Synthesis and Structure of a Series of Oligo[1,1-(2,3,4,5-tetramethylsilole)]s

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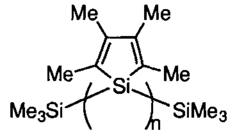
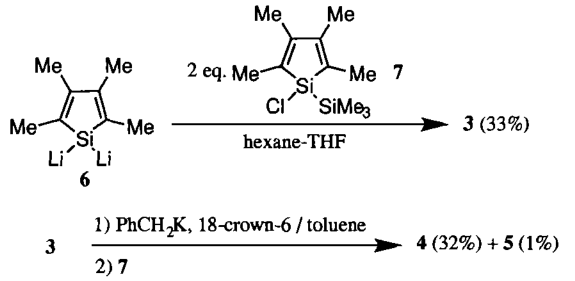
A series of oligo(1,1-silole)s, $Me_3Si[SiC_4Me_4]_nSiMe_3$ (**3**: n = 3, **4**: n = 4, **5**: n = 5) were synthesized and characterized. X-ray diffraction analysis of tersilole **3** revealed that the pentasilane backbone has almost *all-trans* conformation. The oligo(1,1-silole)s show distinct UV absorptions due to σ–σ^*, σ–π^*, and π–π^* transitions.

Polysilane high polymers having saturated all-silicon backbone have attracted remarkable attention recently because of the unique spectroscopic and optoelectronic properties due to σ–conjugation.[1] Polysilanes with catenation of the silole-ring silicons are fascinating polymers, because well-known σ^*–π^* interaction[2] between the silicon-chain σ^*–orbitals and *cisoid*-butadiene π^*–orbitals can modify the electronic structure of the silicon backbone to induce unique photochemical and photophysical properties. Quite recently, as models of poly(1,1-silole)s,[3] Tamao et al.[3a] have reported synthesis and properties of a series of oligo[1,1-(2,5-dimethyl-3,4-diphenylsilole)]s, and Boudjouk et al.[4] have reported the synthesis of a tergermole, germanium analogue of oligo(1,1-silole)s. We now report the synthesis, structure, and UV spectral feature of a series of oligo[1,1-(2,3,4,5-tetramethylsilole)]s **1**–**5**; among them, monosilole **1** and bisilole **2** have already prepared by West[5] and Tilley,[6] respectively. Because we have chosen a methyl substituent on each carbon atom of the butadiene moiety to exclude aromatic substituent effects, distinct UV absorptions due to σ–σ^*, σ–π^* and π–π^* transitions were observed.



1: n = 1, **2**: n = 2, **3**: n = 3, **4**: n = 4, **5**: n = 5



A reaction of 1,1-dilithio-2,3,4,5-tetramethylsilole (**6**)[5] with 2 equivalents of 1-chloro-1-trimethylsilyl-2,3,4,5-tetramethylsilole (**7**)[7] gave tersilole **3** in 33% yield.[8] The treatment of **3** with $PhCH_2K$/18-crown-6[6] in toluene followed by the addition of **7** produced the corresponding quatersilole **4**[9] in 32% yield together with a small amount of quinquesilole **5**[10] (1% yield).

Figure 1 shows an ORTEP drawing of the molecular structure of **3**.[11] The conformation of the pentasilane chain of **3** is almost *all-trans* but slightly deformed in order to avoid the steric repulsion between tetramethylsilole rings [torsion angles: Si1-Si2-Si3-Si4 = 166.90 (3) °, Si2-Si3-Si4-Si5 = 173.74 (3) °]. Two terminal silole units are faced with almost parallel arrangement of the ring planes; the face-to-face distance is ca. 3.7 Å. Usual values are taken to all the bond lengths and bond angles of **3**.

