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Preparation and structural study of naphtho- and anthrocyclobutene derivatives which have extremely long C–C bonds

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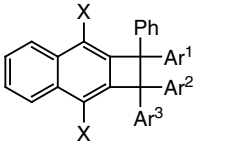
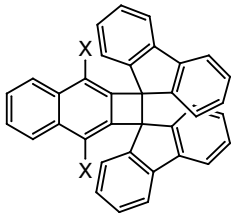
Abstract—1,1,2,2-tetraphenyl-3,8-diiodobuta[*b*]naphthalene (**1c**), 1,1,2,2-(2,2′-biphenyl)-3,8-dibromobuta[*b*]naphthalene (**2b**), 1,1,2,2-(2,2′-biphenyl)-3,8-diiodobuta[*b*]naphthalene (**2c**), and 1,1,2,2,6,6,7,7-octaphenyl-3,5,8,10-tetrachloro-4,9-dimethyldicyclobutaanthracene derivatives (**3a**–**3d**) were prepared. X-Ray analysis of **1b**, **1c**, **2c** and **3a** showed extremely long C–C bond lengths, 1.712 (5), 1.734 (5), 1.724 (5) and 1.726 (7) Å, respectively.

1. Introduction

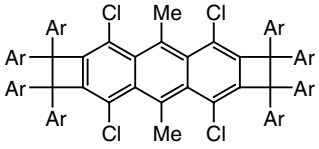
Extremely long C–C single bonds deviated from standards values have attracted a great deal of attention since they provide a new insight into the fundamental chemical bonding.[1] Recently, we have reported extremely long bond lengths, 1.720 Å in 1,1,2,2-tetraphenyl-3,8-dichlorobuta-[*b*]naphthalene (**1a**)[2] and 1.729 Å in 1,1-di-*tert*-butyl-2,2-diphenyl-3,8-dichlorocyclobuta[*b*]naphthalene (**1e**)[3]. The latter bond length is the longest which has so far been reliably determined. These extremely lengthened C–C bonds are proven to be reasonable by theoretical calculations. However, the origin of this unusual bond elongation is still unclear. Herges[4] and Siegel[5] estimated a steric repulsion among the phenyl groups on the cyclobutane ring, while Schleyer[6] estimated a π–σ–π through-bond interaction between the two phenyl groups located at the trans-positions. Here, we report the synthesis and X-ray crystal structure determination of naphthocyclobutene (**1c**), fluorenyl substituted naphthocyclobutene (**2a**–**b**) and anthrodicyclobutene derivatives (**3**). The novel crystal-to-crystal thermal cyclization reactions of tetraallene (**10**) to anthrodicyclobutene derivative (**3**) are also reported (Scheme 1).

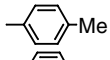


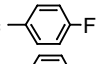
1 a: X=Cl; Ar^1=Ar^2=Ar^3=Ph
b: X=Br; Ar^1=Ar^2=Ar^3=Ph
c: X= I; Ar^1=Ar^2=Ar^3=Ph
d: X=Cl; Ar^1=Ar^3=*t*-Bu; Ar^2=Ph
e: X=Cl; Ar^1=Ph; Ar^2=Ar^3=*t*-Bu

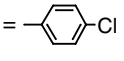


2 a: X=Br
b: X= I



3 a: Ar = Ph
b: Ar = 

c: Ar = 

d: Ar = 

2. Results and discussion

2.1. Preparation of naphthocyclobutene derivatives (1b–c and 2a–b)

1,1,2,2-tetraphenyl-3,8-dibromobuta[*b*]naphthalene (**1b**)

Keywords: 1,1,2,2-tetraphenyl-3,8-diiodobuta[*b*]naphthalene; 1,1,2,2-(2,2′-biphenyl)-3,8-dibromobuta[*b*]naphthalene; 1,1,2,2-(2,2′-biphenyl)-3,8-diiodobuta[*b*]naphthalene.

