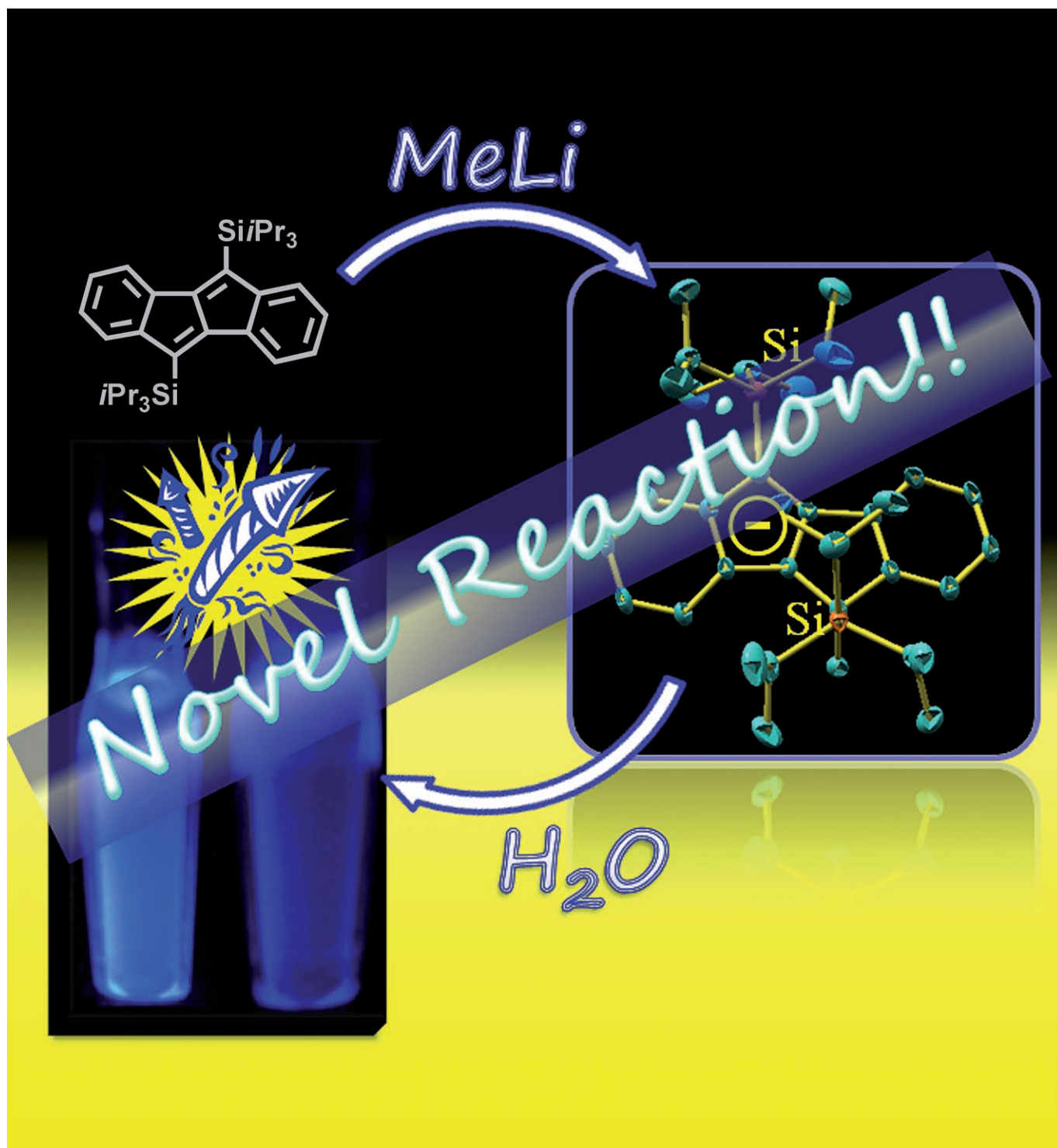


New Reactions of a Dibenzo[*a,e*]pentalene

Masaichi Saito,* Michio Nakamura, and Tomoyuki Tajima^[a]

Dedicated to Professor Robert West on the occasion of his 80th birthday



Abstract: Reduction of dibenzo[*a,e*]pentalene **3** (denoted as dibenzopentalene hereafter) with excess lithium gave dilithium dibenzopentalenide **1**. Since oxidation of **1** with iodine gave **3**, redox behavior between **1** and **3** is controllable and reversible. Reaction of **3** with methyllithium gave lithium 5-

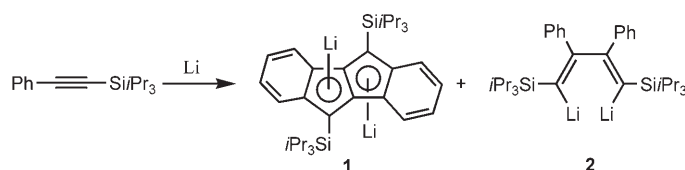
methylidibenzopentalenide **5**, the formation of which was evidenced by some trapping experiments and X-ray

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crystallographic analysis. Reactions of **3** with halogens gave 5,10-dihalodibenzopentalenes, **8** and **9**. Some optical properties of novel dibenzopentalene derivatives are also demonstrated.

