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Synthesis, Structural, Spectral, and Photoswitchable Properties of *cis*- and *trans*-2,2,2′,2′-Tetramethyl-1,1′-indanylindanes[1]

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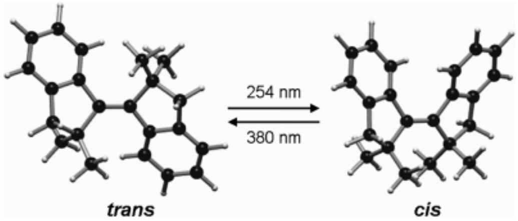
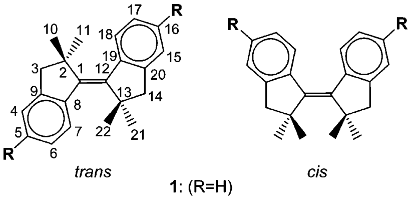


As versatile synthetic intermediates for new photoswitchable molecules with a tetramethylindanylindane (*stiff*-stilbene) core, the cis and trans isomers of 5,16-dibromo-2,2,13′,13′-tetramethylindanylindanes **2** were synthesized by the Barton−Kellogg coupling. The bromine atoms of *trans*-**2** could be readily replaced with alkyl (sp^3), aryl (sp^2), and ethynyl (sp) groups. The cis isomers of the parent tetramethylindanylindane **1** and its bromo derivative **2** were isolated, and their structural and photophysical properties were examined for the first time. Clean and efficient trans−cis and cis−trans photochemical isomerization processes were observed in **1**.

2,2,2′,2′-Tetramethylindanylindane **1**[2,3] has an overcrowded C═C double bond (Chart 1), and potential applications of this unique double bond character in new photochemical switching systems have been examined.[1] Although the X-ray crystal structure and UV/vis spectral properties of the parent *trans*-**1** have already been published,[2c] those of *cis*-**1** have not yet been reported. In a previous article, we described the synthesis and structural, chiroptical, photoswitchable, and anion binding properties of the chiral 5,5′-BINOL appended tetramethylindanylindanes as new types of photoswitchable molecules, and these compounds showed potentials for the highly efficient trans−cis photochemical switching system.[1] However, we could not isolate the pure cis isomer because of the rapid reverse photochemical isomerizarion (cis to trans) in the presence of visible light. Thus, the study of the structural and photophysical properties of the *cis*-tetramethylindanylindanes still remained to be completed. For the synthetic modification of the tetramethylindanylindane core, *trans*-5,16-dibromo-2,2,13′,13′-tetramethylindanylindane **2** was considered to be one of the most versatile synthetic intermediates because the bromine atoms would be readily replaced with the aryl and ethynyl groups via the Suzuki−Miyaura, Sonogashira, and other metal-catalyzed coupling reactions. We would like to now report the synthesis and fundamental structural, photophysical, and photoswitchable properties of the cis isomers of the indanylindanes **1** and **2** for the first time. In addition, synthetic modification of the tetramethylindanylindane core by the organometal-catalyzed coupling reactions of *trans*-**2** will also be reported.

CHART 1



1: (R=H)
2: (R=Br)

Lenoir and Lemmen first reported the synthesis of the parent *trans*-**1**[2a] by the McMurry coupling[4] of 2,2-dimethylindanone **7** in THF (Scheme 1). We also attempted the synthesis of the bromo-substituted indanylindane **2** by the similar McMurry coupling of 5-bromo-2,2-dimethylindanone **3**[1] but failed. We then used the Barton−Kellogg double bond formation reaction.[5,6] 5-Bromoindanone **3** was dissolved in toluene, 0.5 mol equiv of Lawesson's reagent was added, and the mixture was refluxed for 14 h. The resulting mixture was purified by column chromatography (SiO_2, hexane) to give the thioketone **4** as a purple oil (57%). On the other hand, the indanone **3** was converted to the hydrazone **5** (89%) by treatment with hydrazine monohydrate in ethanol at reflux. The diazo compound, which was generated from hydrazone **5** by treatment with Ag_2O at −25 °C, was reacted with **4** to afford thiirane **6** as a mixture of the cis and trans isomers. They were transformed into the desired indanylindane **2** by the reductive double bond formation with Cu powder in toluene to give a mixture of the *cis*- and *trans*-indanylindanes **2** (48% in three steps based on the hydrazone **5**), which were separated by column chromatography (SiO_2, hexane) followed by recrystallization of the resulting mixture (cis/trans = 1/5) from hexane to give the pure *trans*-**2**. The structure of *trans*-**2** was confirmed by the ^1H and ^{13}C NMR, mass spectra, and X-ray crystal analysis.

