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CYCLIC POLYSILANES

X *. GEOMETRICAL ISOMERS AND ELECTRONIC PROPERTIES OF 1,2,3,4-TETRA-t-BUTYLTETRAMETHYLCYCLOTETRASILANE

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Summary

Three of the four possible geometrical isomers of the four-silicon ring 1,2,3,4-tetra-t-butyltetramethylcyclotetrasilane, $(t\text{-BuMeSi})_4$, are formed in the alkali metal-assisted coupling of $t\text{-BuMeSiCl}_2$. The conformations of the *trans-trans-trans*, *cis-trans-trans*, and *cis-trans-cis* isomers are correlated with their ^1H NMR spectra. Extreme electronic properties associated with the strained silicon σ-bonding framework include the longest wavelength UV transition and the lowest first ionization potential yet observed in alkyl polysilanes and multiple charge-transfer bands with TCNE.

The cyclopolysilanes are of special interest because they exhibit unusual electronic properties thought to result from (a) low energy of the Si—Si σ-bonding electrons; (b) electron delocalization in the σ-framework [2]; and (c) the presence of low-energy unfilled MO's [3]. For instance, permethylcyclopolysilanes have been shown to act as donors in charge-transfer complexation with π-acceptors [4,5] and to form electron-delocalized anion-radicals resembling those of aromatic hydrocarbons [6].

Sterically-hindered peralkylpolysilanes have received very little study to date. A brief note reports the isolation of $(i\text{-Bu}_2\text{Si})_5$ as the only cyclic product from condensation of diisobutyldichlorosilane [7]. The discouragingly low 1% yield of this product indicates that the condensation reaction may be expected to reflect the steric loads imposed upon it. However, a system with only one bulky substituent on each silicon might be better able to accomodate the vicinal and transannular compressions which develop upon ring formation. The presence of two different alkyl substituents gives rise to the possibility of geometrical isomers, which have not yet been observed in cyclopolysilanes [8].

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* For part IX see ref. 1.

We have investigated the condensation of t-butylmethyldichlorosilane and report in this paper the identification of three of the four possible isomers of 1,2,3,4-tetra-t-butyltetramethylcyclotetrasilanes (I), (t-BuMeSi)$_4$. Prior to this work the only four-membered alkyl cyclopolysilane known was octamethylcyclotetrasilane, (Me$_2$Si)$_4$, formed as a labile minor product during photolytic ring contraction of (Me$_2$Si)$_6$ [9]. The strained silicon framework in these new four-membered rings gives rise to extreme electronic properties which are discussed below [10]. Accompanying papers treat the reactivity [11] and the photoelectron spectrum of (t-BuMeSi)$_4$ and related compounds [12].

Experimental

All reactions involving Na/K alloy were carried out under atmospheres of prepurified nitrogen using standard techniques with oven-dried glassware. THF and hydrocarbon solvents were distilled prior to use from Na/K alloy.

Combustion analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. All melting points are uncorrected. Gas chromatographic (GLC) separations were performed on a Varian A-700 chromatograph using a 15' × 1/4" 20% Dexsil column. High pressure liquid chromatographic (HPLC) separations were performed on a DuPont 830 chromatograph at 1200 psi using a 1m × 2mm ID "Permaphase ODS" (octadecylsilane reverse-phase) column with an 87% MeOH/13% H$_2$O mobile phase.

Spectra were recorded by means of the following instruments: infrared, Perkin—Elmer 457; ^{1}H NMR, JEOL MH-100; mass spectra, AE 1-MS-902 at 70 eV; UV-visible, Cary 14; ESR, Varian 4502-13; photoelectron spectra, Varian IEE-15.

