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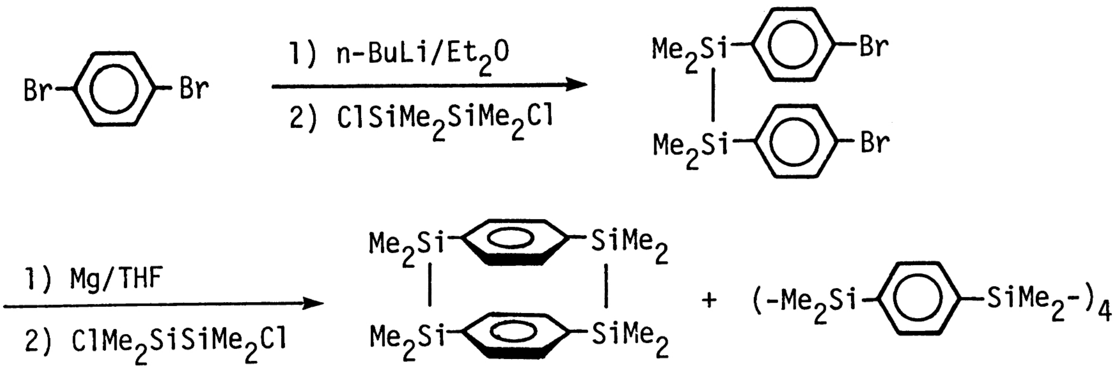
Octamethyltetrasila[2.2]paracyclophane. Cyclophanes Bridged by Polysilanes[1)]

Hideki SAKURAI,* Satoshi HOSHI, Akihiko KAMIYA, Akira HOSOMI, and Chizuko KABUTO†
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980
†Instrumental Analysis Center for Chemistry, Faculty of Science
Tohoku University, Sendai 980

1,1,2,2,9,9,10,10-Octamethyl-1,2,9,10-tetrasila[2.2]paracyclophane, the first [2.2]paracyclophane bridged by heteroatoms, has been prepared. UV, IR, and ^{1}H- ^{13}C- and ^{29}Si-NMR spectral together with X-ray crystallographic data are recorded. The compound displays a strong $\sigma\pi$ mixing between Si-Si bonds and aromatic rings as evidenced by a large red shift in UV spectra.

There is currently intense interest in the chemistry of cyclophanes,[2)] in part due to the expected intriguing physical and chemical properties based on through-space and through-bond interactions between separated π systems. Recently we have reported 3,3,4,4,7,7,8,8-octamethyl-3,4,7,8-tetrasilacyclooctadiyne and related compounds as examples of strongly $\sigma\pi$ mixed system[3)] and have pointed out that interesting spectroscopic properties due to the strong through-bond interactions should be expected for a [2.2]paracyclophane bridged by two Si_2Me_4 units,[4)] the preparation and properties of which are the subject of this paper.

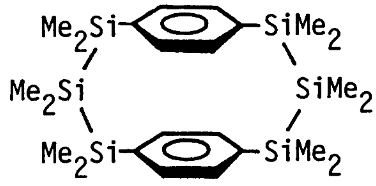
Di(p-bromophenyl)tetramethyldisilane, prepared from p-dibromobenzene and 1,2-dichlorotetramethyldisilane, was converted to the corresponding Grignard reagent which was subsequently subjected to the reaction with 1,2-dichlorotetramethyldisilane under high dilution conditions to give 1,1,2,2,9,9,10,10-octamethyl-1,2,9,10-tetrasila[2.2]paracyclophane (**1**) in 1.6% yield. (Scheme 1)



1

Scheme 1.

We have examined other possible routes to **1** such as those through 1,1,2,2,3,3,10,10,11,11,12,12-dodecamethyl-1,2,3,10,11,12-hexasila[3.3]paracyclophane (**2**) and 1,1,2,2,3,3,10,10,11,11-decamethyl-1,2,3,10,11-pentasila[3.2]paracyclophane (**3**) by photochemical silylene extrusion, and through a diacetylene compound (**4**) by a possible Diels-Alder reaction, but only the most direct way shown in Scheme 1 was successful so far, although the yield was very low. Since we have already prepared 1,1,2,2,9,9,10,10-octamethyl-1,2,9,10-tetrasila[2.2]meta- (**5**) and orthophane (**6**) in a different way,[5)] comparisons of physical and chemical properties of these isomers will be very much intriguing.



