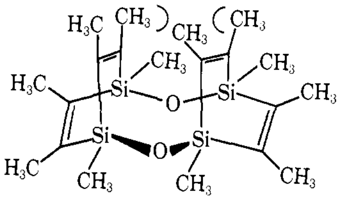


3

Since the nmr spectrum of **1** (CS_2 solvent, TMS internal standard) shows only two single lines in a ratio of 2:1 at δ 1.7 and 0.15 ppm, respectively, the rings in **1** are probably planar. On the other hand, rapidly interconverting boats (**4**, **4′**) may give rise to the observed spectrum. Inspection of molecular models, however, reveals severe nonbonded interactions between methyl groups on opposite rings in the base of the basket-like structures.



4



4′

The chemical shift of the carbon-bound methyl hydrogens is 0.2 ppm upfield relative to the chemical shift of the carbon-bound methyl hydrogens in 1,4-dimethoxyhexamethyl-*p*-disiline. This observation, coupled with the results of Janzen and coworkers[8] might imply the existence of a ring current associated with *p*-disilines. If that were the case, the carbon-bound methyl hydrogens in **1** are probably within the shielding zone of the transannular ring.

The ir spectrum revealed the expected absorptions at 2950 (C–H), 1250 (Si–CH_3), 1012 (Si–O),[9] and 850 (Si–CH_3) cm^{-1}. The ultraviolet spectrum showed λ_{max} (end absorption) at 200 mμ and a shoulder at 220 mμ.

Additional confirmation for the proposed structure of **1** was obtained from the esr spectrum of its radical anion. A green radical anion was obtained by reduction of **1** with potassium in 1,2-dimethoxyethane at −80°. The radical anion was stable for several hours at −80° but decayed rapidly when warmed to room temperature. The experimental esr spectrum obtained is well reproduced by the spectrum simulation program SESRS[10] (assuming that $a^{H}{}_{CCH_3} = 2.50$ G and $a^{H}{}_{SiCH_3} = 1.25$ G), except for a slight alternation in peak heights. This might arise from small deviations of the coupling constant ratio from **2** or from an alternating line width effect[11] caused by time-dependent motions of the cation.

Assuming that the coupling constants for the carbon-bound methyl groups can be described by a McConnell-type relation,[8] $a^{H} = Q^{H}{}_{CCH_3}\rho_i$, the spin density on the ring carbons can be calculated. The total spin density on ring carbon atoms is thus 20.0 G/Q, and Q is normally chosen between 20 and 30 G for systems of this type[8,12] giving a total ring carbon spin density between 0.67 and 1. This leaves less than 0.17 of an unpaired electron for each $\geqslant$Si–O–Si$\leqslant$ portion of the molecule. It has been proposed[11] for disilanes and other organosilicon compounds that $Q^{H}{}_{SiCH_3}$, the Q value for silicon bound methyl groups, is in the range 1–1.25 G. However, this is clearly inconsistent with our coupling of 1.25 G, so the hybridization of the silicon orbitals must be different from that encountered in previous radicals.

The small negative shift in g value ($g = 2.00169$) with respect to the free electron is at least unexpected since previous measurements on silicon radicals such as dodecamethylcyclohexasilane[13] have shown positive shifts. This implies a negative spin density on silicon which is consistent with the small Si–O–Si total spin density calculated above.

Experimental Section

1,4-Dichlorohexamethyl-*p*-disiline. This compound was prepared according to a known procedure.[4] We have never isolated

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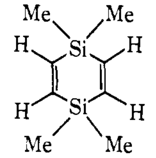
(6) (a) N. Ya, Cheruyak, *et al.*, *Zh. Obshch. Khim.*, 36, 96 (1966); (b) *ibid.*, 36, 89 (1966); (c) W. P. Weber, R. A. Felix, and A. K. Willard, *J. Amer. Chem. Soc.*, 91, 6544 (1969).

(7) M. E. Volpin, Yu. D. Koreshkov, V. G. Dulova, and D. N. Kursanov, *Tetrahedron*, 18, 107 (1962).