Synthesis of 1,2,3,4-tetra-t-butyltetramethylcyclotetrasilanes (I)

In a typical reaction, [illegible]00 ml three-necked round-bottom flask was equipped with a mechanical stirrer, pressure-equalized addition funnel and reflux condenser. To the flask were added potassium (41.4 g, 1.06 g-atom) and sodium (11.6 g, 0.503 g-atom). Tetrahydrofuran (250 ml) was added and the solution was stirred until silvery beads of sodium/potassium alloy formed. A THF solution (100 ml) of naphthalene (5.45 g, 0.0425 mol) was added and the mixture was brought to reflux. From the addition funnel was added dropwise a solution of t-BuMeSiCl$_2$ [13] (120.1 g, 0.708 mol) in THF (250 ml) over a 2.5 h period, during which time the reaction mixture turned from green-black to red-brown. After 1.5 h of additional reflux, a THF solution (25 ml) of naphthalene (2.7 g) was added and the refluxing was continued for 0.5 h. The mixture was cooled and treated with Me$_3$SiCl (200 ml) to deactivate the metals. The supernatant solution was drawn off under suction through a sintered-glass filter and joined with three filtered THF washings (100 ml each) of the solid residue. The combined THF solution was concentrated; the residue was taken up in ether and this solution was washed (H$_2$O), filtered, dried (MgSO$_4$), and concentrated to give a semi-solid residue (62 g). Crystallization from acetone gave crude I (18 g, 25% yield). Recrystallization from acetone gave a 3/2 mixture of Ia and Ib as colorless needles: m.p. 228.5—230°C (sealed cap). Further crystallization from acetone or ethanol did not significantly alter the ratio of isomers.

Isolation of Ia. Slow partial evaporation of an ether solution of I, in which Ia was present as the major component either through prior recrystallization or partial (kinetic) resolution [11], gave crystals of pure Ia: m.p. 232—232.5°C (sealed cap); IR (CsI): 2965, 2950, 2925, 2890, 2870, 2850, 1470, 1460, 1410, 1380, 1360, 1355, 1240, 1185, 1005, 1000, 935, 930, 810, 750, 670, 580, 455, 390 (Si—Si), 325, 300 cm^{-1}; UV λ_{max} (ϵ, 2,2,4-trimethylpentane): 198, (42 000), 245 (3400), 257(sh) (3200), 300 nm (290); ^{1}H NMR (CCl_4): δ 1.03 (s, 3H, Si—$C(CH_3)_3$), 0.46 ppm (s, 1H, Si—CH_3) and (C_6D_5): δ 1.09 (s, 3H, Si—$C(CH_3)_3$), 0.49 ppm (s, 1H, Si—CH_3); mass spectrum, selected *m/e* (relative intensity) 403(0.8), 402(2.7), 401(5.3), 400(13, M^+), 346(0.9), 345(1.7), 344(4.4, $M - C_4H_8$), 343(0.8), 289(0.85), 288(1.8), 287(2.7), 245(5.5), 231(12), 213(9.0), 171(14), 157(8.2), 141(8.1), 131(9.0), 117(8.4), 73(100), 59(20); exact mass, 400.28320 (calcd. for $C_{20}H_{48}{}^{28}Si_4$, 400.28398). Isomer Ia could just barely be separated from isomer Ib by preparative GLC (220°C, 70 ml He/min; retention time Ia, 19 min; ratio of retention times Ia/Ib = 0.95). Preparative HPLC offered a better means of separation (retention time Ia, 26 min; ratio of retention times Ia/Ib = 1.6).

Anal. found for mixed isomers: C, 59.85; H, 11.79; Si, 27.92. Found for Ia: C, 60.14; H, 12.31; Si, 27.08. $C_{20}H_{48}Si_4$ calcd.: C, 59.91; H, 12.07; Si, 28.02%.

Photolytic generation of Ic from Ia and Ib

A solution of I (Ia/Ib = 1.5, 0.11 g, 0.27 mmol) in freshly distilled and degassed cyclohexane (150 ml) was photolyzed in a Rayonet photochemical reactor at 254 nm with a 15°C cooling coil for 1.5 h. The solution was concentrated and I was recovered by preparative GLC. Its ^{1}H NMR spectrum indicated the presence of isomers Ia, Ib and Ic in equimolar amounts (±5%). Longer reaction times or the absence of the cooling coil accelerated the decomposition of I.

