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Separation of Orientational Disorder in the X-Ray Analysis of the Kinetically Stabilized 2-Silanaphthalene

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The crystal structure of the stable 2-silanaphthalene was refined more adequately by the separation of the disorder of overlapped two 2-silanaphthalene moieties. The bond lengths of the 2-silanaphthalene ring were in fairly good agreement with the theoretically calculated values which we previously reported.

Cyclic electron delocalization of aromatic compounds distinctly appeared in their structure as bond length equalization.[1] For example, the D_{6h} symmetric hexagonal structure is one of the most important features of benzene. In view of the proximity in the periodic table, silicon analogues of aromatic compounds are expected to show similar structural features. However, silaaromatic compounds are highly reactive and have been observed only in low-temperature matrices or in the gas phase, except for charged systems.[2]

During the course of our study on neutral silaaromatic compounds, we have succeeded in the synthesis of stable 2-silanaphthalene **1**[3] and silabenzene **2**[4] by taking advantage of an extremely bulky 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter) group (Chart 1). The structures of both **1** and **2** were determined by X-ray crystallographic analysis. The structural parameters of silabenzene **2**[4b] were obtained with sufficient accuracy; however, the severe disorder around the 2-silanaphthalene ring of **1** prevented us from discussing the detailed structure of **1** based on the X-ray analysis.[3] Although the aromatic character of 2-silanaphthalene **1** was strongly suggested by the spectroscopic data and theoretical calculations,[3b] the definite structural determination of **1** is still required. Here, we report the refined crystallographic structural analysis of **1** by the separation of the overlapped disorder of the 2-silanaphthalene ring.

The 2-silanaphthalene ring of **1** was disordered even at −180 °C. After many trials of the structural refinement, the disorder mode of 2-silanaphthalene **1** was finally revealed as shown in Fig. 1 by careful assignment of the atoms to two parts and refinement with SHELXL-97 program.[5] Thus, two overlapped 2-silanaphthalene moieties were found in 2 : 1 ratio. While the crystallinity of **1** seems to be mainly controlled by the extremely bulky Tbt group, the bulkiness of the large Tbt group may also provide some space for the relatively small silanaphthalene ring to be disordered around the central silicon atom, as can be seen in the packing diagram. The analysis of the disorder was highly difficult since many atoms in the 2-silanaphthalene rings were very close to each other. The ORTEP drawing of the major fragment (Fig. 2) is very different from that we previously reported,[3] showing the importance of the separation of the disorder.

In Table 1 are shown the refined observed structural parameters of 2-silanaphthalene **1** together with the calculated (B3LYP/6-311G(d,p)) bond lengths for the parent 2-silanaphthalene **3** which we previously reported. The experimental bond lengths and angles for **1** here obtained are quite different from those given by the structural analysis without considering the disorder[3] and in fairly good agreement with those theoretically calculated. Although two Si–C bond lengths of **1** (1.728(3) and 1.800(3) Å) are in the middle between those of Si–C double and single bonds (1.70 and 1.89 Å, respectively),[6] these Si–C bonds as well as the C–C bonds in the 2-silanaphthalene ring were slightly localized to show a bond alternation as in the case of naphthalene.

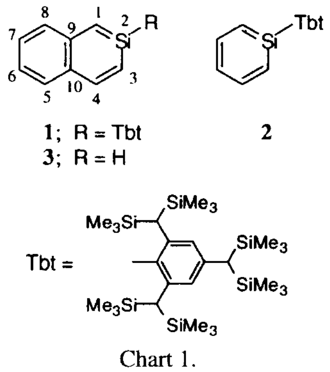

Chart 1.

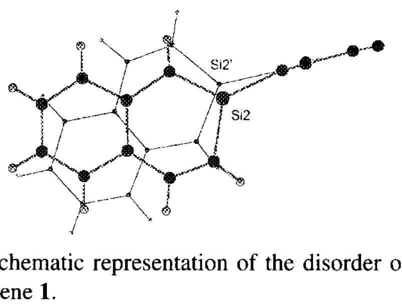

Fig. 1. Schematic representation of the disorder of 2-silanaphthalene **1**.

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Table 1. Observed and Calculated Bond Lengths (Å) of 2-Silanaphthalenes (Si–C lengths are described in bold type.)