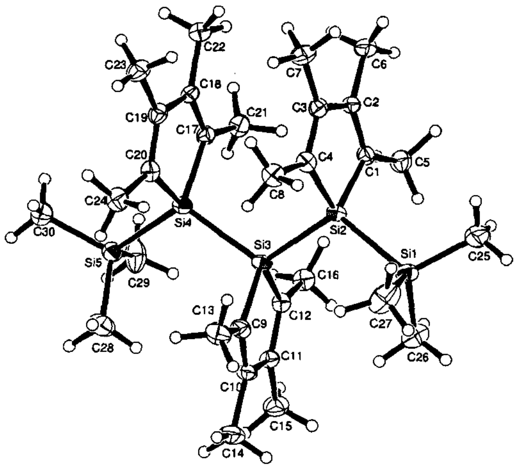


Figure 1. ORTEP drawing of **3**. Selected bond lengths (Å) and bond angles (deg.): Si1 - Si2 = 2.353 (1), Si2 - Si3 = 2.346 (1), Si3 - Si4 = 2.346 (1), Si4 - Si5 = 2.346 (1); Si1 - Si2 - Si3 = 111.33 (4), Si2 - Si3 - Si4 = 111.10 (4), Si3 - Si4 - Si5 = 111.12 (4).

As shown in Figure 2, UV spectrum of monosilole **1** in hexane at rt shows two maxima at 257 and 299 nm. The latter band will be easily assigned to the π–π^* transition of the silole ring because a similar absorption band is found in 1,1-di-*t*-butyl-2,3,4,5-tetramethylsilole (**8**)[12] (λ_{max} = 294 nm). The shorter wavelength band of **1** can be assigned to the intramolecular charge-transfer transition from oligosilane σ–HOMO to diene π^*–LUMO (σ–π^* transition), because the corresponding band is missing in **8** with no Si–Si σ–bonds, and significantly red-shifted in 1,1-bis(pentamethyldisilanyl)-2,3,4,5-tetramethylsilole (**9**, λ_{max} = 272 nm)[13] whose σ–HOMO level is higher than that of **1** due to the longer silicon chain. On this basis, the absorption bands at around 280 nm of **2**–**5** would consist of the two overlapping σ–π^* and π–π^* bands; the absorption wavelengths are apparently invariant with the oligosilane chain lengths, while the absorption coefficients increase. The results suggest that no significant through-space interaction exists between these silole rings, as expected from the face-to-face distance between diene moieties of **3**. The absorption maximum of **2** at 223 nm shifts red with increasing silicon chain length, being assignable to the σ–σ^* transitions of oligosilane chains. Actually, a good linear relationship is found between the σ–σ^* band maxima of **2**–**5** and those of the corresponding

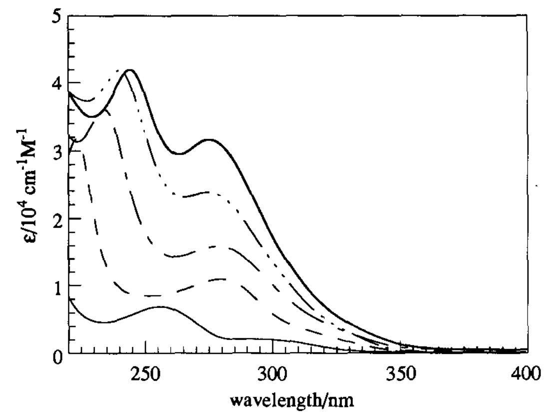


Figure 2. UV spectra of **1-5** in hexane at rt. (**1**: ——— , **2**: - - - - - , **3**: — — — , **4**: —···— , **5**: ———).

permethyloligosilanes, while the slope is less than unity (0.60); λ_{max}/nm of Me(SiMe$_2$)$_n$Me: n = 3, 215; n = 4, 235; n = 5, 250; n = 6, 220 and 260; n = 7, 230 and 266.5.[14]

