Intramolecular charge-transfer fluorescence of 1-phenyltridecamethylbicyclo[2.2.2]octasilane†

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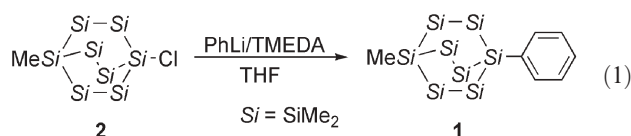
1-Phenyltridecamethylbicyclo[2.2.2]octasilane (1) is prepared by the reaction of the corresponding 1-chlorotridecamethylbicyclo[2.2.2]octasilane with phenyllithium in the presence of *N,N,N′,N′*-tetramethylethylenediamine and the molecular structure of **1** is determined by X-ray crystallography. Phenyloligosilane 1 shows dual fluorescence even in non-polar hexane though the TICT-like mechanism is not applicable.

Much attention has been focused on the photophysics and photochemistry of aryloligosilanes that exert unique effective conjugation between an aromatic π system and an oligosilane σ system (σ–π conjugation).[1] Typically, introduction of a pentamethyldisilanyl group to benzene causes remarkable red-shift of the ^1L_a band of benzene and unique dual fluorescence from the local excited state (LE) and the intramolecular charge transfer (ICT) state.[2,3] In a jet-cooled condition, the nature of the ICT state of *p*-cyanophenylpentamethyldisilane (CPDS) has been revealed to be formed by the electron transfer from Si–Si σ to aromatic π* orbitals.[4] The most distinct structural change during the ICT process of CPDS was suggested to be elongation of the Si–Si bond instead of twisting of the Si–Si bond around C(Ar)–Si bond,[4] while we have previously proposed an in-plane geometry of the Si–Si bond and aryl ring plane (OICT geometry)[2] similar to TICT[5] geometry proposed for *p*-dimethylaminobenzonitrile (DMABN). We wish herein to report the synthesis, structure and electronic spectra of 1-phenyltridecamethylbicyclo[2.2.2]octasilane **1**. Although bicyclo[2.2.2]octasilane-1,4-diyl has a rigid σ framework with three-fold symmetry around the axis through two bridgehead silicon atoms, and hence, the σ–π conjugation between the oligosilane framework and an aromatic π system should not depend on the conformation around the C(aromatic)–Si bond, **1** showed the ICT fluorescence even in a non-polar solvent like hexane.

1-Phenyltridecamethylbicyclo[2.2.2]octasilane **1** was obtained in 56% yield by the reaction of phenyllithium in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) with the corresponding chlorosilane **2** in THF at room temperature; the reaction of phenyllithium with **2** did not take place in the absence of TMEDA. Chlorosilane **2**[6] was synthesized by the chlorination of permethylbicyclo[2.2.2]octasilane[7] using BCl_3. Recrystallization of **1** from acetone–hexane (1 : 1) mixture gave single crystals

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† Electronic supplementary information (ESI) available: X-ray analysis of **1** and fluorescence spectra of **4** in various solvents. See http://dx.doi.org/10.1039/b505109f
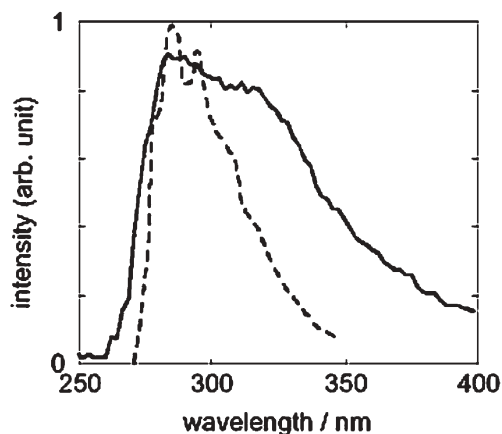
suitable for X-ray structural analysis. Fig. 1 shows the molecular structure of **1**. The lengths of all Si–Si bonds (2.3395(8) ∼ 2.3930(8) Å) in **1** are in the range of a typical Si–Si single bond length (2.372(40) Å) found in cyclic disilanes.[8] Three Si–Si bridge bonds are not parallel but slightly twisted by 13°–21° to avoid steric repulsion among methyl groups.

$$\text{MeSi} \underset{\text{Si}-\text{Si}}{\overset{\text{Si}-\text{Si}}{\diagup}} \text{Si-Cl} \quad \xrightarrow[\text{THF}]{\text{PhLi/TMEDA}} \quad \text{MeSi} \underset{\text{Si}-\text{Si}}{\overset{\text{Si}-\text{Si}}{\diagup}} \text{Si} \quad \bigcirc \qquad (1)$$