The corresponding cis isomers of the *trans*-**1** and **2** were isolated by irradiation ($\lambda = 365$ nm) of the benzene solution of the trans isomer, followed by recrystallization of the resulting

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(1) Photoswitchable host molecules, part 2. For part 1, see: Shimasaki, T.; Kato, S.; Ideta, K.; Goto, K.; Shinmyozu, T. *J. Org. Chem.* **2007**, *72*, 1073−1087.

(2) For *trans*-**1**, see: (a) Lenoir, D.; Lemmen, P. *Chem. Ber.* **1980**, *113*, 3112−3119. (b) Yeung, L. L.; Yip, Y. C.; Luh, T.-Y. *J. Org. Chem.* **1990**, *55*, 1874−1881. (c) Ogawa, K.; Harada, J.; Tomoda, S. *Acta Crystallogr., Sect. B* **1995**, *B51*, 240−248.

(3) For *cis*-**1**, see: Lenoir, D.; Lemmen, P. *Chem. Ber.* **1984**, *117*, 2300−2313.

(4) For reviews of McMurry coupling reactions, see: (a) McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513−1524. (b) McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405−411.

(5) (a) Barton, D. H. R.; Willis, B. J. *J. Chem. Soc., Chem. Commun.* **1970**, 1225−1226. (b) Barton, D. H. R.; Smith, E. H.; Willis, B. J. *J. Chem. Soc., Chem. Commun.* **1970**, 1226. (c) Barton, D. H. R.; Willis, B. J. *J. Chem. Soc., Perkin Trans. 1* **1972**, 305−310.

(6) (a) Buster, J.; Wassenaar, S.; Kellogg, R. M. *J. Org. Chem.* **1972**, *37*, 4045−4060. (b) Kellogg, R. M. *Tetrahedron* **1976**, *32*, 2165−2184.

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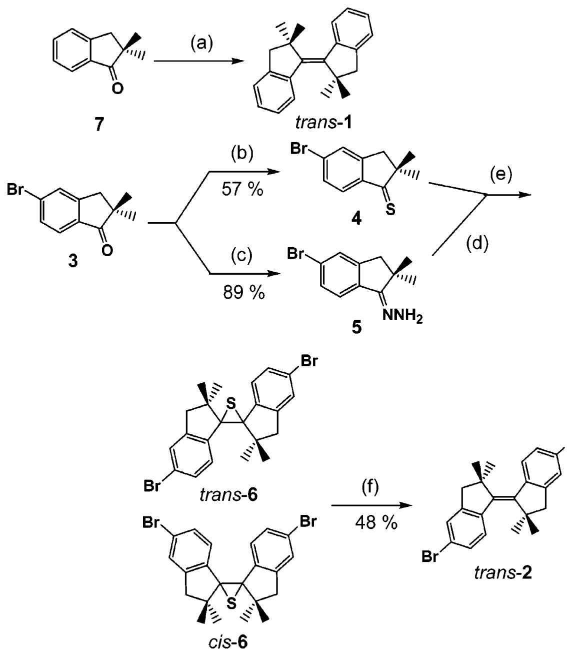
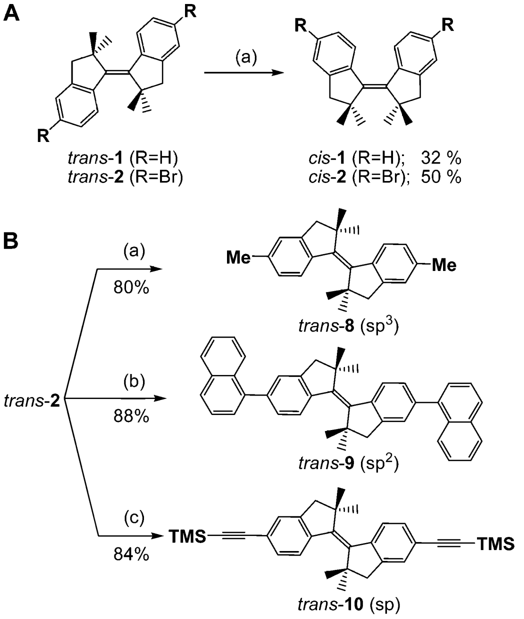
SCHEME 1. Synthesis of Tetramethylindanylindane 1 and Dibromotetramethylindanylindane 2[a]