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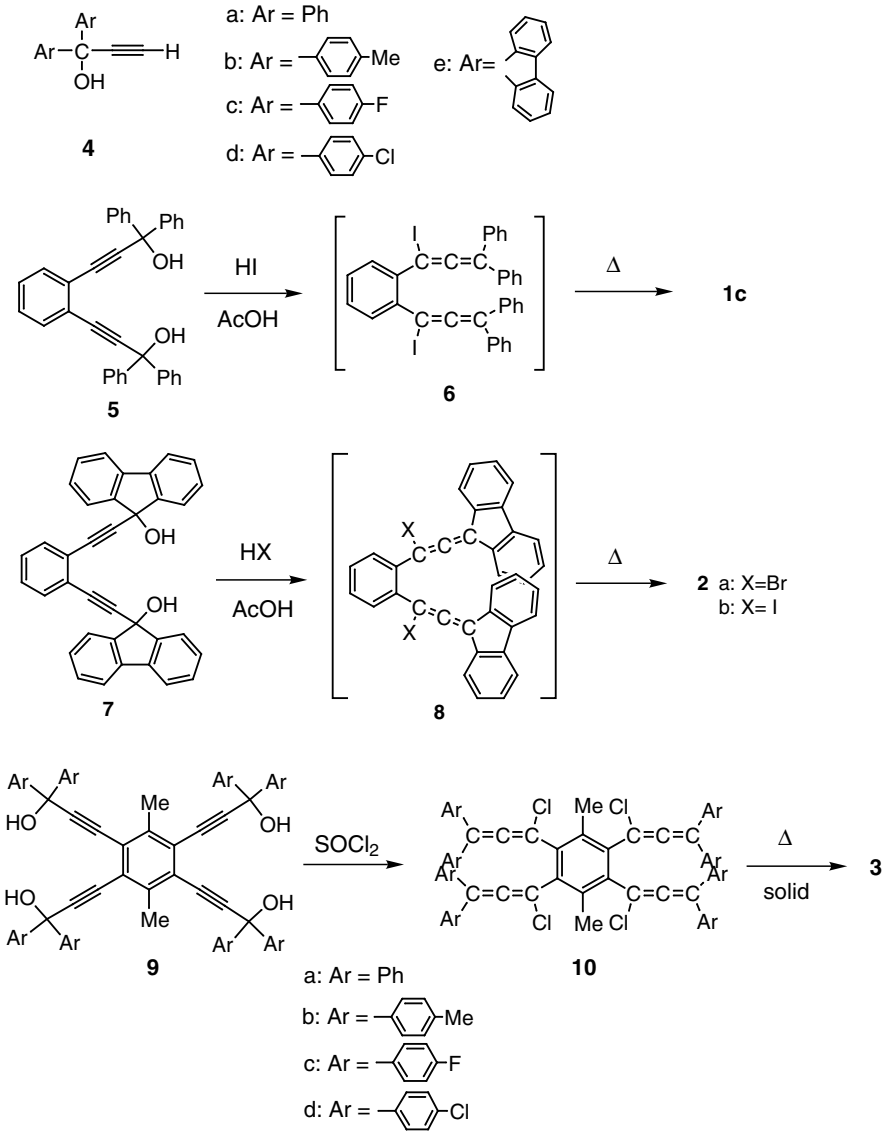

Scheme 1.

was prepared according to the previously reported method.[1] 1,1,2,2-tetraphenyl-3,8-diiodobuta[*b*]naphthalene (**1c**) was prepared by treatment of **5** with hydriodic acid in AcOH as colorless prisms. 1,1,2,2-(2,2′-Biphenyl)-3,8-dibromobuta[*b*]naphthalene (**2b**) was prepared as yellow prisms by treatment of **7** with hydrobromic acid in AcOH. The same treatment of **7** with hydriodic acid in AcOH gave 1,1,2,2-(2,2′-biphenyl)-3,8-diiodobuta[*b*]naphthalene (**2c**) as colorless prisms.