Charge-transfer complexation of I with tetracyanoethylene (TCNE)

When freshly sublimed TCNE (0.023 g, 0.18 mmol) was added to a solution of I (Ia/Ib = 1.5, 0.12 g, 0.29 mmol) in CH_2Cl_2 (5 ml), purified prior to use by passage through a column (10 cm × 2 cm) of activated alumina, a purple color developed. The UV spectrum of this solution, taken against 0.038 *M* TCNE (CH_2Cl_2) as reference, exhibited three weak absorptions with apparent maxima at 395 (sh, br), 460 (br) and 510 (sh, br) nm. Solutions with ten-fold lower concentrations of I and TCNE were colorless.

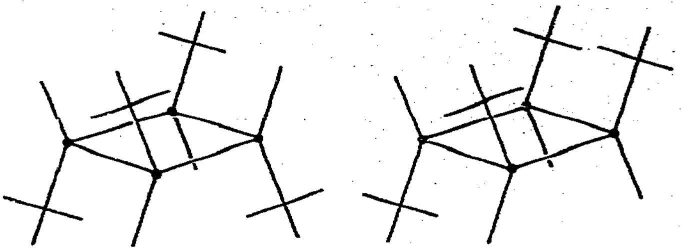
Results and discussion

Preparation and isolation of t-butylated cyclotetrasilanes

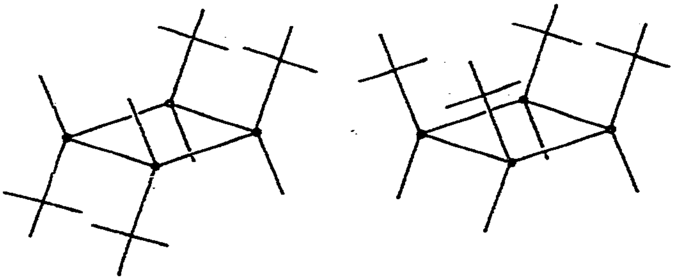
Reductive coupling of t-butylmethyldichlorosilane, t-$BuMeSiCl_2$ [13], with Na/K alloy in tetrahydrofuran (THF) with naphthalene as catalyst [10], conditions previously reported for cyclization of Me_2SiCl_2 [14], gave only one cyclopolysilane, 1,2,3,4-tetra-t-butyltetramethylcyclotetrasilane (I).

$$\text{t-BuMeSiCl}_2 + \text{Na/K} \xrightarrow[(C_{10}H_8)^{\dot{-}}]{\text{THF}, \Delta} \underset{\text{(I)}}{(\text{t-BuMeSi})_4}$$

Optimum crude yields of I of approximately 25% were obtained after 4 h of



Ia (trans-trans-trans) Ib (cis-trans-trans)



Ic (cis-trans-cis) Id (cis-cis-cis)

Fig. 1. The geometrical isomers of (t-BuMeSi)$_4$ in planar conformations (•, Si; +, t-Bu; —, Me).

reflux. Shorter or longer reaction times gave much less I and appreciably more products with Si—O and Si—H functionality. No cyclopolysilanes other than I were ever observed, in contrast to condensations of Me_2SiCl_2, for example, which always yield a mixture of cyclopolysilanes in which $(Me_2Si)_6$ predominates [14]. Presumably I represents a uniquely favorable balance between destabilization from steric load and ring strain on the one hand and stabilization from steric shielding on the other [11].

Recrystallization of crude I from acetone gave pure I identified by ^1H NMR as a 3/2 mixture of isomers (Ia and Ib in Fig. 1). This ratio could not be altered by further recrystallization. Slow partial evaporation of ether solutions of this mixture afforded pure Ia. Incomplete reaction of I with acetyl chloride/aluminum chloride [11] also afforded samples of unreacted I enriched in Ia (>90%). Alternately, Ia could be separated from Ib (and from Ic when it was present) by preparative GLC or HPLC. Slow evaporation of recrystallization mother liquors ultimately gave samples enriched in the very minor isomer Ic but with Ib still present as the major component. Once combined with Ic, isomer Ib could not be separated from it by GLC or HPLC.