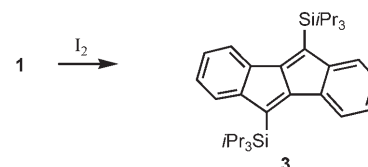
Introduction

The pentalene dianion has received considerable attention recently in terms of its synthetic utility as a ligand of sandwich-type transition-metal complexes^[1–3] and the antiaromaticity of its neutral derivative.^[4] However, the dibenzopentalene dianion,^[5] which is more π -extended than the pentalene dianion, has received less attention in spite of its recent potential use as a building block of ladder-type π -conjugated molecules, which are of growing interest.^[6] Very recently, we succeeded in the first X-ray characterization of a dilithium dibenzopentalenide **1**, prepared by reduction of a phenyl-(triisopropylsilyl)acetylene with lithium (Scheme 1).^[7] Although the yield of dilithium dibenzopentalenide **1** was low,



Scheme 1. Formation of dilithium dibenzopentalenide **1**.

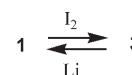
isolation of **1** by recrystallization from a reaction mixture containing a major product, the 1,4-dilithio-1,3-butadiene **2**, was very easy. The dilithium dibenzopentalenide **1** was oxidized by iodine to give dibenzo[*a,e*]pentalene (denoted as dibenzopentalene hereafter) **3** (Scheme 2).^[7] Hence, our novel synthetic method enables us to develop new chemistry for dibenzopentalenes. Herein, we report novel reactions of dibenzopentalene **3** and X-ray structural analysis of a lithium 5-methylidibenzopentalenide, a novel type of indenyl anion, formed by the reaction of **3** with methyllithium. Electronic absorption and fluorescence spectra of novel dibenzopentalene derivatives are also demonstrated.



Scheme 2. Formation of dibenzopentalene **3** by oxidation of **1**.

Results and Discussion

Reduction of dibenzopentalene 3: Treatment of dibenzopentalene **3** with excess lithium in ether followed by recrystallization gave dilithium dibenzopentalenide **1** in 77% yield (Scheme 3). Since dilithium dibenzopentalenide **1** was oxidized by iodine to give dibenzopentalene **3** in 89% yield, redox behavior between dibenzopentalene **3** and dilithium dibenzopentalenide **1** was controllable and reversible.



Scheme 3. Redox behavior between **1** and **3**.

Reaction of dibenzopentalene 3 with methyllithium: trapping of the intermediate: For the synthesis of dilithiodibenzopentalene, a key precursor of dibenzopentalene derivatives with various substituents on the 5- and 10-positions, reaction of dibenzopentalene **3** with methyllithium was carried out. When a THF solution of **3** was treated with methyllithium, the color of the solution changed from brownish red to green, which suggested the formation of an anionic species. After treatment of the resulting mixture with H₂O, 5,10-dihydro-5-methyl-dibenzopentalenes **4** were obtained as a mixture of *cis* and *trans* stereoisomers in 34 and 50% yields, respectively and the expected parent dibenzopentalene was not obtained (Scheme 4). The stereochemistry of *trans*-**4** was established by X-ray crystallographic analysis (Figure 1 and Table 1). To gain more insight into an intermediate of this reaction, treatment of **3** with methyllithium followed by D₂O afforded the corresponding deuterio derivatives, *cis*- and *trans*-**4D** in 31 and 40% yields, respectively.^[8] Thus, the intermediate was lithium 5-methylidibenzopentalenide **5**. By using iodomethane instead of water as a trapping reagent, 5,10-dimethyl derivative **6** was obtained as a single isomer in 72% yield. In the ¹H NMR spectra, the methyl protons of

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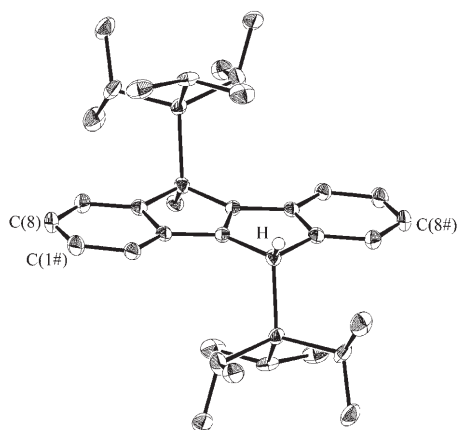
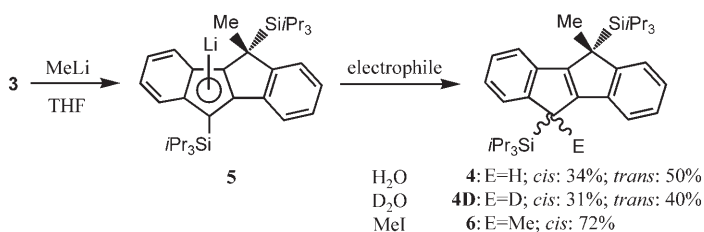


Figure 1. ORTEP drawing of *trans*-4 with thermal ellipsoid plots (40% probability for non-hydrogen atoms).

