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

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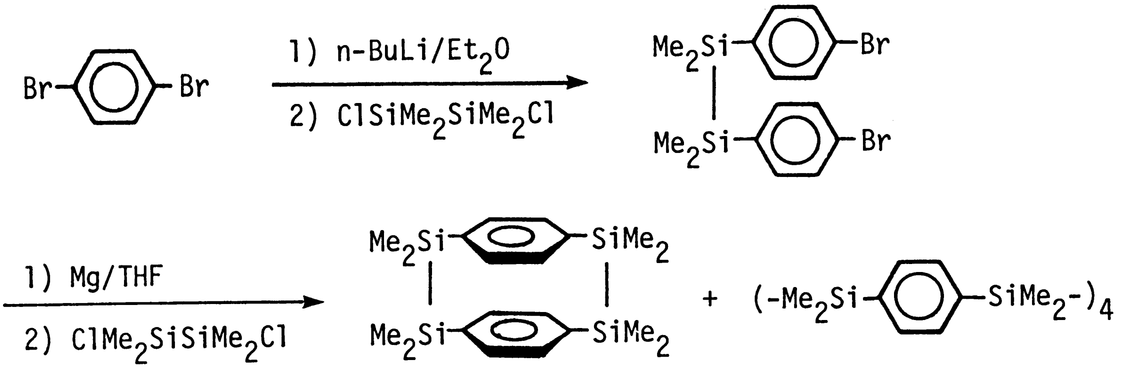
1,1,2,2,9,9,10,10-Octamethyl-1,2,9,10-tetrasila[2.2]paracyclophane, the first [2.2]paracyclophane bridged by heteroatoms, has been prepared. UV, IR, and ^{1}H- ^{13}C- and ^{29}Si-NMR spectral together with X-ray crystallographic data are recorded. The compound displays a strong σπ mixing between Si-Si 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 σπ 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.

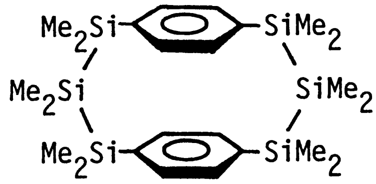
Di(p-bromophenyl)tetramethyldisilane, prepared from p-dibromobenzene and 1,2-dichlorotetramethyldisilane, was converted to the corresponding Grignard reagent which was subsequently subjected to the reaction with 1,2-dichlorotetramethyldisilane under high dilution conditions to give 1,1,2,2,9,9,10,10-octamethyl-1,2,9,10-tetrasila[2.2]paracyclophane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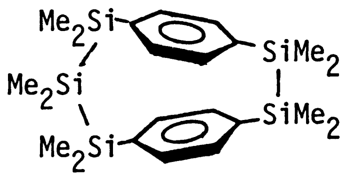

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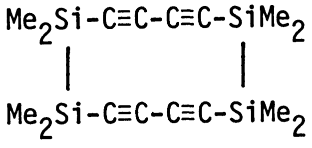

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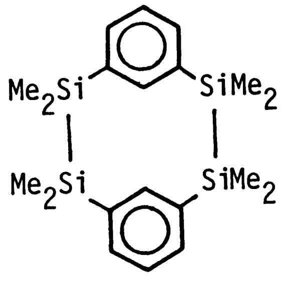

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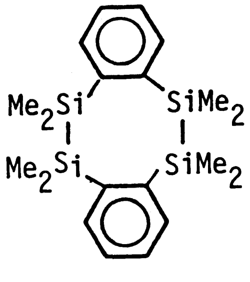

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1 is highly sublimable colorless crystals; mp 268-269 °C, ^{1}HNMR (CCl_4) δ/ppm 6.75 (8H,s), 0.50 (24H, s), ^{13}CNMR (CCl_4) δ/ppm 138.58 (s), 133.36 (d), -4.77 (q), ^{29}SiNMR (CCl_4) δ/ppm 6.45, IR (KBr) ν/cm^{-1} 3060 (w), 3020 (w), 2980 (m) 2920 (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},