2.2. Preparation of anthrodicyclobutene (3) by thermal cyclization reactions of tetraallenes (10) in the crystalline state

Tetrakis(3-hydroxy-3,3-diaryl-1-propynyl)-*p*-xylene derivatives (**9a**–**d**) were prepared from tetrabromo-*p*-xylene and **4a**–**d** according to the previously reported method.[1] Treatment of **9a**–**d** with $SOCl_2$ gave the corresponding tetraallene derivatives (**10a**–**d**). Heating of **10a**–**d** at 140∼200°C in the solid state gave anthrodicyclobutene derivatives (**3a**–**d**). For example, when **10a** was recrystallized from THF–toluene, a 1:2 inclusion complex of **10a** and toluene was obtained as colorless prisms. Heating the colorless crystals of the 1:2 inclusion complex (**11**) at 180°C on a hot plate for 30 min gave the yellow crystals of anthrodicyclobutene derivative (**3a**) in quantitative yield. The differential scanning calorimetry (DSC) measurement of the crystal **11** showed a peak for an endothermic process at around 106°C, which is attributable to the release of toluene from the complex, and a broad peak for an exothermic process at 189°C, which is attributable to the thermal cyclization of **10a** to **3a**. When the IR spectrum of **11** was measured continuously every 15 min at 180°C, the signal at ν=1946 cm^{-1} (C═C═C) gradually decreased and finally disappeared (Fig. 1). The conversion from crystal-to-crystal was monitored through a microscope (Fig. 2). Similarly, **3b**∼**3d** were obtained in quantitative yields upon heating of **10b**∼**10d** on a hot plate.

2.3. Crystal structures of 1b, 1c, 2b, 10a in 11, and 3a in 12

The structures of dibromo and diiode derivatives of

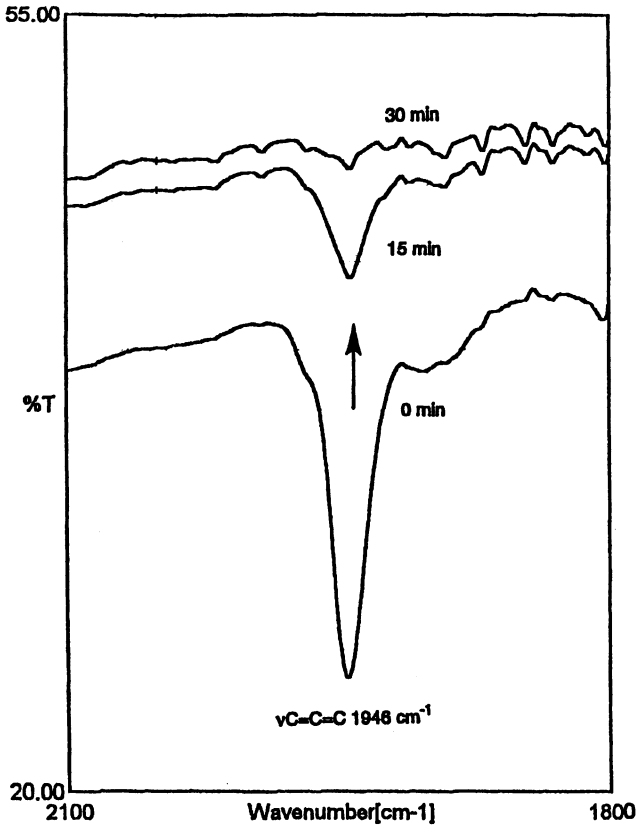

Figure 1. IR spectral changes of tetraallene (**11**) upon heating at 180°C in the solid state.

naphthocyclobutene were determined in order to investigate the effects of the substituents to the elongation of the C–C bonds. The crystal structures of **1b** and **1c** are essentially the same as that of the dichloro compounds **1a**[2,5], all of which belong to the space group of No. 14. Figs. 3 and 4 show the molecular structures for **1b** and **1c**, respectively. The bond lengths between C1 and C2 are found to be 1.712 (5) Å for **1b** and 1.734 (5) Å for **1c**. These bond lengths are extremely long being comparable to that found for **1a** (1.720 (4) Å at room temperature).[2] As is the case for **1a**, the temperature factors of C1 and C2 for **1b** and **1c** are quite normal and there is no possibility of disorder. There seems a tendency that the C–C bond length for the diiodo derivative (**1c**) is longer than that for **1a**, whereas it is shorter for the dibromo derivative (**1b**). It would be attributed to the difference in the deformation of the cyclobutene rings from the molecular plane of naphthalene. For **1c**, the cyclobutene ring takes a gauche-type deviation as shown in Fig. 4b, whereas the conformation for **1b** is an eclipsed-type (Fig. 3b), which makes the C–C bond length of **1b** a little shorter than that of **1a**. Nevertheless, it has been elucidated that these are the remarkable group of the compounds having the longest C–C bonds. For these compounds, the steric crowding due to the four phenyl groups would be the most important factor for the elongation of the C–C bond. The C–C bond lengths of the cyclobutene derivatives with fewer phenyl groups are no more than1.64 Å.[5] Those found for **12**, which contains four phenyl groups on the C–C moiety, also support this conclusion (Fig. 5, C1–C2=1.723 (7) Å and C10–C11=1.730