[a] (a) TiCl$_4$, Zn powder, THF, reflux, 52%; (b) Lawesson's reagent, toluene, reflux, 57%; (c) NH$_2$NH$_2$·H$_2$O, CH$_2$Cl$_2$, reflux, 89%; (d) MgSO$_4$, Ag$_2$O, saturated KOH in methanol, −25 °C; (e) **5**, CH$_2$Cl$_2$, −25 °C to room temperature; (f) Cu powder, toluene, reflux, 48% based on compound **5** (three steps).

SCHEME 2. Preparation of *cis*-Indanylindanes 1 and 2 (A)[a]



[a] (a) $\lambda = 365$ nm, benzene, room temperature, 1 h, then recrystallization from CH$_2$Cl$_2$/hexane, 32% (*cis*-**1**) or 50% (*cis*-**2**). (B) (a) ^{n}BuLi, THF, MeI, −78 °C to room temperature, 80%; (b) 1-naphthyl boronic acid, toluene, saturated Na$_2$CO$_3$ aq, Pd(PPh$_3$)$_4$ (20 mol %), reflux, 88%; (c) TMS acetylene, NEt$_3$, Pd(PPh$_3$)$_4$, CuI, reflux, 84%.

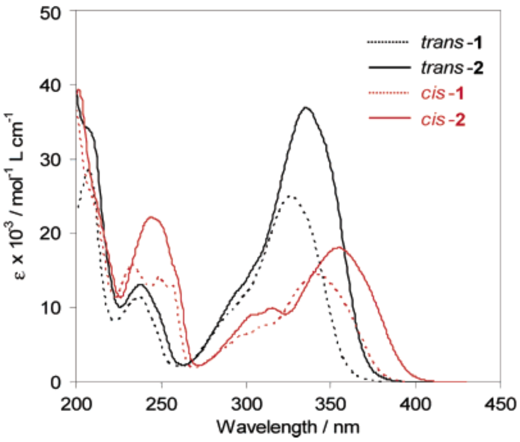


FIGURE 1. UV−vis absorption spectra of *trans*-**1** (dotted black line), *trans*-**2**, (black l line), *cis*-**1** (dotted red line), and *cis*-**2** (red line) in CH$_3$CN at 23 °C.

