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OCTANEOPENTYLCYCLOTETRASILANE. SYNTHESIS AND UNUSUAL PROPERTIES

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The entitled compound was synthesized and its molecular structure was determined by X-ray crystallography. Its unusual properties include the lowest energy CT band with TCNE yet observed for cyclotetrasilanes and the easiness of the decomposition of the Si_4 framework on electron-impact fragmentation and thermolysis.

Recently, preparation of the first peralkylcyclotrisilane, hexaneopentylcyclotrisilane, by the reaction of dichlorodineopentylsilane with lithium has been reported from our laboratories.[1)] In connection with this compound, we have studied the reaction of 1,2-dichlorotetraneopentyldisilane with lithium and found that the reaction unexpectedly afforded octaneopentylcyclotetrasilane (1) in a good yield (Eg. 1). Here we report the synthesis, structure, and properties of this particular cyclotetrasilane which differs discernibly in both structure and properties from other cyclotetrasilanes.[2)]

$$\mathrm{Cl({}^tBuCH_2)_2SiSi(CH_2Bu^t)_2Cl} \xrightarrow{\mathrm{Li}} \underset{\underline{1}}{\mathrm{[({}^tBuCH_2)_2Si]_4}} \qquad (1)$$

A solution of the dichlorotetraneopentyldisilane (9.0 g, 22 mmol) in DME was treated with lithium (30% dispersion, 1.2 g, 55 mg-atom) at room temperature for 7 h under argon. Work-up and recrystallization from ethanol afforded an analytically pure sample of 1 (3.5 g, 43% yield) as colorless crystals (monoclinic): Mp 264-290 °C (partially decomposed); ^1H NMR ($CDCl_3$) δ 1.09 (s, 72H) and 1.39 ppm (s, 16H); ^{13}C NMR ($CDCl_3$) δ 31.80 (t and s, CH_2 and $\underline{C}Me_3$) and 34.03 ppm (q, CH_3); ^{29}Si NMR (C_6D_6) δ -23.56 ppm; UV (c-hexane) λ_{max} 286 nm (ε 440); Anal. Found: C, 70.50; H, 13.02 %. Calcd for $C_{40}H_{88}Si_4$: C, 70.31; H, 12.99 %.

An X-ray analysis of 1 (Fig. 1) reveals a value of 2.409 Å (average) for the Si-Si bond length which is the largest among the values yet observed for cyclotetrasilanes[3),4)] and even larger than that of the cyclotrisilane $[({}^tBuCH_2)_2Si]_3$.[4)] Further, the Si_4 framework assumes a highly folded structure with a dihedral angle of 38.8°, which compares with those in $({}^tBuMeSi)_4$ (36.8°)[3)] and $({}^iPr_2Si)_4$ (37.1°).[5)]

Its unusual properties are as follows: (1) 1 shows CT band with TCNE at 600 nm (in CH_2Cl_2) which is the lowest energy transition yet observed for cyclotetrasilanes [e.g., 510 nm in $({}^tBuMeSi)_4$[6)] and 510 nm in $({}^iPr_2Si)_4$[7)]]. (2) 1 fragments under

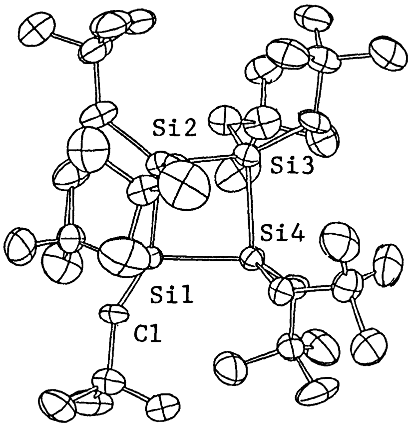

Fig. 1. A Perspective Drawing for 1. Principal bond lenghts (Å) and bond angles (deg): Si(1)-Si(2) 2.433, Si(2)-Si(3) 2.403, Si(3)-Si(4) 2.401, Si(4)-Si(1) 2.398, Si(1)-C(1) 1.91; Si(1)Si(2)Si(3) 86.3, Si(2)Si(3)Si(4) 86.9, Si(3)Si(4)Si(1) 87.1, Si(4)Si(1)Si(2) 86.3.

electron-impact mass spectroscopic conditions (30 eV) in a manner consistent with the formation of tetraneopentyldisilene. 1 gives a peak with m/z 340 (corresponding to the disilene) as the base peak (Eg. 2). The fragmentation of this type

$$\begin{array}{ccc} [({}^{t}\mathrm{BuCH_2})_8\mathrm{Si_4}]^{+\cdot} & \xrightarrow{\qquad\qquad} & [({}^{t}\mathrm{BuCH_2})_4\mathrm{Si_2}]^{+\cdot} \\ m/z\ 680\ (80\%) & & m/z\ 340\ (100\%) \end{array} \qquad (2)$$

is not observed for peralkylcyclotetrasilanes such as $({}^{i}\mathrm{Pr_2Si})_4$ and $({}^{t}\mathrm{BuMeSi})_4$, in which the $\mathrm{Si_4}$ units remain intact until most of the alkyl groups on silicon are eliminated.7) (3) 1 is much less thermally stable compared to $({}^{i}\mathrm{Pr_2Si})_4$. For instance, heating a solution of 1 in decalin at 250°C for 24 h in a sealed tube led to 68% decomposition with the formation of 1,2-dihydrotetraneopentyldisilane (4%), while the perisopropyl derivative remained intact under nearly the same conditions.

Comparison of $[({}^{t}\mathrm{BuCH_2})_2\mathrm{Si}]_4$ with $[({}^{t}\mathrm{BuCH_2})_2\mathrm{Si}]_3$ is of interest and a work along this line is now underway.

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