Brief, gentle photolysis offered a useful route to Ic. When cold dilute cyclohexane solutions of Ia and Ib, with or without Ic, were photolyzed for no more than 1.5 h, the isomeric ratio of I recovered by preparative GLC was found to have shifted in favor of isomers Ib and especially Ic at the expense of Ia. This short term build-up of Ic is consistent with a competitive process involving ring opening, rotation of one silicon radical terminus, and reclosure. The *cis*-

substituted isomers Ib and Ic would be expected to photolyze faster than Ia [15]. In this way Ia, initially the major component, generates Ib, which in turn gives rise to Ic (and some Ia); photolysis of Ic regenerates Ib. However, conservation of the all-silicon ring by self-quenching ring reclosure is only one of several ongoing photolytic processes, including oxidations to linear and ring-expanded siloxanes [11] and quenching by solvent to give linear hydrosilanes. Even under optimum conditions, considerable ring cleavage was unavoidable; with longer irradiations and higher temperatures the cyclotetrasilane system was rapidly and completely destroyed. Hence the amount of Ic is initially built-up by self-quenching ring reclosure of Ib and later decays.

Geometrical isomers of I

The four possible isomers of I are shown in planar conformation in Fig. 1 (Ia—Id). Of these, only Ia, Ib and Ic were evern observed. Molecular models indicate that the alkyl—alkyl eclipsing interactions in I are severely destabilizing and are best alleviated by a "butterfly" folding of the ring across the diagonal which generates pseudo-equatorial and pseudo-axial substituent orientations. Working against this are critical 1,3-diaxial alkyl—alkyl compressions which then arise. In the absence of other factors, I should prefer folded conformations which accomodate the bulky t-butyl groups in the less hindered equatorial orientations.

There are few quidelines for the conformational analysis of these silicon systems. The introduction of silicon into a carbon chain can have drastic effects on bond lengths, torsional strains, and the nature of the Van der Waals' interactions in linear and cyclic systems. For example, 2-silabutane, in sharp contrast to butane, prefers the *gauche* conformation over the *anti*, attesting to substantial attractive Van der Waals' interactions in the silane [16].

With regard to cyclic systems, Ouellette has predicted on the basis of force field calculations that the most stable conformation of *cis*-4-methyl-1-t-butylsilacyclohexane has the t-butyl group on silicon *axial* and the methyl group equatorial [17]. The methyl group at silicon in 1-methylsilacyclohexane is predicted to prefer an axial orientation [18]. In cyclohexane the t-butyl group acts as an effective conformation lock with an overriding preference for the equatorial orientation [19]. Interestingly, the t-butyl group on carbon in 4-t-butyl-1-methylsilacyclohexane, now in a more cyclohexane-like environment, will lock into the equatorial orientation [20]. However, in cyclobutanes where smaller conformational alkyl ΔG values prevail, the t-butyl group is a poor conformational lock. Thus, in and of itself, the t-butyl group cannot be considered an effective conformational lock in cyclopolysilanes such as I and we might expect I to be conformationally mobile.

Isomer Ia (trans-trans-trans)

The all-*trans* isomer, Ia, can fold in only one direction across either (equivalent) diagonal to offset vicinal eclipsing interactions without incurring prohibitive 1,3-diaxial t-Bu—t-Bu interactions. X-ray diffraction analysis of crystalline Ia [21] showed a folded conformation with a relatively large 36.8° dihedral angle between the two halves (Fig. 2, left). The t-butyl groups, occupying pseudo-equatorial positions above and below the ring, are *trans* to each other and symmetrically equivalent. The methyl groups occupy the remaining symmetrically