Table 1. Selected bond lengths [Å] and angles [°] of *trans*-4.

C1–C2	1.389(2)	C2–C3	1.390(2)	C3–C4	1.460(2)
C4–C5	1.505(2)	C5–C6	1.518(2)	C6–C7	1.392(2)
C7–C8	1.386(3)	C1–C8#	1.381(3)	C3–C6#	1.415(2)
C4–C4#	1.349(3)				
Si1–C5–C18	106.97(15)	C4–C5–C6	100.28(13)	Si1–C5–C6	108.44(11)

cis and *trans*-4 resonated at $\delta = 1.65$ and 1.91 ppm, respectively. The signal assignable to the methyl protons of **6** was observed at $\delta = 1.65$ ppm, and hence the stereochemistry of **6** could be assigned as *cis*. The preferential formation of *cis*-**6** can be reasonably interpreted by steric hindrance of the triisopropylsilyl group at the 5-position, which prevents attack of the anionic moiety on iodomethane. On the other hand, when the electrophile was water, it was sufficiently small to react with **5** from both sides of the five-membered ring, which resulted in an almost 1:1 ratio of *cis* and *trans* isomers (Scheme 4).



Scheme 4. Reaction of dibenzopentalene **3** with methyllithium.

Reaction of dibenzopentalene **3 with methyllithium: monitoring the intermediate by NMR spectroscopy:** When the reaction of dibenzopentalene **3** with methyllithium was monitored by NMR spectroscopy, a single product was observed in the NMR spectra. Therefore, lithium 5-methyldibenzopentalenide **5** was formed quantitatively from **3**. In the ^7Li NMR spectrum, an upfield resonance was observed at $\delta = -7.4$ ppm, which suggested that the anionic moiety of **5** should be highly aromatic.^[9] The carbon atom at the 9-position

of some fluorenyllithiums was reported to resonate at about $\delta = 80$ ppm.^[10] Likewise, in the ^{13}C NMR spectrum, a ^{13}C signal at $\delta = 80.47$ ppm can be assigned to a carbon atom at the 1-position in the anionic moiety of **5**. Following the previous report that a 6,6-dimethylfulvene derivative reacted with methyllithium to give the corresponding lithium *t*-butylcyclopentadienide,^[11] dibenzopentalene **3** reacted with methyllithium as a fulvene to give **5**.

Structure of lithium 5-methyldibenzopentalenide **5:** We succeeded in the first X-ray characterization of lithium 5-methyldibenzopentalenide **5**, a novel type of indenyl anion. Single crystals of lithium 5-methyldibenzopentalenide **5** were obtained by recrystallization from a THF solution of **5** in the presence of [12]crown-4 at -30°C . The lithium cation is coordinated with two [12]crown-4 molecules, hence [5([12]crown-4)] has a solvent-separated ion-pair structure in the solid state. An ORTEP drawing and selected bond lengths and angles of the anionic moiety of **5** are shown in Figure 2 and Table 2, respectively. The tetracyclic framework deviates slightly from planarity and has a bow shape.

The carbon–silicon bond between the cyclopentadienyl anion moiety and the triisopropylsilyl group deviates slightly from the plane of the five-membered ring and turns toward

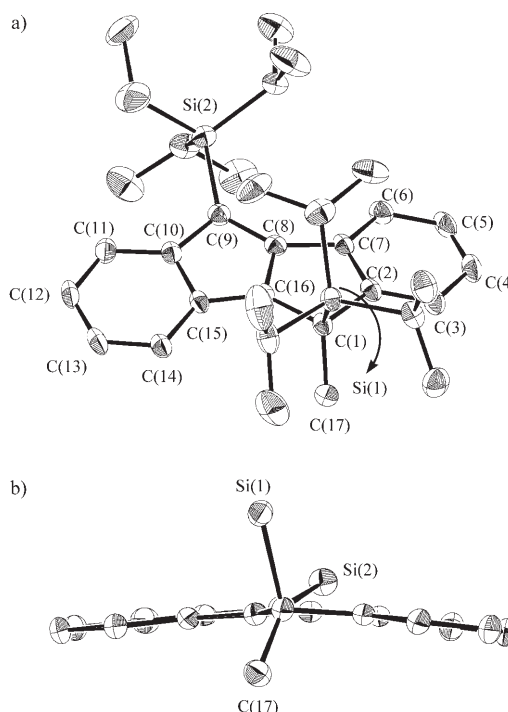


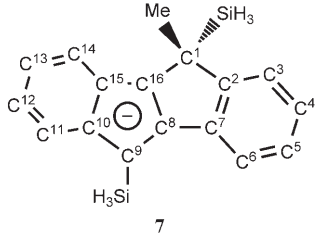
Figure 2. ORTEP drawings of [5([12]crown-4)] with thermal ellipsoid plots (40% probability for non-hydrogen atoms). a) Top view and b) side view. The lithium atom, and THF and [12]-crown-4 molecules are omitted for clarity.