cis−trans mixture from hexane as colorless crystals (*cis*-**1**: 32% from *trans*-**1**; *cis*-**2**: 50% from *trans*-**2**) (Scheme 2A). Their structures were confirmed by the spectral properties and X-ray crystal structural analysis. Modifications of the *trans*-tetramethylindanylindane core by replacing the bromine atoms of *trans*-**2** with methyl, 1-naphthyl, and ethynyl groups were successfully accomplished (Scheme 2B). The lithiated *trans*-indanylindane was treated with MeI in THF to give *trans*-5,17-dimethylindanylindane (*trans*-**8**) (80%). 1-Naphthyl groups were introduced at the 5,16-positions of *trans*-**2** by the Suzuki−Miyaura coupling via boronic acids to give *trans*-5,26-bis(1-naphthyl)indanylindane (*trans*-**9**) (88%). The Sonogashira coupling of *trans*-**2** with TMS acetylene smoothly proceeded under reflux conditions in NEt$_3$ to give *trans*-5,21-bis(trimethylsilylethynyl)-indanylindane (*trans*-**10**) (84%). Thus, the bromine-substituted *trans*-tetramethylindanylindane **2** was confirmed to be a versatile synthetic intermediate for the synthesis of new photoswitchable molecules having the tetramethylindanylindane core.

The crystal and calculated structural data of several indanylindane analogues were summarized (Table S3). The crystal structure of *trans*-**1** has already been reported by Ogawa et al.[2c] The crystal structure of *trans*-**2** was determined by X-ray diffraction at −160 °C (Figure S1) along with that of *trans*-**1** as a reference (Figure S2). There were two molecules (A and B) lying at inversion centers in the unit cell in both cases. Structure A in the ORTEP drawings of *trans*-**2** was expected to be more stable than structure B by 3.25 kcal/mol on the basis of DFT calculations (B3LYP/6-311+G** level of theory), while a much smaller energy difference (0.30 kcal/mol) was expected for *trans*-**1**. The ethylene double bond length of *trans*-**2** was comparable to that of *trans*-**1**, whereas the twist of the double bond of *trans*-**2** was slightly more significant than that of *trans*-**1**. The average twist angle of the phenyl rings of A and B (>A−B) of the two structures of *trans*-**2** was smaller than that of *trans*-**1** (Figure S3). Crystal structures of *cis*-**1** and **2** were also determined by X-ray diffraction at −160 °C (Figure S4). The ethylene double bond length of *cis*-**1** was almost the same as that of *trans*-**1**, while it was more twisted than that of *trans*-**1** (ca. 4°). The C═C bond length of *cis*-**2** was slightly longer than that of *cis*-**1** and *trans*-**2** (0.008 Å), while the dihedral angle around the C═C double bond of *cis*-**2** was comparable to that of *cis*-**1** but was larger than those of *trans*-**2** (ca. 3°). The twist angle between the phenyl rings of A and B of *cis*-**1** was larger than that of *cis*-**2** (ca. 12°). The crystal structure of *trans*-**8** has almost the same bond lengths and angles around the C═C bond compared to those of *trans*-**1** (Figures S5−S7, Table S3). In *trans*-**9**, a little bit longer bond length but smaller twist angle around the C═C bond were observed (Figures S8 and S9).