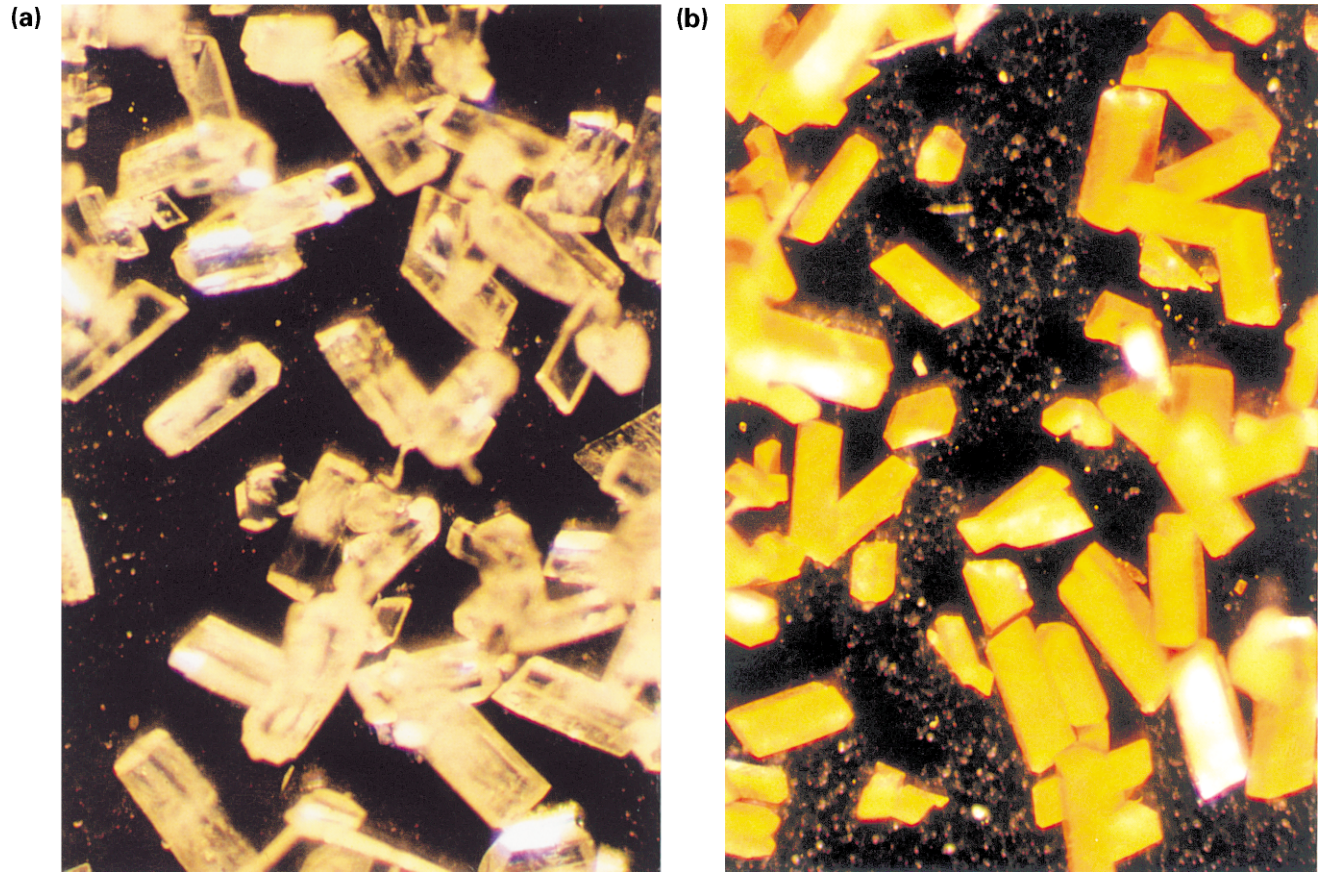

Figure 2. The thermal reaction of a crystal of **11** to a crystal of **3a** as observed through a microscope. The photos show the crystal before heating (a) and after 30 min at 180°C (b).