Table 2. Selected bond lengths [Å] and angles [°] of **5** ([12]crown-4).

C1–C2	1.522(3)	C2–C3	1.388(3)	C3–C4	1.386(3)
C4–C5	1.374(4)	C5–C6	1.397(4)	C6–C7	1.402(3)
C7–C8	1.478(3)	C8–C9	1.434(3)	C9–C10	1.447(3)
C10–C11	1.418(3)	C11–C12	1.385(4)	C12–C13	1.394(4)
C13–C14	1.374(3)	C14–C15	1.421(3)	C15–C16	1.411(3)
C1–C16	1.513(3)	C2–C7	1.411(3)	C8–C16	1.395(3)
C10–C15	1.441(3)	C1–C17	1.548(3)	C1–Si1	1.950(2)
C9–Si2	1.871(2)				
Si1–C1–C2	109.11(15)	Si1–C1–C16	108.64(15)	C2–C1–C16	99.11(18)
Si2–C9–C8	132.16(18)	Si2–C9–C10	123.90(18)	C8–C9–C10	102.7(2)

the side of the other triisopropylsilyl group, which suggests some localization of the negative charge on the carbon atom bonded to the triisopropylsilyl group. As suggested, the C–C bond lengths of the cyclopentadienyl anion moiety (1.395–1.447 Å) differ slightly; this contrasts the dilithium dibenzopentalenide **1**^[7] and alkali-metal indenides,^[10b,12] which do not show any alternation of the C–C bonds in the five-membered ring. The six-membered ring adjoining the anionic five-membered ring also has different C–C bond lengths (1.385–1.441 Å), as was observed in alkali-metal indenides.^[10b,12] On the other hand, remarkable alternation of the C–C bonds is found in the cyclopentadiene ring of **5** (1.395–1.522 Å), which is similar to that observed in *trans*-**4** (Table 1).

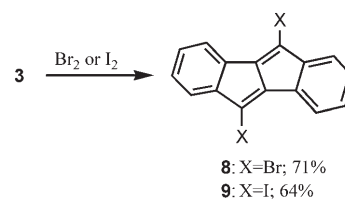
To get more insight into the structure of **5**, theoretical calculations were carried out. Geometrical optimization was carried out with density functional theory at the B3LYP level by using the Gaussian 98 program^[13] and the 6-31G(d) basis set was used for C, Si, and H. The model anion **7** was fully optimized and the calculated C–C bond lengths in the tetracyclic framework are consistent with those found in the X-ray structural analysis, although the calculated tetracyclic framework is almost planar (Table 3). Nucleus-independent chemical shift (NICS) values calculated at 1.0 Å above ($\delta = -12.5$ ppm) and below ($\delta = -12.9$ ppm) the cyclopentadienide ring^[14] of the model anion **7** are negative, which suggests that the cyclopentadienide ring has aromatic character.

Table 3. Selected bond lengths [Å] in the optimized structure of **7**.


C1–C2	1.530	C2–C3	1.390	C3–C4	1.402
C4–C5	1.398	C5–C6	1.398	C6–C7	1.402
C7–C8	1.452	C8–C9	1.426	C9–C10	1.442
C10–C11	1.412	C11–C12	1.388	C12–C13	1.416
C13–C14	1.387	C14–C15	1.412	C15–C16	1.418
C1–C16	1.512	C2–C7	1.426	C8–C16	1.409
C10–C15	1.462				

Reactions of dibenzopentalene

3 with halogens: For functionalization of dibenzopentalene **3**, halogenation of **3** was examined. Reactions of dibenzopentalene **3** with excess bromine at room temperature gave 5,10-dibromo derivative **8**^[15] in high yield (Scheme 5). Heating of dibenzopentalene **3** with excess

Scheme 5. Halogenation of dibenzopentalene **3**.

iodine in ether under reflux gave a novel 5,10-diiodo derivative **9** in high yield (Scheme 5). Although the synthesis of 5,10-dihalodibenzopentalenes has already been reported,^[15,16] the present method is noteworthy as a novel, facile method for the synthesis of 5,10-dihalodibenzopentalenes, which would be key intermediates for derivatives with a dibenzopentalene skeleton.

Absorption and fluorescence spectra of dibenzopentalene derivatives

Optical properties of newly obtained dibenzopentalene **3 and dihydrodibenzopentalenes, *cis*- and *trans*-**4**,** were also investigated (Table 4). The electronic absorption and fluorescence spectra of **3** and *cis*- and *trans*-**4** are shown in Figures 3 and 4, respectively. The two longest absorption maxima of **3** are longer than those of the parent dibenzopentalene,^[17] as was observed in a silyl-substituted triphenylene, the absorption maxima of which are longer than those of the parent triphenylene.^[18] On the other hand, the absorption spectra of *cis*- and *trans*-**4** are similar to that of the parent dihydrodibenzopentalene.^[19] In sharp contrast to the non-fluorescent nature of dibenzopentalene **3**, dihydrodi-

Table 4. Photophysical properties of **3**, *cis*-**4**, and *trans*-**4**.