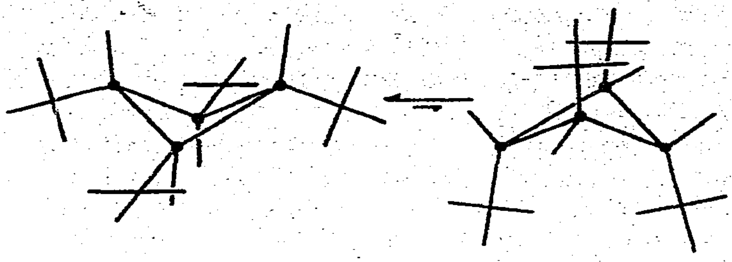


Fig. 2. Extreme folded conformations of Ia.

equivalent pseudo-axial psoitions. Consistent with this structure, the ^{1}H NMR spectrum (CCl_4) of Ia (Fig. 3, top) showed only one singlet at δ 1.03 ppm in the t-butyl region and only one singlet at δ 0.46 ppm in the methyl region. These observed chemical shifts presumably reflect the net equatorial environment of the four equivalent t-butyl groups and the net axial environment of the four equivalent methyl groups in solution. 1,3-Diaxial Me—Me interactions appear to be relatively easily accomodated in the cyclotetrasilane system.

Isomer Ib (cis-trans-trans)

Available to isomer Ib is a conformation involving only one transannular t-Bu—Me compression (Fig. 4, left). That Ib was the second most abundant cyclopolysilane formed in the condensation attests to the ability of the ring to accomodate this interaction. The remaining three t-Bu groups occupy equatorial

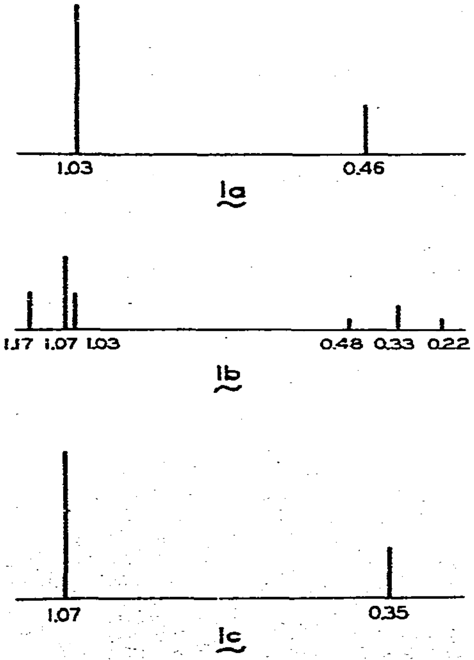


Fig. 3. ^{1}H NMR (δ (ppm), CCl_4) of isomers Ia, Ib and Ic.

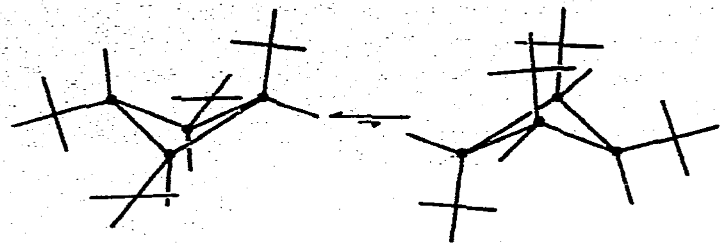


Fig. 4. Extreme folded conformations of Ib.

positions. The ^{1}H NMR spectrum of Ib (Fig. 3, middle) showed the 1/2/1 ratio of t-Bu protons (and of Me protons) corresponding to the overall C_{2v} molecular symmetry.

The methyl singlet at highest field (δ 0.22 ppm) was assigned to the lone pseudo-equatorial methyl which is *cis* to two other methyl groups. The mutual shielding of two methyl groups 1,2-*cis* to each other resulting in shifts to higher field is well documented in cyclohexanes [19]. This phenomenon is also observed in methyl-substituted silacyclobutanes [22,23].