An MO correlation diagram for bisilole **2** with two silole rings and three Si–Si σ–bonds is represented schematically in Figure 3. The energy level of the lowest-energy σ*–orbital of Si$_4$Me$_{10}$ (σ^*_{LU}) remains unchanged in **2** because σ*–π* conjugation between σ^*_{LU} and all of the π*–orbitals does not take place due to the disagreement of the orbital symmetry each other, while interactions of π^*_{LU} with higher-energy σ*–orbitals (σ^*_2 and σ^*_3) are allowed. The π^*_{LU} level will be lowered by the σ*–π* interaction as expected, but elevated by the possible interaction with the highest-energy σ–orbital (σ_{HO}). These opposite interactions may keep the π^*_{LU} levels independent of the silicon chain length, leading to the invariant π–π* transition energy. Another consequence of the σ_{HO}–π* interaction will be lowering the σ_{HO} level to cancel out the elevation of σ_{HO} level by silicon-chain elongation. This may be the origin of the invariant σ–π* transition energy as well as the less sensitive chain length dependence of the σ–σ* transition energy.

Existence of the intense σ–π* intramolecular charge-transfer absorption found in the oligo(l,l-silole)s is highly suggestive of the unique optoelectronic properties like photoconductivity of poly(l,l-silole)s. Related work is in progress.

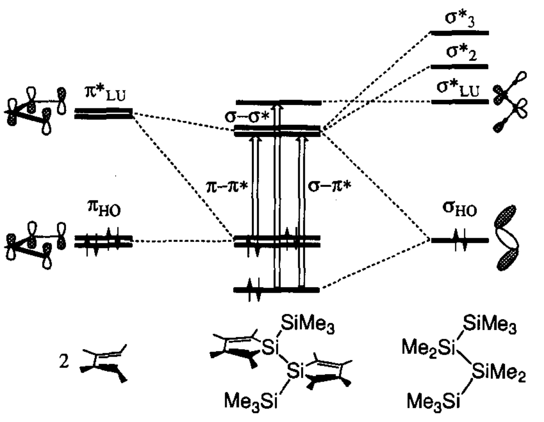


Figure 3. MO correlation diagram of **2**.

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References and Notes

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7 **7** was prepared by a reaction of 2,5-dilithio-3,4-dimethylhexa-2,4-diene with 1,1,1-trichlorotrimethyldisilane in ether at -78 °C (y. 89%). **7**: a colorless oil, bp 50–60 °C/0.01 mmHg (Kugel-rohr distillation); ^{1}H NMR (C_6D_6, δ) 1.85 (s, 6 H), 1.60 (s, 6 H), 0.16 (s, 9 H); ^{13}C NMR (C_6D_6, δ) 150.9, 128.7, 14.1, 13.2, -2.3; ^{29}Si NMR (C_6D_6, δ) 7.0, -16.8; MS (70 eV) m/z(%) 244 (M$^+$, 46), 229 (100); HRMS m/z Calcd for $C_{11}H_{21}Si_2Cl$: 244.0871, Found: 244.0869.

8 **3**: colorless crystals, mp 110–112 °C; ^{1}H NMR(toluene-d_8, δ) 2.08 (s, 6 H), 1.94 (s, 12 H), 1.82 (s, 6 H), 1.77 (s, 12 H), 0.00 (s, 18 H); ^{13}C NMR (toluene-d_8, δ) 150.1, 149.9, 132.8, 131.0, 15.9, 15.5, 14.8, 14.7, -0.8; ^{29}Si NMR (toluene-d_8, δ) -13.1, -34.3, -36.9; MS (70 eV) m/z(%) 554 (M$^+$, 41), 99 (100); HRMS Calcd for $C_{30}H_{54}Si_5$: 554.3072, Found: 554.3068; UV (hexane) λ_{max}/nm (ε) 234 (36000), 280 (16000).

