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Highly Coplanar (*E*)-1,2-Di(1-naphthyl)disilene Involving a Distinct CH–π Interaction with the Perpendicularly Oriented Protecting Eind Group[#]

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An air-stable emissive di(1-naphthyl)disilene protected by the bulky Eind groups (Eind: 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl) has been obtained by reducing the corresponding dibromosilane (Eind)(1-Naph)$SiBr_2$ with lithium naphthalenide. The X-ray crystallography shows a highly coplanar (*E*)-1,2-di(1-naphthyl)disilene skeleton, favorable for the efficient π-conjugation involving the Si=Si unit, together with a distinct CH–π interaction between the *peri*-H atom of 1-naphthyl groups and the aromatic ring of the perpendicularly oriented Eind groups.

A large variety of organic π-electron architectures are currently known; their properties primarily depend on the number and arrangement of the double bonds. In recent years, the incorporation of double bonds of the heavier main group elements into carbon π-conjugated systems have attracted much attention because of their potentially useful properties as functional materials.[1] For example, in organosilicon chemistry, various types of π-conjugated molecules containing a Si=Si double bond have been developed[2–8] by taking advantage of steric protection with the appropriately designed bulky substituents. We have introduced a series of fused-ring bulky "Rind" (1,1,3,3,5,5,7,7-octa-R-substituted-*s*-hydrindacen-4-yl) groups in this field.[9] This paper is concerned with the synthesis of di(1-naphthyl)disilene **1** stabilized by Eind (R = Et) groups (Figure 1).

In 2010, we reported 2-naphthyl counterpart **2** as the first air-stable and room-temperature emissive disilene,[2b] existing as a mixture of two conformers in the crystals, **2**(*s-trans*, *s-trans*) and **2**(*s-cis*, *s-cis*), in the ratio of 6:4. In both isomers, the highly coplanar skeleton including the Si=Si unit is effectively encapsulated by the perpendicularly oriented Eind groups, in which the proximate ethyl side chains interlock with one another above and below the π-framework. In 2012, we demonstrated for the first time that disilene **2** can emit light in an organic light-emitting diode (OLED), which has opened a new platform for the development of functional elemento-organic materials and devices.[2e]

In these previous studies, the 2-naphthyl group was employed rather than the 1-naphthyl group, because the presence of a hydrogen atom at the *peri*-position in the latter might cause twisting of the naphthyl group from the Si=Si double bond.[10] However, we are still interested in examining how much the *peri*-H atom causes the geometrical changes by introducing the 1-naphthyl group in the disilene unit.

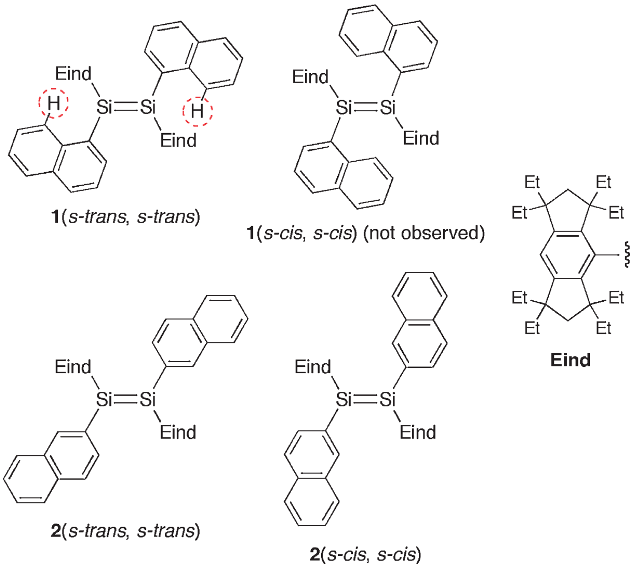
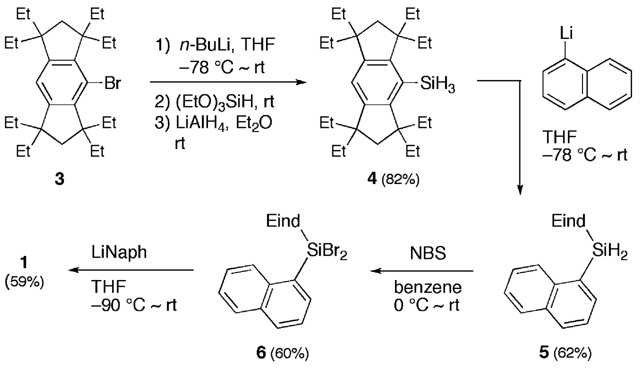


Figure 1. 1,2-Di(1-naphthyl)disilene **1** and 1,2-di(2-naphthyl)disilene **2**.