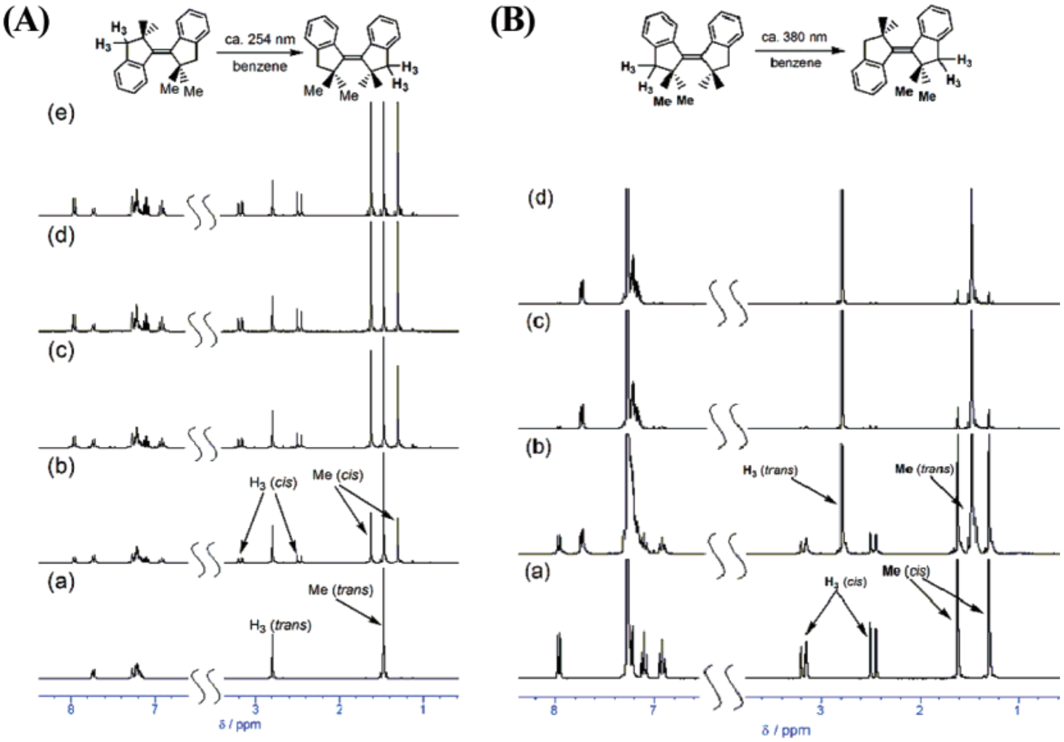


FIGURE 2. (A) ^{1}H NMR spectra of the photoisomerization of *trans*-**1** to *cis*-**1** upon irradiation of ca. 254-nm light in benzene-d_6: (a) 0 min (pure *trans*-**1**), (b) 10 min, (c) 20 min, (d) 40 min, and (e) 60 min [*trans*-**1**/*cis*-**1** = 29/71 (photostationary state)]. (B) ^{1}H NMR spectra of the photoisomerization of *cis*-**1** to *trans*-**1** upon irradiation of ca. 380-nm light in benzene-d_6: (a) 0 min (pure *cis*-**1**), (b) 10 min, (c) 20 min, and (d) 30 min [*trans*-**1**/*cis*-**1** = 97/3 (photostationary state)].

The UV/vis spectra of *cis*- and *trans*-**1** and **2** were measured in CH_3CN at 23 °C (Figure 1). The longest absorption bands (λ_{max}) of *trans*-**1** and **2** appeared at ca. 326 (ϵ 27 400) and 339 nm (ϵ 32 950), respectively, while the λ_{max} of *cis*-**1** (340 nm, ϵ 14 600) appeared in a longer wavelength region as compared to that of *trans*-**1**. A similar red shift was observed in the absorption spectrum of *cis*-**2**, probably due to the more twisted C═C bond of the cis isomer.[7] The DFT (B3LYP) calculations predicted an increase in the HOMO level but a decrease of the LUMO level in the cis isomer and supported the red shift of the cis isomer (Figure S38). The calculated spectra obtained by the time-dependent (TD) DFT method[8,9] at the B3LYP/6-31G* level predicted that the difference of excitation energy between *trans*-**1** and *cis*-**1** was 0.20 eV, which corresponded to ca. 18 nm (excitation energies: *trans*-**1**, 3.77 eV = 330 nm; *cis*-**1**, 3.57 eV = 348 nm). This agreed well with the difference in the λ_{max}'s of the observed spectra (14 nm). Similarly, the observed red shift (19 nm) of the λ_{max} of *cis*-**2** compared to that of *trans*-**2** was in good agreement with the calculated value of 20 nm (excitation energy: *trans*-**2**, 3.61 eV = 343 nm; *cis*-**2**, 3.41 eV = 363 nm). The observed intensity ratio between *cis*-**2** and *trans*-**2** was 0.49, which was comparable to that of the calculated oscillator strengths (0.54). These data indicated the good reproducibility of the UV/vis spectra by TDDFT at the B3LYP/6-31G* level of theory. The assignments of the UV/vis spectra of *trans*- and *cis*-**2** are summarized (Table S13).

