2,3,6,7,10,11-Hexakis(dimethylsilyl)triphenylene

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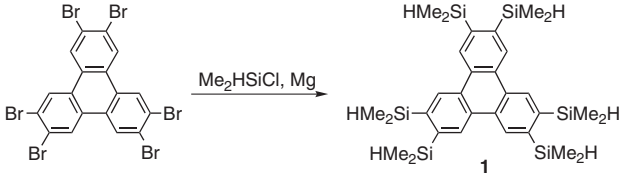
2,3,6,7,10,11-Hexakis(dimethylsilyl)triphenylene (**1**) was synthesized by the silylation of 2,3,6,7,10,11-hexabromotriphenylene with chlorodimethylsilane and magnesium. The absorption and emission spectra of **1** revealed that the silyl substituents modify optical properties of triphenylene.

Triphenylene derivatives have been studied as discotic liquid crystals.[1] For the last decade, their application to optical materials such as photoconductors,[2] light emitting diodes,[3] and optical compensation sheets[4] has been remarkably developed. Most of them have alkoxy, acyloxy, and alkylthio substituents at the 2,3,6,7,10,11-positions of triphenylene. Introduction of a variety of substituents into triphenylene might expand and improve optical properties. In the course of our studies on aromatic compounds with organosilicon substituents, we found that organosilicon substituents perturb the electronic properties of aromatic compounds.[5] We report herein the synthesis, structure, and some optical properties of a novel 2,3,6,7,10,11-hexasilyltriphenylene.[6]

2,3,6,7,10,11-Hexakis(dimethylsilyl)triphenylene (**1**) was synthesized by the silylation of 2,3,6,7,10,11-hexabromotriphenylene with chlorodimethylsilane and magnesium. In this reaction, a mixture of mono- to hexasilyltriphenylenes was obtained, and **1** was isolated from the mixture in 3% yield.[7] The formation of the partially silyl-substituted triphenylenes may be due to the benzyne formation from the *o*-dibromobenzene moieties by magnesium.



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The structure of **1** was analyzed by X-ray crystallography (Figure 1).[8] The triphenylene ring is deformed by silyl substituents. The C(2)–C(3), C(8)–C(9), and C(14)–C(15) bonds (average 1.419 Å) are significantly longer than other C–C bonds of the benzene rings owing to the steric repulsion between the silyl groups. The corresponding C–C bond lengths of triphenylene have been reported to be 1.385 Å on the average.[9] On the other hand, the C(5)–C(18), C(6)–C(11), and C(12)–C(17) bonds (average 1.407 Å) are shorter than the corresponding C–C bonds of triphenylene (average 1.435 Å).[9] One methyl group on each silicon atom is oriented so that the Si–C bond becomes perpendicular to the benzene ring. The perpendicular orientation has the advantage for the effective σ^*–π^* conjugation mentioned below.

The UV spectra of **1** and triphenylene are described in

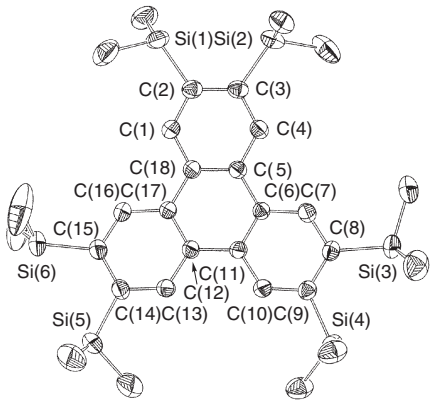

Figure 1. Molecular structure of **1**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

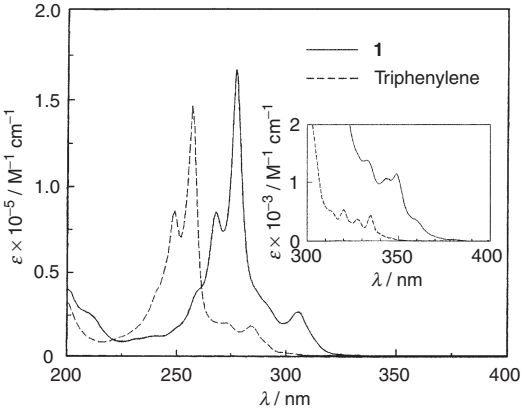

Figure 2. UV spectra of **1** and triphenylene in hexane at room temperature.