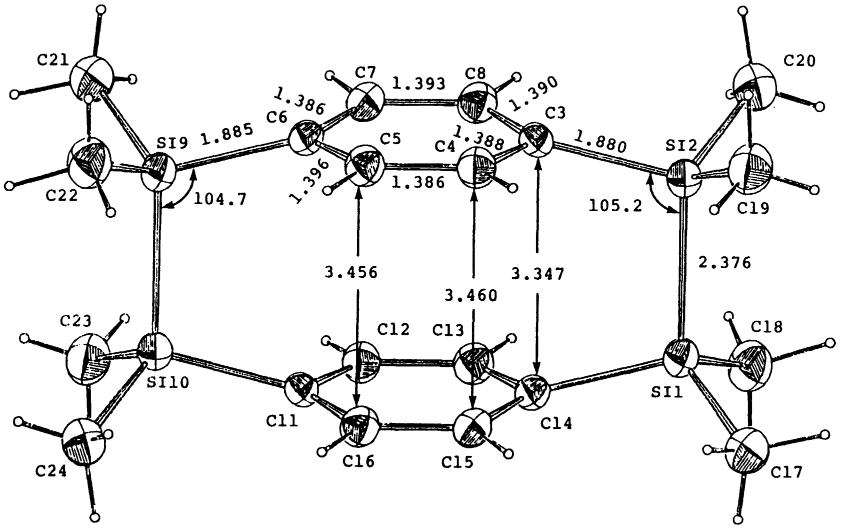

Fig. 1. ORTEP drawing of 1 with pertinent bond lengths and bond angles.

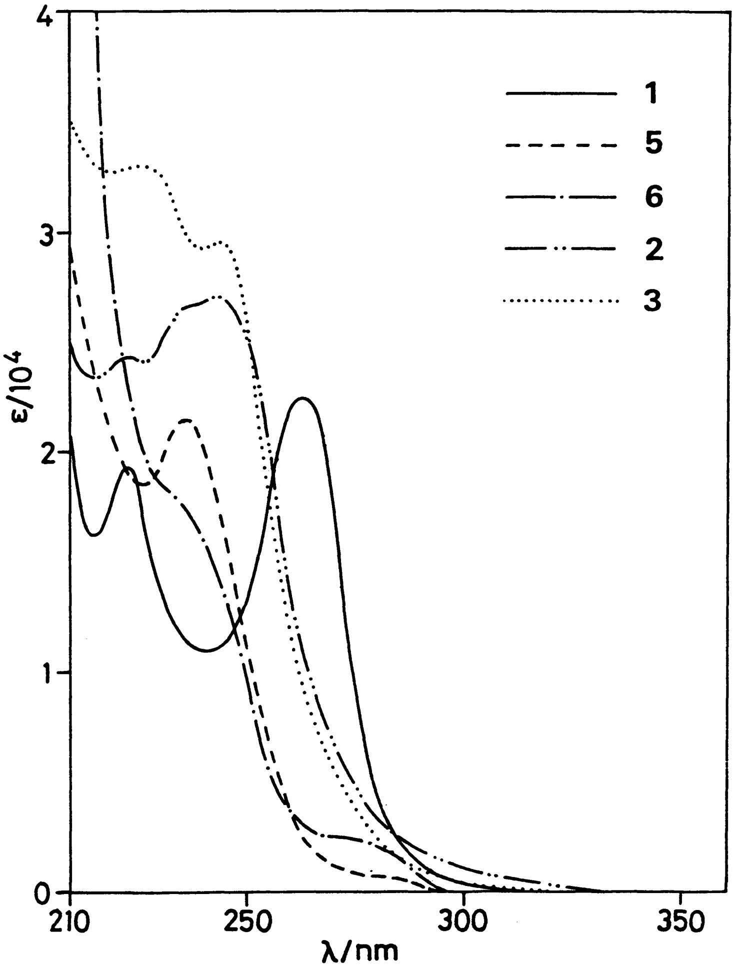

Fig. 2. Electronic spectra of several polysilane-bridged cyclophanes.

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$_\alpha$ 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 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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