The lowest-field singlet (δ 0.48 ppm) was assigned to the axial methyl group at Si(3). Transannular diaxial steric compressions give rise to shifts to lower field in substituted cyclohexanes [19] and in silacyclobutanes [23]. The equatorial t-butyl at Si(3) was assigned to the singlet at δ 1.03 ppm since it is in essentially the same environment as the t-butyl groups in Ia (δ 1.03 ppm). It follows then that the remaining low field singlet (δ 1.17 ppm) corresponds to the axial t-butyl group at Si(1).

We would expect Ib to have a greater net molecular dipole moment than Ia. Indeed, Ib is eluted before Ia from non-polar chromatographic stationary phases (e.g., SE-30 in GLC and ODS in HPLC) but is eluted after Ia from polar and semipolar columns by nonpolar mobile phases (Dexsil in GLC and silica in HPLC).

Isomer Ic (cis-trans-cis)

This isomer of I is formed as a very minor (<5%) product in the condensation. Its ^{1}H NMR spectrum (Fig. 3, bottom) showed one t-butyl singlet at δ 1.07 ppm and one methyl singlet at δ 0.35 ppm. Either one of the two equivalent extreme folded conformations shown in Fig. 5 would give rise to two distinct pseudo-axial

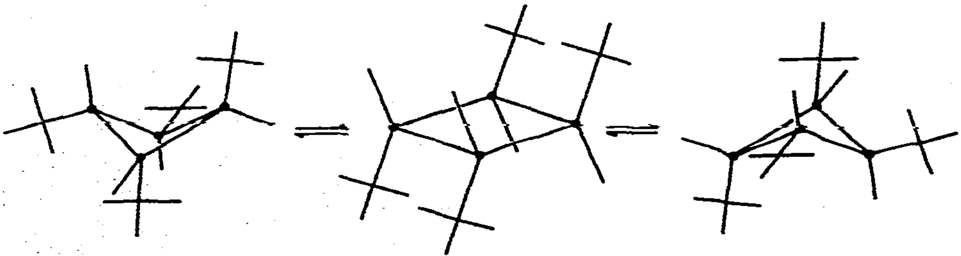


Fig. 5. Planar and folded conformations of Ic.

and pseudo-equatorial substituent environments similar to Si(1) and Si(3) in **Ib**. Rapid flexing of the ring would average these substituent environments, in accord with the lone singlets observed at intermediate positions in their respective regions. The t-butyl and methyl groups in **Ic**, *cis* to methyl on one side and *cis* to t-butyl on the other, are similar to those at Si(2) in **Ib** in this respect and have almost identical chemical shifts.

Electronic properties

Extreme electronic properties are associated with the tetra-t-butylated cyclotetrasilane system compared to previously known cyclopolysilanes. The electrons associated with the delocalized σ-bonding framework are known to exhibit several UV absorptions arising from either $\sigma(\text{Si—Si}) \rightarrow \sigma^*$ [24] or $\sigma(\text{Si—Si}) \rightarrow \pi^*$ [3] excitations. Decreasing the ring size in permethylcyclopolysilanes destabilizes these bonding levels and shifts these absorptions to longer wavelengths. For example, the lowest energy transitions observed for $(Me_2Si)_6$ and $(Me_2Si)_5$ occur at 252 nm (ϵ = 1200) and 272 nm (ϵ = 970), respectively [6]. In **I** this long wavelength absorption is shifted to 300 nm (ϵ = 290). To our knowledge this is the longest wavelength UV transition observed in any cyclic or linear alkyl polysilane with an all silicon σ framework, representing a relatively small ground state first excited state energy difference (Fig. 6).

Information bearing on the ground state of **Ia** was obtained from its photoelectron spectrum which showed ionization from three Si—Si σ-bonding levels at 7.43, 7.85 and 8.13 eV, with a weighted occupancy of 1/2/1, respectively. The first ionization potential is the lowest value yet reported for any polysilane, 0.36 eV lower than the most easily ionized Si—Si bonding electrons in $(Me_2Si)_6$. Further interpretation of the photoelectron spectrum is set forth in the accompanying paper [12].