The fluorescence spectrum of *trans*-**1** was an almost mirror image of the absorption spectrum, and the Stokes shift and quantum yield (Φ_f) were 12 nm and <0.001, respectively (Figure S40), whereas that of *cis*-**1** appeared in a longer wavelength region and it was more complicated than that of trans isomer.[10] A similar phenomenon was observed in the fluorescence spectrum of *trans*- and *cis*-**2**, and all UV−vis and fluorescence data were summarized (Tables S16 and S17).

The photochemical isomerization process of **1** was examined. The deoxygenated benzene-d_6 solution of *trans*-**1** was irradiated with a sterilizing lamp (λ = 254 nm) in a quartz NMR tube at 23 °C, and the reaction was monitored by the ^{1}H NMR spectra, and the trans/cis ratio was determined by the integral intensities of the benzylic proton signal (H_3) of the indanylindane moiety (Figure 2A). The reaction reached the photostationary state after a 60 min of irradiation with the trans/cis ratio of 29/71. The reverse photochemical isomerization was also examined (Figure 2B). The deoxygenated benzene-d_6 solution of *cis*-**1** was irradiated with an ultrahigh-pressure Hg lamp (λ = ca. 380 nm) in a Pyrex NMR tube at 23 °C. The reaction reached the photostationary state after 30 min of irradiation with the trans/cis ratio of 97/3. Thus, a smooth and clean photochemical isomerization was observed in *cis*- and *trans*-2,2,2′,2′-tetramethylindanylindanes. No isomerization occurred during benzene reflux in *cis*-**1**, and this result indicated that the energy barrier for the thermal cis−trans isomerization of *cis*-**1** should be much higher than that of azobenzene.

Moreover, to check the stability of the indanylindane core to the photochemical trans/cis interconversion, resistance against photo fatigue experiments were carried out in deoxygenated

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[7] Newman, M. S. *Steric Effects in Organic Chemistry*; Wiley & Sons: New York, 1956; Chapter 11.

[8] Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J. *J. Chem. Phys.* **1998**, *109*, 8218−8224.

[9] (a) Dierksen, M.; Grimme, S. *J. Phys. Chem. A* **2004**, *108*, 10225−10237. (b) Improta, R.; Santoro, F. *J. Phys. Chem. A* **2005**, *109*, 10058−10067. (c) Clark, A. E. *J. Phys. Chem. A* **2006**, *110*, 3790−3796.

[10] Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Sausalito, CA, 1991; p 113.

CH_3CN solution and monitored by the UV spectra. As a result, no decrease in the band intensities could be observed even after 30 times switching operations, and this indicated that the system **1** has good resistance against photo fatigue.

As described above, pure *cis*-**1** and **2** were isolated for the first time, and their structural, photophysical, and photoswitchable properties were examined in detail and compared to the corresponding trans isomers. The crystal structures of the *cis*- and *trans*-tetramethylindanylindanes indicated that the cis isomers had almost similar C═C bond lengths but more twisted bond angles around the C═C bonds relative to those of the trans isomers. The λ_{max} (stilbene band) of the UV/vis spectrum of the cis isomer appeared in a longer wavelength region compared to that of the corresponding trans isomer. A clean trans−cis and cis−trans photochemical isomerization was observed for the parent **1** in benzene-d_6 without decomposition. Easy introduction of methyl, aryl, and ethynyl groups at the 5,16-positions of *trans*-**1** indicated the potential to prepare derivatives with λ_{max} in the expected wavelength region.

Experimental Section

***trans*-2,2,13,13-Tetramethyl-1,12-indanylindane (*trans*-1).** *trans*-**1** was prepared (52%) according to previously reported procedures:[2a] mp 129−130 °C (lit. 129−130;[2a] 127−129 °C[2b]).