(8) E. G. Janzen, J. B. Pickett, and W. H. Atwell, *J. Amer. Chem. Soc.*, 90, 2719 (1968), recorded the nmr spectrum of iii and found that the vinyl protons appear at exceptionally low fields (6.84 ppm relative to TMS).



iii

(9) L. J. Bellamy, "The Infra-red Spectra of Complex Organic Molecules," 2nd ed, Wiley, New York, N. Y., 1958, p 339.

(10) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 38, 1999 (1963).

(11) P. D. Sullivan and J. R. Bolton, *Advan. Magn. Resonance*, 4, 39 (1970).

(12) M. D. Curtis and A. L. Allred, *J. Amer. Chem. Soc.*, 87, 2554 (1965).

(13) E. Carberry, R. West, and G. E. Glass, *ibid.*, 91, 5446 (1969).

the material in its pure state but have confirmed its structure *via* its chemical reactions (*vide infra*). Thus the white sublimate, obtained upon treatment of 1,4-dimethoxyhexamethyl-*p*-disiline[3] with acetyl chloride followed by removal of methyl acetate and excess acetyl chloride, was reconverted to 1,4-dimethoxyhexamethyl-*p*-disiline in an exothermic reaction with methanol and triethylamine. The dichloride was also prepared by Atwell.[14]

1,4-Dihydroxyhexamethyl-*p*-disiline. Acetyl chloride (2 cm^3) was heated to reflux overnight with 450 mg of 1,4-dimethoxyhexamethyl-*p*-disiline. The excess acetyl chloride and methyl acetate were removed under vacuum. The residue was dissolved in 30 cm^3 of dry tetrahydrofuran (distilled from LAH and used immediately). To this solution was added, with stirring, 0.5 cm^3 of triethylamine (distilled from phenyl isocyanate) and 0.04 cm^3 of water in 30 cm^3 of dry THF. The mixture was allowed to stir overnight at room temperature. After the triethylamine hydrochloride was removed by filtration, the solvent was removed to afford the dihydroxide in quantitative yield. The white solid sublimes at 230°, is soluble in MeOH and DMSO, slightly soluble in ether, and insoluble in petroleum ether: mass spectrum (*m/e*) 228 (parent, 20%) 213 (M − 15, 70%), 195 (50%), 173 (100%), 159 (80%), 119 (50%), 97, 99 (20%), 75 (60%), 61 (20%), 45 (60%); nmr (DMSO-d_6, δ, external TMS) 0.05 (s, 6), 1.8 (s, 12), 3.4 (s, 1), 5.45 (s, 1). Therefore the dihydroxide exists as a 50/50 cis–trans mixture of isomers, where the difference in chemical shift between the isomeric hydroxyl hydrogens is ~2 ppm. Glpc (2-ft, 0.25-in. 10% SE-30 on silanized chromosorb W 30–60 mesh) showed two peaks of approximately equal intensity.

Dodecamethyldioxa[1.1]di-*p*-disilinocyclophane. Into a small, dry sublimer were placed 0.519 g of 1,4-dimethoxyhexamethyl-*p*-disiline and 1 cm^3 of acetyl chloride. The mixture was heated to reflux overnight. The volatile components were then evaporated under a fast stream of dry argon gas and the residue was sublimed at 70° (1 mm). The sublimer pot was exchanged quickly and the sublimate was washed into the new pot with 15 cm^3 of dry THF. The THF solution was treated with 0.25 cm^3 of hydrazine and allowed to sit for 48 hr. Upon evaporation of the solvent, the residue was washed several times with ether. The ether washings were stored at −15° overnight and deposited 20–50 mg of colorless, hexagonal prisms (sublimation point >268°). The compound is slightly soluble in THF, DMSO, and ether and insoluble in petroleum ether. Glpc (2 ft × 0.25 in. column; 10% SE-30 on silanized chromosorb W 30–60 mesh; injection, 300°; column, 200°; detection, 300°) showed a single component. Elemental analysis was done *via* mass spectroscopy.[15] *Anal.* Calcd for $C_{20}H_{36}O_2Si_4$: 420.1801. Found: 420.1792; error, 2 ppm. Nmr (CS_2, δ relative to TMS internal standard) 0.15 (s, 1), 1.7 (s, 2); ir (KBr) 2950, 1250, 1012, 850 cm^{-1}.