Figure 2. Compound **1** shows an intense ^1B_b band at 278 nm (ε 170000 $M^{-1}\,cm^{-1}$), a ^1L_a band at 305 nm (ε 27300 $M^{-1}\,cm^{-1}$), and a weak ^1L_b band at 349 nm (ε 1200 $M^{-1}\,cm^{-1}$). Since the corresponding bands of triphenylene are observed at 257 (ε 148000 $M^{-1}\,cm^{-1}$), 285 (ε 18100 $M^{-1}\,cm^{-1}$), and 335 nm (ε 300 $M^{-1}\,cm^{-1}$), the ^1B_b, ^1L_a, and ^1L_b bands of **1** show bathochromic shifts of 21, 20, and 14 nm, respectively. Also, the extinction coefficients of these bands of **1** are larger than those of triphenylene. In order to obtain more information about these results, molecular orbital calculations (B3LYP/6-31G*) were carried out. The energy level of the HOMO of **1** is almost the same as that of triphenylene, whereas the energy level of the LUMO of **1** is much lower than that of triphenylene because of the σ^*–π^* conjugation[10] between Si–C(methyl) σ^* orbitals and

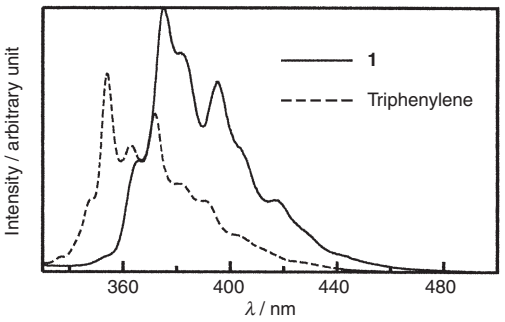

Figure 3. Fluorescence spectra of **1** and triphenylene in 3-methylpentane at room temperature.

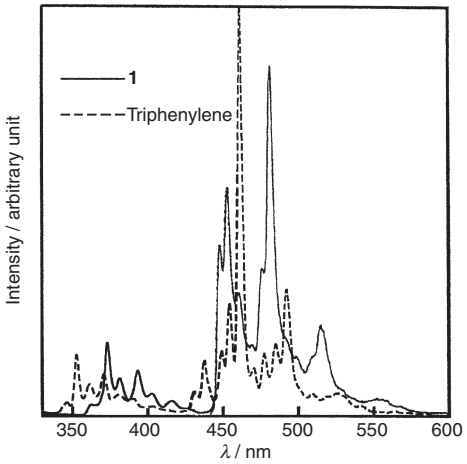

Figure 4. Emission spectra of **1** and triphenylene in 3-methylpentane at 77 K.

a π^* orbital of triphenylene.

The fluorescence spectrum of **1** measured at room temperature is shown in Figure 3. A bathochromic shift compared with the fluorescence of triphenylene is observed. The intensity of the fluorescence of **1** is greater than that of triphenylene; the fluorescence quantum yield (Φ_F) of **1** is 0.14, while that of triphenylene has been reported to be 0.09.[11] The higher fluorescence quantum yield of **1** corresponds to the more intense UV absorption in Figure 2 and is ascribed to the effect of the silyl groups.

Compound **1** shows weak fluorescence in the region of 360–440 nm and intense phosphorescence in the region of 440–600 nm at 77 K (Figure 4). The phosphorescence quantum yield of **1** ($\Phi_P = 0.6$) is higher than that of triphenylene ($\Phi_P = 0.41$).[12] Since Φ_P is expressed by the following equation, where Φ_{ST}, k_P, and k_{TS} represent the intersystem crossing quantum yield from the S_1 state to the T_1 state, the phosphorescence radiative rate constant, and the intersystem crossing rate constant from the T_1 state to the S_0 state, the twice greater k_P value of **1** than the k_{TS} value leads to the higher phosphorescence quantum yield (Table 1).

$$\Phi_P = \Phi_{ST} k_P / (k_P + k_{TS})$$

Table 1. Photophysical parameters of **1** and triphenylene in 3-methylpentane at 77 K

Compound	Φ_F	Φ_P	Φ_{ST}[a]	τ_T/s	k_P/s^{-1}	k_{TS}/s^{-1}
1	0.08	0.6	0.92	3	0.2	0.1
Triphenylene	0.07[b]	0.41[b]	0.93	14	0.03	0.04

[a]$\Phi_{ST} \approx 1 - \Phi_F$. [b]Ref. 12.

References and Notes

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7 **1**: mp 130–131 °C; ^{1}H NMR (C_6D_6) δ 0.51 (d, 36H, $J = 3.7$ Hz), 5.13 (sep, 6H, $J = 3.7$ Hz), 9.20 (s, 6H); ^{13}C NMR (C_6D_6) δ −2.5, 129.8, 129.9, 142.8; ^{29}Si NMR (C_6D_6) δ 69.8; IR (NaCl, cm^{-1}) 2950, 2130, 1250, 1140, 890; MS m/z (%) 576 (M^+, 100), 561 (23), 517 (38); HRMS. Found: 576.2374. Calcd for $C_{30}H_{48}Si_6$: 576.2372.

8 Crystal data for **1**: $C_{30}H_{48}Si_6$, $M_r = 577.22$, monoclinic, space group $P2_1/c$, $a = 13.545(2)$, $b = 12.703(1)$, $c = 21.565(3)$ Å, $\beta = 101.192(3)°$, $V = 3639.9(7)$ Å^3, $Z = 4$, $D_c = 1.053$ g·cm^{-3}, $R1 = 0.060$ and $wR2 = 0.150$ ($I > 2\sigma(I)$), $R1 = 0.094$ and $wR2 = 0.157$ (all data). Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-213164.

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