***cis*-2,2,13,13-Tetramethyl-1,12-indanylindane (*cis*-1).** The benzene (8 mL) solution of *trans*-**1** (100 mg, 348 μmol) in a Pyrex sample tube was deoxygenated with Ar bubbling for 5 min. The solution was irradiated with black light (λ = ca. 365 nm) for 60 min at 23 °C. After removal of the solvent, the residue was purified by repeated recrystallization from hexane to give the pure *cis*-**1** as colorless crystals (32.1 mg, 32%): mp 160−161 °C (lit. mp 178−180 °C);[3] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (6H, s, methyl) 1.64 (6H, s, benzyl-H_2), 2.52 (2H, d, J = 14.7 Hz, Ar−H) 3.13 (2H, d, J = 14.5 Hz, Ar−H), 6.85 (2H, t, J = 7.4 Hz, Ar−H), 7.05 (2H, t, J = 7.3 Hz, Ar−H), 7.16 (2H, d, J = 7.5 Hz, Ar−H), 7.56 (2H, d, J = 7.9 Hz, Ar−H); ^{13}C NMR (75 MHz, $CDCl_3$,) δ 26.3, 28.8, 49.9, 52.5, 124.5, 124.6, 126.7, 126.9, 143.6, 144.7, 144.9; UV (CH_3CN); λ_{max} (ϵ) 340 (14 600), 312 (7800, sh), 299 (6500, sh), 256 (13 300), 249 (14 300), 233 (15 900), 211 (24 500) nm; HRMS (FAB) m/z calcd for $C_{22}H_{24}$ 288.1878 [M$^+$], found 288.1877. Anal. Calcd for $C_{22}H_{24}$: C, 91.61; H, 8.39. Found: C, 91.42; H, 8.39.

***trans*-2,2,13,13-Tetramethyl-5,16-dibromo-1,12-indanylindane (*trans*-2).** To a toluene solution (20 mL) of 5-bromoindanone **3** (1.00 g, 4.20 mmol) was added Lawesson's reagent (1.01 g, 2.52 mmol) under an Ar atmosphere. After the mixture was refluxed for 14 h, the cooled reaction mixture was concentrated under reduced pressure, and the concentrate was purified by column chromatography on silica gel with hexane to afford 2,2-dimethyl-5-bromoindane-1-thione **4** (606 mg, 57%) as a purple oil. **4**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34 (6H, s, methyl), 3.10 (2H, s, benzyl-H_2), 7.44−7.48 (1H, m, Ar−H), 7.61−7.62 (1H, m, Ar−H), 7.77 (1H, dd, J = 0.4 and 8.1 Hz, Ar−H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.62, 29.68, 46.2, 56.8, 100.5, 126.1, 129.4, 130.4, 131.3, 143.9, 153.4; IR (neat): 1080 (C═S) cm^{-1}; HRMS (FAB) m/z calcd for $C_{11}H_{11}BrS$ 254.9843 [M$^+$], found 254.9841. Anal. Calcd for $C_{11}H_{11}BrS\cdot 0.04$hexane: C, 52.20; H, 4.51. Found C, 52.28; H, 4.45.

A mixture of the bromoindanone **3** (1.00 g, 4.20 mmol), ethanol (10 mL), and hydrazine monohydrate (1.10 g, 21.0 mmol) was refluxed for 15 h under an Ar atmosphere, and the yellow reaction mixture was allowed to cool to room temperature. After removal of the solvent, the yellow residue was extracted with CH_2Cl_2, and the combined CH_2Cl_2 extracts were concentrated under reduced pressure to give 2,2-dimethyl-5-bromoindane-1-hydrazone **5** (947 mg, 89%) as a yellow oil, which was used in the next reaction without further purification: HRMS (FAB) m/z calcd for $C_{11}H_{13}N_2{}^{79}Br$ 253.0340 [M$^+$], found: 253.0339.