Si = SiMe₂

2   **1**

Whereas two representative rotational conformations around Si1–C1 bond for **1**, perpendicular (A) and bisected (B), should be almost identical in energy, only A-type conformation was observed in the solid state; dihedral angle Si7–Si1–C1–C2 = 96.9(2)°. Intermolecular interaction between the phenyl ring and a methyl group on Si7 of a neighboring molecule may prevent the free rotation of the phenyl ring.
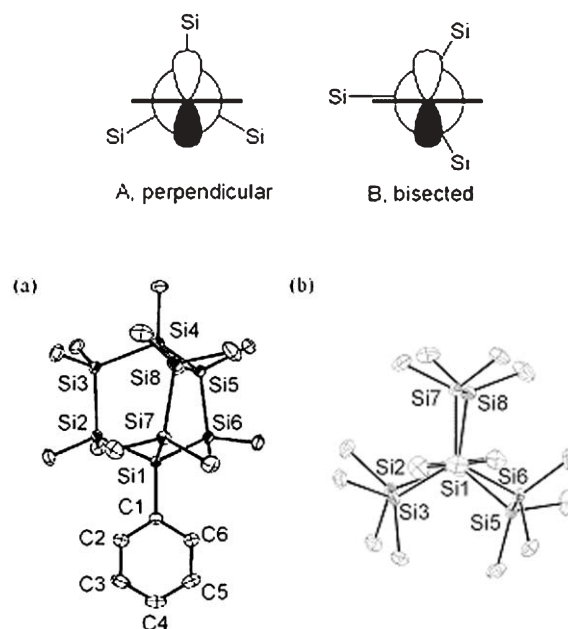
Fig. 1 Molecular structure of 1-phenyltridecamethylbicyclo[2.2.2]octasilane **1** determined by X-ray crystallography; (a) top view and (b) a view obtained by looking down the axis through Si1 and Si4. Hydrogen atoms are omitted for clarity (30% thermal ellipsoids). Selected bond lengths (Å), angles (°), and dihedral angles (°); Si1–C1 1.906(2); Si1–Si2 2.3573(8); Si2–Si3 2.3591(8); Si3–Si4 2.3402(8); Si4–Si5 2.3395(8); Si5–Si6 2.3442(8); Si1–Si7 2.3404(8); Si7–Si8 2.3930(8); S18–Si4 2.3753(8); C1–Si1–Si2 111.48(7); Si1–Si2–Si3 109.59(3); Si1–Si2–Si3–Si4 16.10(4); Si7–Si1–C1–C2 96.9(2).

Fig. 2 Fluorescence spectra of 1-phenylbicyclo[2.2.2]octasilane (**1**, solid line) and tris(trimethylsilyl)silylbenzene (**4**, dashed line) in hexane solution (*ca.* 1×10^{-6} M).

Phenyltridecamethylbicyclo[2.2.2]octasilane **1** showed an intense absorption band at 241 nm (ε 23500) due to σ–π conjugation, whereas permethylbicyclo[2.2.2]octasilane **3** having a *syn*-tetra-silane framework[9] shows only a weak absorption band at *ca.* 245 nm (ε 4000) in hexane. Fig. 2 shows the fluorescence spectra of **1** and a reference compound, tris(trimethylsilyl)silylbenzene (**4**), in hexane. Because the OICT mechanism[2] for the ICT fluorescence of aryldisilanes requires the orthogonal arrangement between ben-zene pπ orbital and Si–Si σ orbital in the emitting state, neither **1** nor **4** having three-fold symmetric Si–Si bonds should show the ICT fluorescence. As expected, no ICT fluorescence was found for **4** in hexane.[10] However, **1** shows a dual fluorescence in hexane with two bands at 290 nm and 320 nm as shown in Fig. 2. They are assigned to be the LE and CT emission bands, respectively, because the band maxima are comparable to those found for phenylpentamethyldisilane (295 and 330 nm in isooctane).[2]