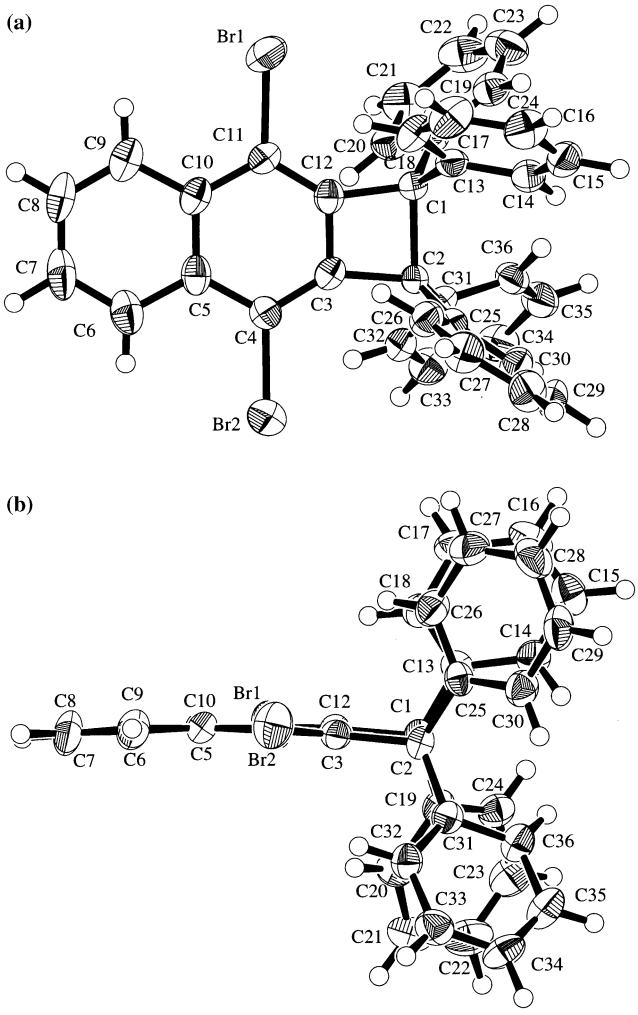

Figure 3. Molecular structure of **1b**: (a) the view from the normal of the naphthalene ring, (b) the view along the naphthalene plane.

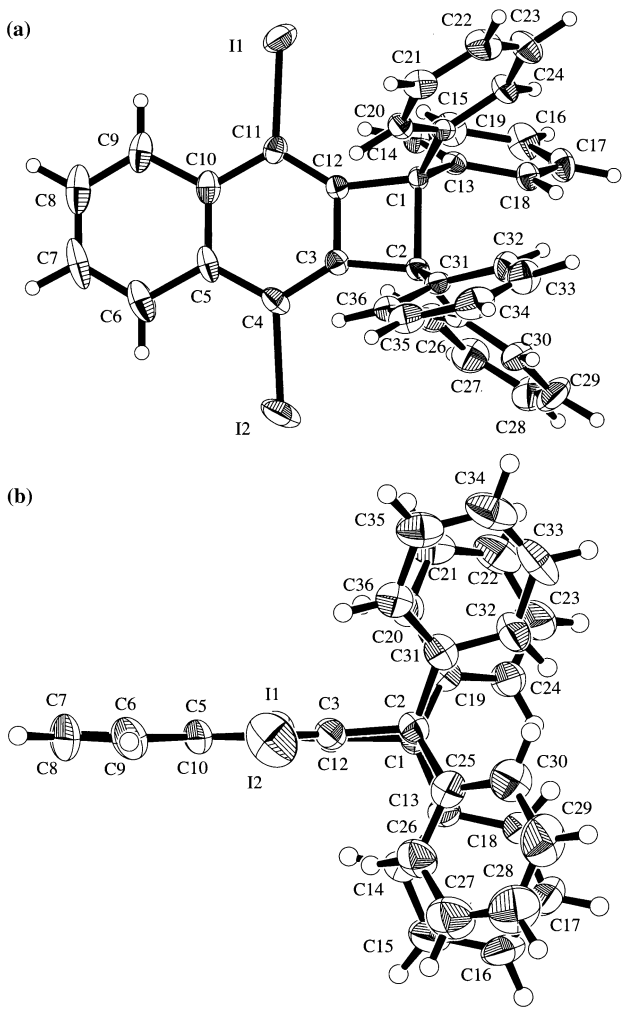

Figure 4. Molecular structure of **1c**: (a) the view from the normal of the naphthalene ring, (b) the view along the naphthalene plane.