A dilute THF solution of freshly prepared 1,4-dichlorohexamethyl-*p*-disiline (*vide supra*) was treated with a dilute THF solution of 1,4-dihydroxyhexamethyl-*p*-disiline (mixture of isomers). Triethylamine was added and the mixture stirred overnight. Glpc analysis (*vide supra*) indicated the presence of **1** plus telomers.

Electron Spin Resonance Spectroscopy. The green radical anion was prepared by reduction of ~2 mg of **1** with a potassium mirror in 1,2-dimethoxyethane (DME) under high vacuum. The potassium mirror was prepared by five consecutive distillations of the metal under vacuum and the DME was dried over sodium–potassium alloy under vacuum until a stable blue color from the dissolving metal was obtained.

The esr spectra were recorded on a Varian-4502 spectrometer equipped with a 12-in. magnet and variable-temperature control. They were calibrated with a Ventron G-502 gaussmeter. Simulated spectra were calculated on a CDC-6400 computer using a suitably modified SESRS[10] program.

Acknowledgment. We acknowledge support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also wish to thank Mr. Patrick Gallagher for recording the esr spectra and the SUNY institutional fund for computer time. The mass spectra and exact mass measurements were performed by the Battelle Memorial Institute Mass Spectrometry Laboratory under the sponsorship of Professor A. Padwa's NIH grant.

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[14] W. H. Atwell, private communication.

[15] Mass spectrum and computer work done by Battelle Memorial Institute; *cf.* Acknowledgment.

Thermodynamic and Kinetic Properties of an Iron–Porphyrin System

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Abstract: The synthesis and characterization of an iron (ferric)-porphyrin monomer and dimer system are described in this paper. A water-soluble porphyrin—the tetrasulfonated tetraphenylporphine (TPPS)—was employed to study the system in aqueous solutions. The magnetic susceptibility and visible absorption spectra of both the iron monomer tetraphenylporphine and the iron monomer of the sulfonated tetraphenylporphine were studied; the dimers of both these systems were also studied. The comparison of the data of the sulfonated and nonsulfonated tetraphenylporphine systems has led to the assignment to both of a monomer $Fe^{III}TPPS$ species and of an oxo-bridged dimer species in aqueous solutions. The equilibrium constant of the dimerization was determined at constant ionic strength ($\mu = 0.10$) and found to be (25°) $K_D = 0.79 \times 10^{-8}\ M$, where K_D is defined by $2Fe^{III}(OH_2)TPPS \rightleftharpoons O\text{-}[Fe^{III}TPPS]_2 + 2H^+ + H_2O$ (K_D). The rate of breakdown of the dimer into monomer (at $\mu = 0.10$, 25°) was studied and led to a rate law $d[\text{dimer}]/dt = \{k_{21} + k_{21}'[H^+]\}[(FeTPPS)_2O]$, with $k_{21} = 41\ sec^{-1}$ and $k_{21}' = 840\ M^{-1}\ sec^{-1}$.

The iron–porphyrin system is central to the functioning of many biological systems and thus an understanding of the chemical and physical properties of this system is desirable. The relation of the structural aspects of metalloporphyrins to some of their properties has recently been reviewed.[1] This paper continues the study of the chemistry of a water-soluble porphyrin ligand[2] when it is complexed to iron(III).

(1) E. B. Fleischer, *Accounts Chem. Res.*, **3**, 105 (1970).

(2) E. B. Fleischer, *Inorg. Chem.*, **1**, 493 (1962); E. B. Fleischer, E. Choi, P. Hambright, and A. Stone, *ibid.*, **3**, 1284 (1964); E. B. Fleischer, S. Jacobs, and S. Mestichelli, *J. Amer. Chem. Soc.*, **90**, 2527 (1968).