The synthetic route to disilene **1** starting from (Eind)Br (**3**) is outlined in Scheme 1.[11] Disilene **1**, isolated as a red powder, is air-stable in the solid state for more than 2 years, similar to **2**, while a solution of **1** gradually decomposes upon exposure to air, as monitored by the ^1H NMR spectroscopy.

Disilene **1** was found by X-ray analysis to form two pseudo-polymorphs (forms I and II) of red crystals, depending on the crystallization conditions. Although fine microcrystals of form I were obtained from a dilute benzene solution of **1** with no crystal solvent, form II with 3 equiv of crystal THF was crystallized from a suspension of **1** in THF. The geometry of **1** in both polymorphs is nearly identical, having a coplanar (*E*)-1,2-di(1-naphthyl)disilene skeleton with an inversion center at the center of the Si=Si bond. Thus, only the molecular structure of form II is presented in Figure 2. Rather surprisingly, the *peri*-



Scheme 1. Synthesis of 1,2-di(1-naphthyl)disilene **1**.

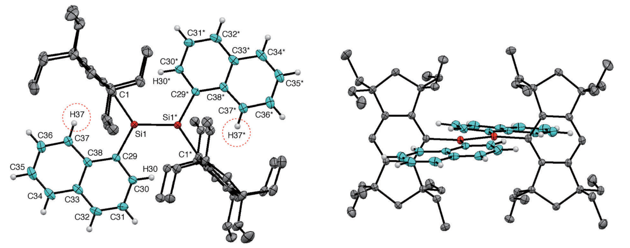


Figure 2. Molecular structures of **1** (form II): top view (left) and side view (right). Hydrogen atoms of Eind groups and THF molecules are omitted for clarity. Selected atomic distances (Å), bond angles (deg), and torsion angle (deg): Si1–Si1* = 2.1688(7), Si1–C1 = 1.8955(13), Si1–C29 = 1.8831(14), C37⋯C1 = 3.284(2), H37⋯C1 = 2.457, C1–Si1–Si1* = 124.77(5), C29–Si1–Si1* = 117.82(5), C29–Si1–C1 = 117.39(6), Si1*–Si1–C29–C30 = 4.93(12).

H atoms do not cause any steric repulsion with the Eind-containing disilene moiety, but seems to participate in the CH–π interaction with the benzene ring of the perpendicularly oriented Eind groups (vide infra).

Some structural features (given below) are mentioned only for form II. (1) An *s-trans*, *s-trans* conformer of **1**, theoretically 8.85 kcal mol^{-1} more stable than the *s-cis*, *s-cis* isomer,[11] has been found only in the crystals in contrast to the 2-naphthyl counterpart **2**,[2b] probably because of the presence of the *peri*-H atom of the 1-naphthyl groups and/or the crystal packing situation. (2) The 1-naphthyl groups are highly coplanar with the Si=Si bond having a Si–Si–C–C torsion angle of 4.93(12)°, similar to that of 9.57(11)° in **2**(*s-trans*, *s-trans*).[2b] The Si=Si bond length of 2.1688(7) Å is in the standard range of those for disilenes.[1c] (3) It is noteworthy that the *peri*-H atom of the 1-naphthyl group is in close contact with the benzene ring of the Eind group in the crystals, judging from the three pertinent parameters for the CH–π interaction (Figure 3), defined by Takahashi, Nishio, and their co-workers.[12] Thus, form II has D_{pln} = H37⋯π = 2.46 Å, D_{px1} = 1.14 Å, and α = angle C37–H37⋯π = 153°. These data are all consistent with the intrinsic nature of the CH–π interaction.[12] It is further noted that the observed D_{pln} of 2.46 Å is the shortest edge for a large number of known C(sp^2)–H⋯π distances and in an about 1 kcal mol^{-1} stabilized region.[12]

Table 1 summarizes the photophysical data of **1** together with those of **2** for comparison. Several features are found as follows: (1) The UV–vis spectrum of **1** in THF shows an absorption peak at 521 nm ($\varepsilon = 9.5 \times 10^3$), which is 17 nm red-shifted from that of **2** (504 nm),[2b] indicating the efficient π-conjugation over the di(1-naphthyl)disilene skeleton. (2) Disilene **1** exhibits a rather weak emission at room temperature, both in solution and in the solid state (Figure 4). The emission maximum of **1** appears at 614 nm in THF. The Stokes shift of **1** is estimated to be 2910 cm^{-1}, similar to that of **2** (2780 cm^{-1}),[2b] indicating the rigid framework of di(1-naphthyl)disilene.