	Absorption wavelength [nm] (ϵ)		
3	283(53 800)	420(13 200)	442(11 300)
<i>cis</i> - 4	325(24 000)		
<i>trans</i> - 4	324(24 800)	339(19 600)	
	Fluorescence		
	Excitation [nm]	Emission [nm]	Absolute quantum yield
3	– ^[a]	– ^[a]	– ^[a]
<i>cis</i> - 4	325	386	0.57 ^[b]
<i>trans</i> - 4	300	368	0.48 ^[c]

[a] No fluorescence was observed. [b] 1.22×10^{-4} mol L⁻¹. [c] 1.07×10^{-4} mol L⁻¹.

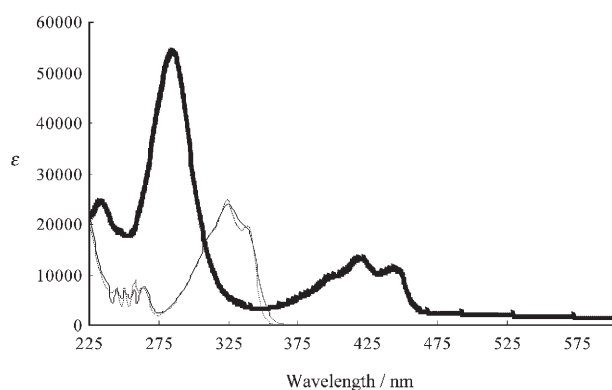


Figure 3. Electronic absorption spectra of **3** (—), *cis*-**4** (---), and *trans*-**4** (----) in hexane at room temperature.

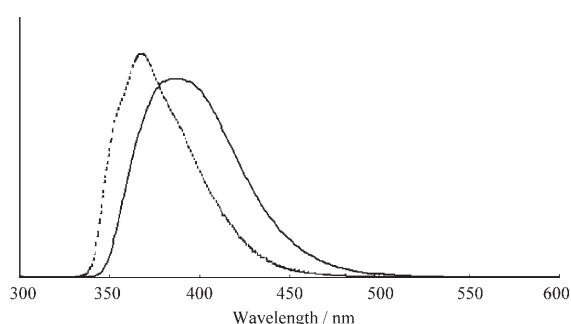


Figure 4. Fluorescence spectra of *cis*-**4** (—, excited at 325 nm) and *trans*-**4** (----, excited at 300 nm) in hexane at room temperature.

benzopentalenes **4** each reveal a fluorescent nature at room temperature. Each fluorescence of *cis*- and *trans*-**4**, excited at 325 and 300 nm, respectively, appears in the same region as that of the parent dihydrodibenzopentalene,^[19] which suggests that the effect of silyl substituents on the optical properties of **4** is small, although a bathochromic shift in the fluorescence of *cis*-**4** (386 nm) is observed, compared with that of *trans*-**4** (368 nm).

Conclusion

Reactions of novel dibenzopentalene **3** were investigated. Reduction of **3** with excess lithium gave dilithium dibenzopentalenide **1**. Thus, dibenzopentalene **3** and dilithium dibenzopentalenide **1** showed a reversible redox behavior. Reaction of **3** with methyllithium gave novel lithium 5-methyl-dibenzopentalenide **5**. The X-ray and NMR spectroscopic analyses indicated that the anionic moiety of **5** has considerable aromatic character, although partial localization of the negative charge is suggested. Reaction of **3** with bromine or iodine gave the corresponding halogenated compounds. A bathochromic shift was observed in the electronic absorption spectrum of **3**, compared with that of the parent dibenzopentalene, whereas the silyl substituents had little effect

on the absorption and fluorescence spectra of **4** relative to those of the parent dihydrodibenzopentalene.

Experimental Section

General: All reactions were carried out under an argon atmosphere. THF, diethyl ether, and C₆D₆ used in the synthesis or NMR spectroscopic analyses were distilled from sodium benzophenone ketyl under an argon atmosphere followed by distillation from a potassium mirror by using a trap-to-trap technique. ¹H (400 MHz), ¹³C (101 MHz), and ⁷Li NMR (156 MHz) spectra were recorded on a Bruker DPX-400 or a DRX-400 spectrometer. Preparative gel-permeation chromatography (GPC) was carried out on an LC-918 (Japan Analytical Ind.) with JAIGEL-1H and -2H columns. Column chromatography was carried out with Merck Kieselgel 60 (silica gel). Melting points were determined on a Mitamura Riken Kogyo MEL-TEMP apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of Molecular Analysis and Life Science Center, Saitama University (Japan). UV/Vis spectra were measured on a JASCO V-560 spectrometer. Fluorescence spectra and absolute quantum yields were measured on a JASCO FP-6300 spectrometer and a Hamamatsu Photonics absolute PL quantum yield measurement system C9920-02, respectively.