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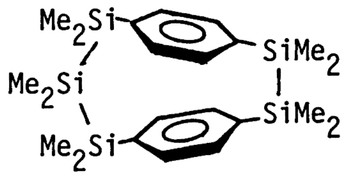

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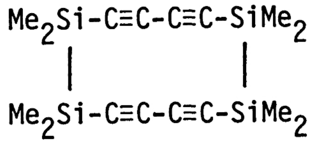

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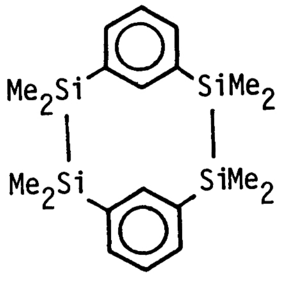

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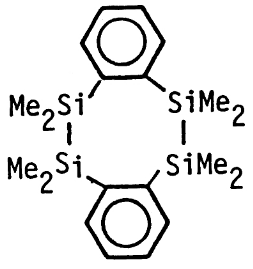

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1 is highly sublimable colorless crystals; mp 268-269 °C, ^{1}HNMR (CCl_4) δ/ppm 6.75 (8H,s), 0.50 (24H, s), ^{13}CNMR (CCl_4) δ/ppm 138.58 (s), 133.36 (d), -4.77 (q), ^{29}SiNMR (CCl_4) δ/ppm 6.45, IR (KBr) ν/cm^{-1} 3060 (w), 3020 (w), 2980 (m) 2920 (w), 1410 (w), 1390 (w) 1260 (s), 1140 (s), 800 (s), UV (n-C_6H_{14}) λ_{max}/nm (ε) 223 (19,100), 263 (22,500), MS m/e (%) 384 (M^+, 100), 369 (58), 191 (18) 177 (25), 73 (14).

The X-ray structure of **1** is shown in Fig. 1.[6)] **1** is highly symmetric with a center of symmetry. The Si-Si bond lengths (3.376 Å) deviate slightly from the normal values (3.34 Å). The 3 and 6 (and 11 and 14) carbon atoms of the aromatic rings are displaced slightly out of the plane of the other four atoms inward. The degree of the displacement was 4.3° which is far smaller than that of the [2.2]-paracyclophane (12.6°), indicating a smaller degree of distortion of the benzene rings of **1**.[7)] However, the silicon atoms of the bridges are displaced appreciably from the aromatic ring toward the cyclophane cavity. The degree of this displacement is 15.0°, larger than that of [2.2]paracyclophane (11.2°).[7)] The distances between aromatic rings, 3.347 Å for C_3-C_{14} and 3.456-3.460 Å for C_4-C_{15} and C_5-C_{16},

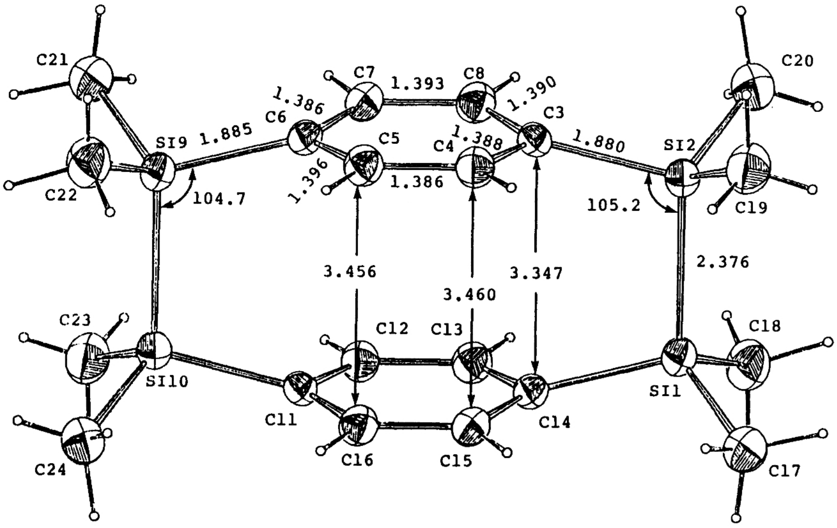

Fig. 1. ORTEP drawing of **1** with pertinent bond lengths and bond angles.