The ICT nature of the longer-wavelength band of **1** is confirmed by the significant solvent effects. As shown in Fig. 3, in the fluorescence spectra of **1**, no LE band is observed but the ICT band red-shifts remarkably in polar solvents; the ICT band maximum is 335 and 380 nm in dichloromethane and acetonitrile, respectively.
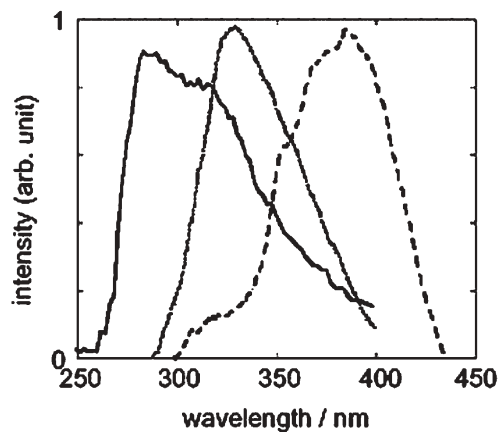

Fig. 3 Fluorescence spectra of 1-phenyltridecamethylbicyclo[2.2.2]octa-silane (**1**); (a) in hexane (left, solid line); (b) in dichloromethane (center, dotted line); (c) in acetonitrile (right, dashed line).

Neither the OICT[2] nor the 2pπ–3dπ (Si–Si) mechanism[3] is applicable to the ICT emission of **1** having three-fold symmetric Si–Si bonds. Because the theoretical calculations at the RHF/3–21G* level[11] showed that the HOMO of permethylbicyclo[2.2.2]oc-tasilane **3** is mostly localized on the three bridge Si–Si σ bonds, the positive charge in the ICT state of **1** would be accommodated in the bridge Si–Si bonds to attain the charge separation and hence the long life-time of the ICT state. More detailed studies will be required for the elucidation of the ICT mechanism.‡

Notes and references

‡ **1**: A mixture of phenyl lithium (0.21 mmol) and *N*,*N*,*N*′,*N*′-tetrametnyl-1,2-diaminoethane (TMEDA, 20 mg, 0.17 mmol) in cyclohexane (0.22 ml) was added to 1-chlorobicyclo[2.2.2]octasilane **2** (36 mg, 0.08 mmol) in tetrahydrofuran-d_8 (0.5 ml) in an NMR tube. The mixture was kept at room temperature and the reaction was monitored by ^{1}H NMR spectroscopy. Hydrolysis, extraction with diethyl ether, drying over MgSO$_4$, removal of the volatile materials *in vacuo* and then flash silica-gel chromatography (eluent: hexane) followed by recrystallization from acetone gave colorless crystals of **1** (22 mg, 0.044 mmol) in 56% yield. **1**: colorless crystals; mp >400 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 0.22 (s, 3H), 0.27 (s, 18H), 0.30 (s, 18H), 7.22–7.25 (m, 5H); ^{13}C NMR (150 MHz, CDCl$_3$) δ −14.6, −3.58, −2.77, 127.4, 127.7, 135.6, 136.2; ^{29}Si NMR (59 MHz, CDCl$_3$) δ −81.9 (SiMe), −70.8 (SiPh), 40.0 (SiMe$_2$), −39.8 (SiMe$_2$); MS (EI, 70 eV) *m*/*z* (%) 496 (*M*$^+$, 100); HRMS Calcd. for C$_{19}$H$_{44}$Si$_8$: 496.1597, Found: 496.1598; UV-vis λ_{max}/nm 241 (ε 23500). Crystal data for **1**: C$_{19}$H$_{44}$Si$_8$, *M* = 497.26, colorless prism, 0.3 × 0.2 × 0.1 mm^3, monoclinic, space group *P*2$_1$/*n*, *a* = 9.9526(5), *b* = 16.4089(9), *c* = 18.566(1) Å, β = 92.026(3)°, *V* = 3030.1(3) Å^3, *Z* = 4, *D*$_c$ = 1.090 g cm^{-3}, MoKα (λ = 0.7107 Å), *T* = 173(2) K; 6868 unique reflections (2θ_{max} = 55.0°) were collected. The structure was solved by direct methods (SIR92). It was refined by full-matrix least squares (SHELXL-97) on *F*^{2} with anisotropic temperature factors for non-hydrogen atoms. Final *Goof* = 1.064, *R1* = 0.043 for 5475 [*I* > 2σ (*I*)] observed reflections, 244 parameters. CCDC 269601. See http://dx.doi.org/10.1039/b505109f for crystallographic data in CIF or other electronic format.

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10 Compound **4** showed a very weak ICT fluorescence band at 340 and 360 nm in polar CH_2Cl_2 and CH_3CN solvents, respectively. The spectra are shown in the Supplementary Information. In our previous papers,[2] it has been shown that in polar solvents, the stabilization of the ICT state is achieved by a mechanism different from the OICT mechanism.

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