Reduction of dibenzopentalene 3 with lithium (excess): A solution of dibenzopentalene **3** (421.4 mg, 0.82 mmol) in diethyl ether (10 mL) was added to lithium (85.6 mg, 12.3 mmol). The resulting mixture was degassed by freeze-pump-thaw cycles, sealed, and then stirred for 2 days. In a glovebox, insoluble materials were filtered off and hexane (5 mL) was added to the filtrate. Recrystallization of the filtrate at -30°C gave dilithium dibenzopentalenide **1** (426.5 mg, 77%).

Oxidation of dilithium dibenzopentalenide 1 with iodine: A solution of iodine (41.3 mg, 1.63 mmol) in diethyl ether (5 mL) was added to a solution of dilithium dibenzopentalenide **1** (56.1 mg, 0.083 mmol) in diethyl ether (5 mL). The resulting mixture was stirred for 3.5 h. After removal of volatile substances, insoluble materials in dichloromethane were filtered off. The residue was subjected to GPC to give 5,10-bis(triisopropylsilyl)dibenzo[*a,e*]pentalene (**3**) (38.0 mg, 89%). **Product 3:** M.p. 208–210°C; ¹H NMR (CDCl₃): δ = 1.19 (d, *J*(H,H) = 8 Hz, 36H), 1.64 (sept, *J*(H,H) = 8 Hz, 6H), 6.76–6.84 (m, 4H), 7.08–7.10 (m, 2H), 7.22–7.24 ppm (m, 2H); ¹³C NMR (CDCl₃): δ = 13.26 (d), 19.37 (q), 123.37 (d), 124.90 (d), 125.99 (d), 127.71 (d), 136.35 (s), 140.10 (s), 156.09 (s), 161.72 ppm (s); elemental analysis calcd (%) for C₃₄H₅₀Si₂: C 79.30, H 9.79; found: C 79.25, H 10.09.

Product 5: M.p. 182°C (recrystallized from hexane/ethanol); ¹H NMR (CDCl₃): δ = 0.93–1.03 (m, 42H), 7.05–7.09 (m, 6H), 7.20–7.24 ppm (m, 4H); ¹³C NMR (CDCl₃): δ = 13.75 (d), 19.25 (q), 19.53 (q), 108.57 (s), 126.84 (d), 128.13 (d), 129.40 (d), 139.73 (s), 165.70 ppm (s); elemental analysis calcd (%) for C₃₄H₅₂I₂Si₂: C 52.98, H 6.80; found: C 53.24, H 6.81.

Reaction of dibenzopentalene 3 with methyllithium: trapping of the intermediate by H₂O: Methyllithium (0.98 M in ether; 0.34 mL, 0.33 mmol) was added to a solution of dibenzopentalene **3** (76.5 mg, 0.15 mmol) in THF (3 mL) at room temperature. After the reaction mixture had been stirred for 30 min, the reaction was quenched by the addition of H₂O. The organic layer was then extracted with ether and dried over anhydrous magnesium sulfate. Removal of volatile substances gave a crude product (84.6 mg), which was chromatographed on silica gel (hexane) to afford *cis*- (*cis*-**4**) (27.0 mg, 34%) and *trans*-5,10-dihydro-5,10-bis(triisopropylsilyl)-5-methyl-dibenzo[*a,e*]pentalene (*trans*-**4**) (39.8 mg, 50%).

Product cis-4: M.p. 159°C (decomp); ¹H NMR (CDCl₃): δ = 0.93 (d, *J*(H,H) = 7 Hz, 9H), 1.05–1.09 (m, 18H), 1.12 (d, *J*(H,H) = 8 Hz, 9H), 1.33–1.42 (m, 6H), 1.65 (s, 3H), 3.90 (s, 1H), 7.06–7.13 (m, 2H), 7.21–7.25 (m, 2H), 7.50–7.54 (m, 3H), 7.58 ppm (d, *J*(H,H) = 8 Hz, 1H); ¹³C NMR (CDCl₃): δ = 12.00 (d), 12.12 (d), 19.37 (q), 19.53 (q), 19.97 (q), 20.15 (q), 21.27 (q), 36.97 (d), 45.98 (s), 120.24 (d), 120.67 (d), 122.72 (d), 123.13 (d), 123.88 (d), 124.22 (d), 124.65 (d), 125.34 (d), 140.84 (s), 141.18

(s), 151.39 (s), 152.44 (s), 157.82 (s), 160.49 ppm (s); elemental analysis calcd (%) for $C_{35}H_{54}Si_2$: C 79.17, H 10.25; found: C 79.13, H 10.34.