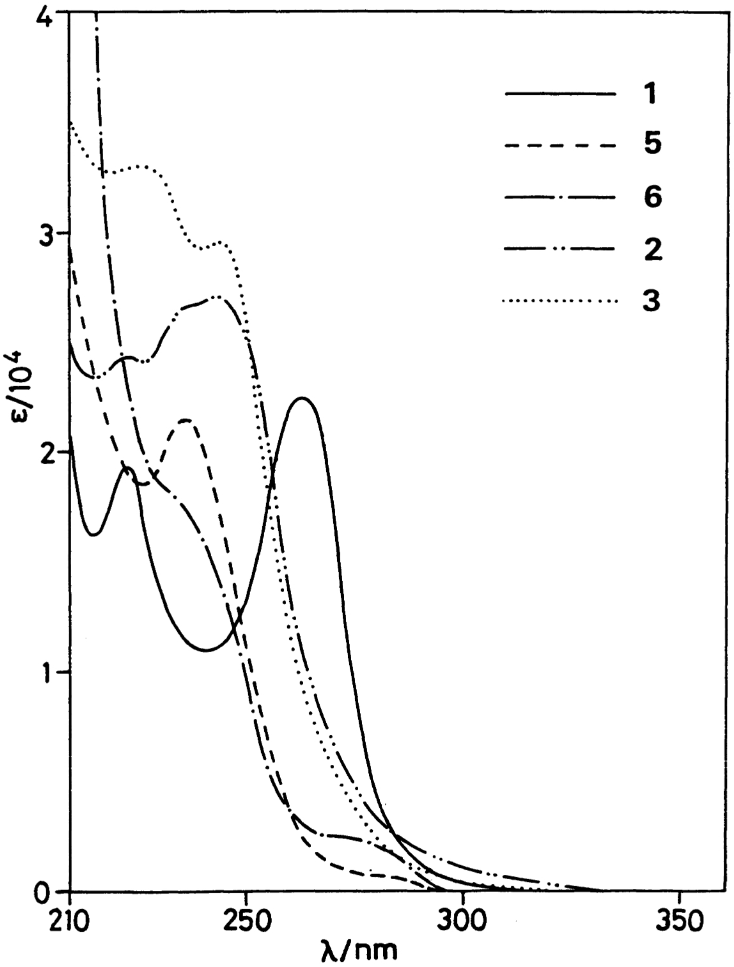

Fig. 2. Electronic spectra of several polysilane-bridged cyclophanes.

are close to that observed in graphite (3.40 Å) and longer than the mean intramolecular aromatic ring separation of [2.2]paracyclophanes around 3.00 Å. Two benzene rings and methyl groups eclipse completely.

These structural data show that **1** is a rather less distorted molecule than [2.2]paracyclophane. However, a dramatic effect of the strong σ(Si-Si)-π interaction was observed in UV spectra as shown in Fig. 2.

In an UV spectrum of phenylpentamethyldisilane, an intramolecular σ(Si-Si)-π charge-transfer band appears around 231 nm.8) Octamethyltetrasila[2.2]meta- (**5**) and orthophane (**6**) show similar absorptions but the band is split into two bands at 223 nm (ε = 19100) and 263 nm (ε = 22500) in **1**. This type of red shift in the uv spectra occurs only in **1** among other polysilaparacyclophanes such as **2** and **3**.

Further studies on these new cyclophanes and related compounds will be reported soon.

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6) A colorless crystal with the sizes of 0.2x0.15x0.25 mm^3 was used for the data collection on a Rigaku Denki AFC 6R four circle diffractometer with graphite monochromatized MoK_α radiation (λ = 0.71079 Å). The cell constants are a = 6.789 (1), b = 12.847 (1) and c = 12.847 (1) Å and β = 97.13 (1)°. The space group is $P2_{1/n}$ with two molecules in the unit cell. The calculated density is 1.11 $\mathrm{g/cm}^3$ (mol wt 384.82; $C_{20}H_{32}Si_4$). A total of 3512 reflections within 2θ = 60° were collected by the 2θ-θ scan method with a scan rate of 4°/min. The intensities were corrected for the Lorentz-polarization effects but not for the absorption. The structure was solved by the direct method and refined by the block-diagonal least-squares refinement for non-hydrogen atoms anisotropically. All hydrogen atoms were located by the difference Fourier map and included in the refinement with isotropic temperature factors. The final R factor is 0.065 for 1832 non-zero reflections.

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