To a cooled (−25 °C) mixture of the hydrazone **5** (947 mg, 3.74 mmol) and CH_2Cl_2 (8 mL), $MgSO_4$ (800 mg), Ag_2O (1.78 g, 7.48 mmol), and two drops of a saturated solution of KOH in methanol were added successively under an Ar atmosphere. After the mixture was stirred for 30 min at −25 °C, the color of the solution changed from yellow to bright red. The red solution was filtered, and the filtrate was added dropwise to the mixture of thioketone **4** (606 mg, 2.37 mmol) and CH_2Cl_2 (3 mL) until the purple color disappeared. The mixture was stirred overnight, and the reaction temperature was allowed to warm to room temperature. The reaction mixture was concentrated under reduced pressure, and the concentrate was purified by column chromatography on silica gel with hexane, followed by recrystallization from hexane to give the thiirane **6** as colorless needles as a mixture of the cis and trans isomers, which was used in the next reaction because the separation could not be achieved.

A mixture of the trans and cis isomers of the thiirane **6** was dissolved in toluene (10 mL). To the mixture was added Cu powder (3.01 mg, 47.4 mmol) under Ar, and the mixture was refluxed overnight. After removal of the solvent, the crude product was purified by column chromatography on silica gel with hexane to give **2** as a mixture (cis/trans = 1/5 based on the ^{1}H NMR), which was recrystallized from hexane to give the pure *trans*-**2** (902 mg, 48%) as colorless crystals: mp 197−198 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (12H, s, methyl), 2.51 (4H, benzyl-H_2), 7.22 (2H, d, J = 8.4 Hz, Ar−H), 7.27 (2H, s, Ar−H), 7.28 (2H, d, J = 8.1 Hz, Ar−H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.5, 27.6, 50.9, 51.6, 121.2, 127.4, 127.5, 128.1, 129.1, 141.4, 145.5, 147.4; UV (CH_3CN); λ_{max} (ϵ) 336 (36 900), 239 (12 800) nm; IR (KBr): 1060 (ν C−Br) cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{22}Br_2$ 444.0088 (M$^+$, 51%), found 444.0062 (M$^+$, 50%). Anal. Calcd for $C_{22}H_{22}Br_2$: C, 59.22; H, 4.97. Found: C, 59.10; H, 4.97.

***cis*-2,2,13,13-Tetramethyl-5,16-dibromo-1,12-indanylindane (*cis*-2).** The benzene (5 mL) solution of the pure *trans*-**2** (30.2 mg, 67.7 μmol) was deoxygenated with Ar bubbling for 5 min in a small sample tube. The solution was irradiated with black light (λ = 365 nm) for 60 min at 23 °C. The solvent was evaporated, and the product was purified by recrystallization from hexane to give the pure *cis*-**2** (15.1 mg, 50%) as colorless crystals: mp 168−169 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17 (6H, s, $-CH_3$), 1.61 (6H, s, $-CH_3$), 2.49 (2H, d, J = 15.0 Hz, benzyl-H_2), 3.10 (2H, d, J = 15.0 Hz, benzyl-H_2), 6.98 (2H, d, J = 8.1 Hz, Ar−H), 7.30 (2H, s, Ar−H), 7.36 (2H, d, J = 8.4 Hz, Ar−H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.2, 28.6, 50.2, 51.9, 120.7, 127.78, 127.89, 128.0, 142.3, 147.2, 154.8; UV (CH_3CN); λ_{max} (ϵ) 354.5 (18 100), 315.5 (10 000), 303 (9000, sh), 244.5 (22 100) nm; IR (KBr): 1064.5 (ν C−Br) cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{22}{}^{79}Br_2$ 444.0088 [M$^+$], found 444.0087. Anal. Calcd for $C_{22}H_{22}Br_2$: C, 59.22; H, 4.97. Found C, 59.35; H, 4.87. Detailed synthetic procedures for *trans*-**8**, **9**, and **10** were described in the Supporting Information.

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Supporting Information Available: Experimental (*trans*-**8**, **9**, and **10**), DFT-optimized structural properties, X-ray crystallographic analyses (*trans*-**1**, **2**, **8**, **9**, and *cis*-**1** and **2**), ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectra, coordinates of the theoretical calculations, optimized structures, calculated oscillator strengths, selected data of UV calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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