Product trans-4: M.p. 236–237°C; 1H NMR ($CDCl_3$): δ =0.82 (d, $J(H,H)$ =7 Hz, 9H), 0.86 (d, $J(H,H)$ =7 Hz, 9H), 0.91 (d, $J(H,H)$ =8 Hz, 9H), 0.95 (d, $J(H,H)$ =8 Hz, 9H), 1.27–1.37 (m, 6H), 1.91 (s, 3H), 4.06 (s, 1H), 7.10–7.17 (m, 2H), 7.23–7.28 (m, 2H), 7.51–7.55 (m, 3H), 7.64 ppm (d, $J(H,H)$ =8 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ =11.95 (d), 12.64 (d), 18.67 (q), 18.75 (q), 19.10 (q), 19.48 (q), 19.56 (q), 35.12 (d), 44.96 (s), 120.14 (d), 120.31 (d), 122.81 (d), 123.21 (d), 123.89 (d), 124.35 (d), 124.59 (d), 125.31 (d), 140.14 (s), 140.65 (s), 149.21 (s), 149.98 (s), 156.22 (s), 156.47 ppm (s); elemental analysis calcd (%) for $C_{35}H_{54}Si_2$: C 79.17, H 10.25; found: C 78.69, H 10.26.

X-ray crystallographic analysis of trans-4: Crystals suitable for X-ray diffraction were obtained by recrystallization from a dichloromethane solution of *trans-4* at $-20^\circ C$. The intensity data were collected at $-170^\circ C$ on a Bruker SMART APEX equipped with a CCD area detector with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.71073 \text{ \AA}$) and graphite monochromator. Formula = $C_{35}H_{54}Si_2$; $F_w=530.96$; crystal dimensions = $0.30 \times 0.10 \times 0.10$ mm; monoclinic; space group = $P2_1/n$; $Z=2$; $a=12.1181(12)$, $b=8.7158(9)$, $c=15.8599(16) \text{ \AA}$; $\beta=110.162(2)^\circ$; $V=1572.5(3) \text{ \AA}^3$; $D_{calcd}=1.121 \text{ g cm}^{-3}$; $R_1=0.052$ ($I > 2\sigma(I)$, 2468 reflections), $wR_2=0.138$ (for all reflections) for 2854 reflections and 209 parameters; GOF = 1.076. CCDC-680364 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Reaction of dibenzopentalene 3 with methyllithium: trapping of the intermediate by D₂O: Methyllithium (0.98 M in ether; 0.32 mL, 0.31 mmol) was added to a solution of dibenzopentalene 3 (71.3 mg, 0.14 mmol) in THF (3 mL) at room temperature. After the reaction mixture had been stirred for 20 min, the reaction was quenched by D₂O (0.5 mL). The organic layer was then extracted with ether and dried over anhydrous magnesium sulfate. Removal of volatile substances gave a crude product (71.1 mg), which was chromatographed on silica gel (hexane) to afford *cis-* (22.9 mg, 31%) and *trans-4D* (29.2 mg, 40%).

Reaction of dibenzopentalene 3 with methyllithium: trapping of the intermediate by iodomethane: Methyllithium (1.09 M in ether; 0.48 mL, 0.52 mmol) was added to a solution of dibenzopentalene 3 (128.6 mg, 0.25 mmol) in THF (5 mL) at room temperature. After the reaction mixture had been stirred for 20 min, the reaction was quenched by methyl iodide (0.5 mL, 3.21 mmol). After removal of insoluble materials in dichloromethane by filtration, the filtrate was concentrated to give a crude product (134.9 mg), which was purified by column chromatography on silica gel (hexane) to afford *cis-5,10-dihydro-5,10-bis(triisopropylsilyl)-5,10-dimethyldibenzo[*a,e*]pentalene (cis-6)* (97.6 mg, 72%).

Product cis-6: M.p. 155.5°C (decomp); 1H NMR ($CDCl_3$): δ =0.94 (d, $J(H,H)$ =7 Hz, 18H), 1.10 (d, $J(H,H)$ =7 Hz, 18H), 1.35 (sept, $J(H,H)$ =7 Hz, 6H), 1.65 (s, 6H), 7.13 (dd, $J(H,H)$ =7, 7 Hz, 2H), 7.23 (dd, $J(H,H)$ =7, 7 Hz, 2H), 7.53 (d, $J(H,H)$ =7 Hz, 2H), 7.55 ppm (d, $J(H,H)$ =7 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ =11.81 (d), 20.06 (q), 20.19 (q), 21.29 (q), 46.07 (s), 120.92 (d), 123.10 (d), 123.78 (d), 124.94 (d), 140.30 (s), 158.18 (s), 159.83 ppm (s); elemental analysis calcd (%) for $C_{36}H_{56}Si_2$: C 79.34, H 10.36; found: C 79.11, H 10.49.

Reaction of dibenzopentalene 3 with methyllithium: monitoring the intermediate by NMR spectroscopy: Methyllithium (1.09 M in ether; 0.35 mL, 0.38 mmol) was added to a solution of dibenzopentalene 3 (132.2 mg, 0.26 mmol) in THF (4 mL) at room temperature. After the mixture had been stirred for 20 min, it was degassed by freeze-pump-thaw cycles and sealed. In a glovebox, removal of volatile substances gave a crude product, an aliquot of which was dissolved in C_6D_6 . NMR spectra of the solution revealed the quantitative formation of lithium 5,10-dihydro-5,10-bis(triisopropylsilyl)-5-methyldibenzo[*a,e*]pentalenide (5).