In view of its relatively easily ionized σ electrons, it was not surprising to find

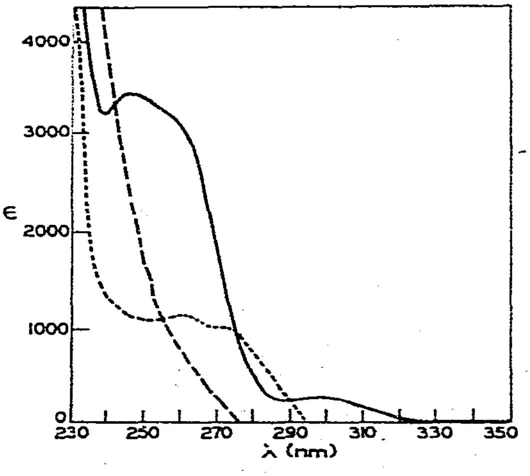


Fig. 6. Ultraviolet spectra of isomer **Ia** of $(t\text{-BuMeSi})_4$ (——), $(Me_2Si)_5$ (. . . . .) and $(Me_2Si)_6$ (- - - -) in 2,2,4-trimethylpentane.

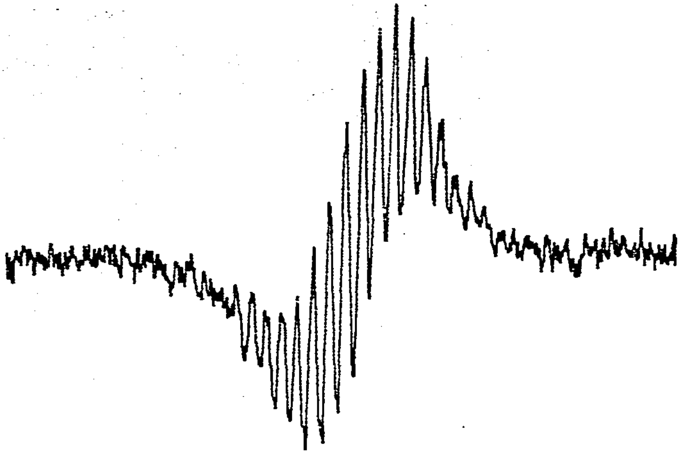


Fig. 7. ESR spectrum of radical anion species from electrolytic reduction of Ia.

that I could act as an electron donor in charge-transfer complexation with a suitable acceptor. Charge-transfer behavior has been observed for other polysilanes with much higher ionization potentials [4,5]. When I was mixed with excess tetracyanoethylene in purified CH_2Cl_2, a purple color developed. The visible spectrum of this colored solution showed three new bands with apparent maxima at 395, 460 and 510 nm, which may arise from charge-transfer from all three occupied Si—Si bonding levels in Ia.

Isomer Ia could be reduced electrolytically at temperatures below —70° C in THF using the spectrometer and techniques previously described [6]. However, the observed ESR spectrum was not consistent with the 13 line pattern expected from splitting of the unpaired electron, delocalized over the ring, by the 12 equivalent methyl protons. Instead we observed a basic singlet (Fig. 7) partially resolved into more than 15 lines with $g = 2.0049$ and an apparent hyperfine splitting constant of 0.47 *G*-values quite in accord with those arising from reduction of other peralkylcyclopolysilanes [6]. We infer from the over-all first-order symmetry and simplicity of the spectrum and the blue color of the electrolyzed solution the presence of a predominant cyclopolysilane-like radical anion species. However even the earliest spectra detectable exhibit a definite asymmetry and corresponding loss of resolution on the far high field side of the multiplet. It appears that a second radical species whose spectrum overlaps that of the major species is present from the outset in low concentration, and persists at that level through to the final spectrum. This could conceivably arise from isomer Ib, present in low concentration (<3%). Even under prolonged electrolysis with the high generating current (4 μA) essential for initial build-up of the major species, a limiting concentration of the radical species could not be exceeded. Without the high current or with temperatures higher than —70° C the spectrum decayed rapidly.

Acknowledgements

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