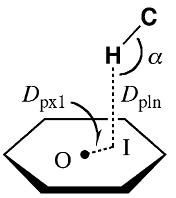


Figure 3. Structural parameters for CH–π interaction defined in ref 12. O: Center of the ring. I: Foot of a perpendicular line from H atom. D_{pln}: Distance of H atom from the π-plane. D_{px1}: Distance between O and I. α: C–H⋯π access angle.

Table 1. Photophysical data of disilenes **1** and **2**

Compd	State[a]	Absorption λ_{max}/nm	ε /cm^{-1} M^{-1}	Emission λ_{max}/nm (Φ_{F})	Stokes shift /cm^{-1}
1	THF	521	9.5×10^3	614 (< 0.01)	2910
	Solid			635 (0.05)	
2	THF	504	2.5×10^4	586 (< 0.01)	2780
	Solid			619 (0.23)	

[a] In a THF solution or in the solid state.

Figure 4. Solid-state color and emission of **1** at room temperature in ambient air.

To elucidate the nature of bonding in di(1-naphthyl)disilene, DFT computations were carried out for **1**(*s-trans*, *s-trans*) at the B3LYP/6-31G** level by using the Gaussian 09 program package.[13] The optimized structure well reproduces the X-ray molecular structure found in the crystals. The missing **1**(*s-cis*, *s-cis*) conformer is also found at an 8.85 kcal mol^{-1} higher level with a distorted di(1-naphthyl)disilene skeleton.[11] The frontier molecular orbitals of **1**(*s-trans*, *s-trans*) are depicted in Figure 5. Although the HOMO is mainly represented by the 3p$_\pi$(Si–Si) orbital, the LUMO involves the substantial contribution of the 3p$_\pi$*(Si–Si)–2p$_\pi$*(1-naphthyl) conjugation, which is essentially the same as that of **2**.[2b] The HOMO and LUMO levels of **1** (−4.209 and −1.572 eV) are, respectively, slightly higher and lower than those of **2**(*s-trans*, *s-trans*) (−4.304 and −1.478 eV).[2b] Thus, the total HOMO–LUMO gap in **1** (2.637 eV) is slightly smaller than that in **2**(*s-trans*, *s-trans*) (2.826 eV), being in agreement with the experimental data, a slightly longer

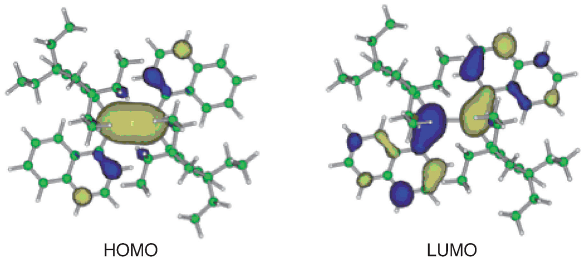


Figure 5. Frontier molecular orbitals of **1**(*s-trans*, *s-trans*) (top view).

absorption $\lambda_{\max}$ in **2**, as mentioned above. This difference is primarily ascribed to the larger HOMO and LUMO lobes at the 1-position than at the 2-position of the naphthalene ring.

In conclusion, we have shown that the installation of two 1-naphthyl groups to the Eind-containing disilene moiety produces the highly coplanar π-conjugated system of (*E*)-1,2-di(1-naphthyl)disilene with the CH–π interaction between the *peri*-H atoms and benzene rings of the Eind groups. The present result further demonstrates the high ability of the fused-ring Eind group (Rind groups in general), by being perpendicular to the Si=Si bond, to provide a space necessary for the central coplanar diaryldisilene skeleton and to make even the *peri*-H-containing 1-naphthyl group coplanar to the Si=Si bond.[10] Further investigations of π-conjugated disilenes with polycyclic aromatic groups are in progress.

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