Product 5: 1H NMR (C_6D_6): δ =0.96 (d, $J(H,H)$ =7 Hz, 9H), 1.10 (d, $J(H,H)$ =7 Hz, 9H), 1.41 (d, $J(H,H)$ =7 Hz, 9H), 1.46 (d, $J(H,H)$ =7 Hz, 9H), 1.60 (sept, $J(H,H)$ =7 Hz, 3H), 2.06 (s, 3H), 2.13 (sept, $J(H,H)$ =7 Hz, 3H), 6.98–7.04 (m, 2H), 7.10 (t, $J(H,H)$ =7 Hz, 1H), 7.26 (t, $J(H,H)$ =7 Hz, 1H), 7.65 (d, $J(H,H)$ =7 Hz, 1H), 8.02 (d, $J(H,H)$ =8 Hz,

1H), 8.11 (d, $J(H,H)$ =8 Hz, 1H), 8.14 ppm (d, $J(H,H)$ =8 Hz, 1H); ^{13}C NMR (C_6D_6): δ =13.30 (d), 14.66 (d), 19.84 (q), 20.01 (q), 20.17 (q), 20.22 (q), 25.54 (q), 41.77 (s), 80.47 (s, C–Li), 116.15 (d), 117.26 (d), 119.20 (d), 121.40 (d), 122.13 (d), 124.14 (d), 124.49 (s), 124.49 (d), 125.37 (d), 132.36 (s), 140.67 (s), 140.95 (s), 142.77 (s), 157.96 ppm (s); 7Li NMR (C_6D_6): δ = -7.4 ppm.

X-ray crystallographic analysis of 5: Crystals suitable for X-ray diffraction were obtained by recrystallization from a THF solution of 5 in the presence of [12]crown-4 at $-30^\circ C$ in a glovebox. The crystal was mounted in a glass capillary. The intensity data were collected at $-170^\circ C$ on a Bruker SMART APEX equipped with a CCD area detector with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.71073 \text{ \AA}$) and graphite monochromator. Formula = $C_{55}H_{93}LiO_9Si_2$; $F_w=961.41$; crystal dimensions = $0.40 \times 0.20 \times 0.15$ mm; monoclinic; space group = $C2/c$; $Z=8$; $a=22.492(3)$, $b=23.964(3)$, $c=22.675(4) \text{ \AA}$; $\beta=114.021(3)^\circ$; $V=11163(3) \text{ \AA}^3$; $D_{calcd}=1.144 \text{ g cm}^{-3}$; $R_1=0.062$ ($I > 2\sigma(I)$, 7201 reflections), $wR_2=0.179$ (for all reflections) for 9903 reflections and 732 parameters; GOF = 1.007. CCDC-680363 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Reaction of dibenzopentalene 3 with bromine: Bromine (0.22 mL, 4.27 mmol) was added to an ether (10 mL) solution of dibenzopentalene 3 (108.7 mg, 0.21 mmol) at room temperature and the resulting mixture was stirred for 6 h. After addition of saturated aqueous sodium sulfite to the reaction mixture, the organic layer was extracted with ether, dried over anhydrous magnesium sulfate, and concentrated to give a crude product (173.9 mg). The residue was chromatographed on silica gel (hexane) to afford 5,10-dibromodibenzo[*a,e*]pentalene (8) (54.1 mg, 71%).

Product 8: M.p. 208°C (decomp); 1H NMR ($CDCl_3$): δ =6.95 (d, $J(H,H)$ =7 Hz, 2H), 6.98–7.06 (m, 4H), 7.33 ppm (d, $J(H,H)$ =7 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ =122.33 (s), 122.05 (d), 122.07 (d), 128.62 (d), 128.81 (d), 132.76 (s), 144.23 (s), 147.40 ppm (s); elemental analysis calcd (%) for $C_{16}H_8Br_2$: C 53.37, H 2.25; found: C 52.90, H 2.08.

Reaction of dibenzopentalene 3 with iodine: A mixture of dibenzopentalene 3 (97.4 mg, 0.19 mmol) and iodine (1.0127 g, 3.99 mmol) in diethyl ether (10 mL) was heated under reflux for 63 h. After the addition of saturated aqueous sodium sulfite to the reaction mixture, the organic layer was extracted with ether, dried over anhydrous magnesium sulfate, and concentrated to give a crude product (154.6 mg). The residue was then washed with hexane to give 5,10-diiododibenzo[*a,e*]pentalene (9) (55.0 mg, 64%).

Product 9: M.p. 197°C (decomp); 1H NMR ($CDCl_3$): δ =6.83 (d, $J(H,H)$ =7 Hz, 2H), 7.00 (ddd, $J(H,H)$ =1, 7, 7 Hz, 2H), 7.06 (ddd, $J(H,H)$ =1, 7, 7 Hz, 2H), 7.42 ppm (d, $J(H,H)$ =7 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ =94.36 (s), 120.83 (d), 123.90 (d), 128.45 (d), 129.08 (d), 133.68 (s), 150.02 (s), 152.01 ppm (s); elemental analysis calcd (%) for $C_{16}H_8I_2$: C 42.32, H 1.78; found: C 42.47, H 1.65.

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