Compound	C1–Si2	Si2–C3	C3–C4	C4–C10	C10–C5	C5–C6	C6–C7	C7–C8	C8–C9	C9–C1	C9–C10
1 (R = Tbt, obsd)[a]	**1.728(3)**	**1.800(3)**	1.359(3)	1.438(3)	1.427(3)	1.374(3)	1.386(4)	1.373(3)	1.415(3)	1.433(3)	1.431(3)
3 (R = H, calcd)[b]	**1.750**	**1.791**	1.379	1.432	1.422	1.376	1.414	1.375	1.428	1.426	1.445
Naphthalene (calcd)[b]	1.374	1.415	1.374	1.420	1.420	1.374	1.415	1.374	1.420	1.420	1.431

a) The major fragment; two overlapped fragments were restrained to have the same structure. b) From Ref. 3b, B3LYP/6-311G(d,p).

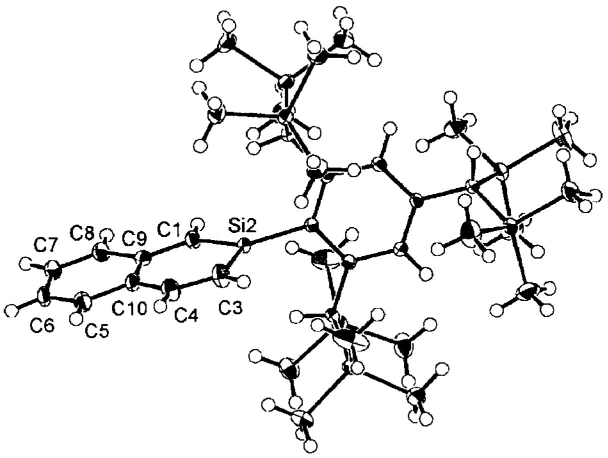

Fig. 2. ORTEP drawing of 2-silanaphthalene **1** (major fragment, 50% probability).

Thus, the structural parameters of 2-silanaphthalene **1** experimentally obtained reinforced the conclusion that the 2-silanaphthalene ring system is highly aromatic, which we have already claimed on the basis of spectroscopic properties and theoretical calculations.[3b]

Experimental

X-Ray Analysis of 2-Silanaphthalene 1. Crystal data: Formula $C_{36}H_{68}Si_7$, monoclinic, a = 12.7099(2) , b = 9.8269(1) , c = 34.3018(4) Å, β = 96.3177(5)°, V = 4258.24(9) Å^3, space group $P2_1/c$, Z = 4, D_{calc} = 1.085 Mg m^{-3}, μ = 0.247 mm^{-1}. Crystals of **1** suitable for X-ray analysis were obtained by slow evaporation of its hexane solution in a glovebox filled with argon. A colorless and prismatic crystal having approximate dimensions of 0.3×0.3×0.2 mm was mounted on a glass fiber. The intensity data were collected on a Rigaku R-AXIS RAPID imaging plate area detector with graphite monochromated Mo $K\alpha$ radiation (λ = 0.71069 Å) at −180 °C (R_{int} = 0.036). Empirical absorption correction (symmetry related method) was applied. The structure was solved by direct method (SHELXS-97) and refined by full-matrix least-squares procedures based on F^2 for all 9771 unique reflections (SHELXL-97).[5] The structures of the overlapped and disordered 2-silanaphthalene rings were restrained to be identical to each other using a SAME instruction (σ = 0.01). The occupancies of each fragment were refined with constraints that their sum is 1 (0.687(2) : 0.313(2)). Hydrogen atoms of 2-silanaphthalene rings and methyl groups of Tbt were placed using AFIX instructions (43 and 137, respectively), while the other hydrogens were refined isotropically. Carbon atoms of the minor fragment were refined isotropically, and all the other carbon and silicon atoms were refined anisotropically. R_1 ($I > 2\sigma(I)$) = 0.034, wR_2 (all data) = 0.096 for 473 parameters and 25 restraints; max/min residual electron density 1.15 and −0.47 e Å^{-3}.[7] Tables of final atomic coordinates and thermal factors together with the atom numbering scheme and packing diagram for compound **1** have been submitted to the Editorial Office as Supporting Information.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 145740. The data are also deposited as Document No. 73049 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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7 One large residual peak was found at 1.633 Å distance from C1 atom, though the other residual peaks were smaller than 0.4 e Å^{-3}. This large peak was probably due to the halogen atom of the precursor of 2-silanaphthalene **1**, a very small amount of which was contaminated in the crystal.