9 **4**: colorless crystals, mp >300 °C; ^{1}H NMR (C_6D_6, δ) 2.07 (s, 12 H), 2.01 (s, 12 H), 1.84 (s, 12 H), 1.83 (s, 12 H), 0.05 (s, 18 H); ^{13}C NMR (C_6D_6, δ) 150.1, 149.7, 132.0, 131.1, 15.8, 15.5, 15.0, 14.9, -0.8; ^{29}Si NMR (C_6D_6, δ) -13.0, -34.1, -37.5; MS (70 eV) m/z(%) 690 (M$^+$, 100); HRMS Calcd for $C_{38}H_{66}Si_6$: 690.3780, Found: 690.3777; UV (hexane) λ_{max}/nm (ε) 238 (41800), 274 (23800).

10 **5**: colorless crystals; ^{1}H NMR (C_6D_6, δ) 2.04 (s, 12 H), 1.99 (s, 6 H), 1.95 (s, 12 H), 1.84 (s, 12 H), 1.82 (s, 12 H), 1.81 (s, 6 H), 0.02 (s, 18 H); ^{13}C NMR (C_6D_6, δ) 150.3, 150.0, 149.5, 132.1, 131.1, 131.0, 15.8, 15.7, 15.5, 15.0 (2C), 14.8, -0.8; ^{29}Si NMR (C_6D_6, δ) -13.0, -33.9, -37.5, -38.1; MS (70 eV) m/z(%) 826 (M$^+$, 100), 696 (21), 373 (28), 237 (50), 179 (28); UV (hexane) λ_{max}/nm (ε) 244 (41900), 275 (31600).

11 Crystal data of **3**: $C_{30}H_{54}Si_5$, FW = 555.18, monoclinic, space group $P2_1/n$ (#14), a = 10.464(3) Å, b = 29.95(2) Å, c = 11.094(4) Å, β = 91.65(2) °, V = 3475(1) Å^3, Z = 4, d_{calc} = 1.061 g/cm^3, temperature 150 K. The structure was solved by direct method using SIR92. Full matrix least-squares refinement yielded the final R value of 0.039 (R_w = 0.043) for 5324 independent reflections [$2\theta \leq 128.2$ °, $I > 3.00\sigma(I)$] measured on a Rigaku AFC5R diffractometer using Cu-Kα radiation (λ = 1.54178 Å) and ω-2θ scan.

12 **8** was prepared by a reaction of 1,1-dilithio-2,3,4,5-tetramethylsilole[6] with 2 equivalents of *t*-butylchloride in THF (y. 10%). **8**: colorless crystals, mp 63–66 °C; ^{1}H NMR (C_6D_6, δ) 1.90 (s, 6 H), 1.73 (s, 6 H), 1.11 (s, 18 H); ^{13}C NMR (C_6D_6, δ) 150.6, 128.8, 29.0, 19.3, 16.0, 13.9; ^{29}Si NMR (C_6D_6, δ) 13.0; MS (70 eV) m/z(%) 250 (M$^+$, 36), 73 (100); UV (hexane) λ_{max}/nm (ε) 294 (2000).

13 **9** was prepared by a reaction of 1,1-dilithio-2,3,4,5-tetramethylsilole[6] with chloropentamethyldisilane (y. 35%). **9**: a colorless oil, bp 90–120 °C/0.01 mmHg (Kugel-rohr distillation); ^{1}H NMR (C_6D_6, δ) 2.02 (s, 6 H), 1.83 (s, 6 H), 0.35 (s, 12 H), 0.06 (s, 18 H); ^{13}C NMR (C_6D_6, δ) 149.5, 132.9, 15.8, 14.7, -1.7, -4.5; ^{29}Si NMR (C_6D_6, δ) -14.2, -33.9, -41.8. MS (70 eV) m/z (%) 398 (M$^+$, 35), 325 (100); UV (hexane) λ_{max}/nm (ε) 234 (sh, 19000), 249 (22300), 272 (sh, 6500), 299 (sh, 2900).

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