(7) Å). Also in the case of **2b** with rigid fluorenyl groups, an extremely long C–C bond is realized (1.724 (5) Å). Interestingly, two fluorenyl groups are bowed to the opposite directions to avoid the steric hindrance (Fig. 6). The molecular structure of **10a** in the crystal **11** is shown in Fig. 7. It is interesting to note that the adjacent diphenylallene groups are completely apart from each other in the crystal. The rotation of the bulky diphenylallene groups is necessary for cyclization reaction and by heating, it would be achieved.

3. Experimental

3.1. Data and compounds

3.1.1. Preparation of 1c. Hydriodic acid (4 ml, 57 wt% in water) was added slowly to a ice-cooled solution of **5** [1] (1.0 g, 2.0 mmol) in THF–AcOH (1:2, 45 ml) and the reaction mixture was stirred for 2 h. The crude crystals formed was corrected by filtration, washed with water and air-dried. The crude crystals chromatographed on silica gel using toluene as an eluent to give pure 1c as colorless prisms (0.22 g, 15% yield). **1c**. Mp: 204–206°C. ^{1}H NMR: δ 8.33–8.30 (m, Ar, 2H), 7.71–7.68 (m, Ar, 2H), 7.00 (brs, Ph, 20H). UV ($CHCl_3$): λ_{max} (ϵ)=258 (24000), 296 (14000), 310 (18000), 324 nm (16000). Anal. Calcd for $C_{36}H_{24}I_2$: C, 60.87; H, 3.41. Found: C, 60.97; H, 3.44.

3.1.2. Preparation of 2a. A mixture of **4e** (19.2 g, 93.2 mmol), 1,2-dibromobenzene (10 g, 42.4 mmol), CuI (0.1 g), [$(Ph_3P)_2PdCl_2$] (0.6 g), PPh_3 (0.87 g), and NEt_3

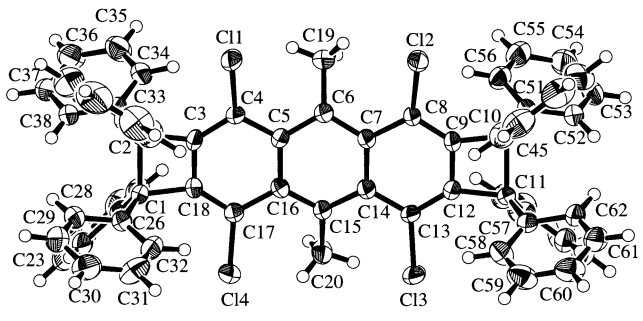

Figure 5. Molecular structure of **3a** in **12**.

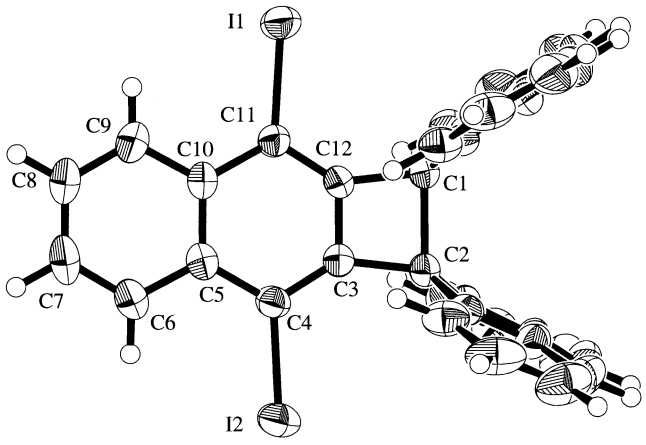

Figure 6. Molecular structure of **2b**.

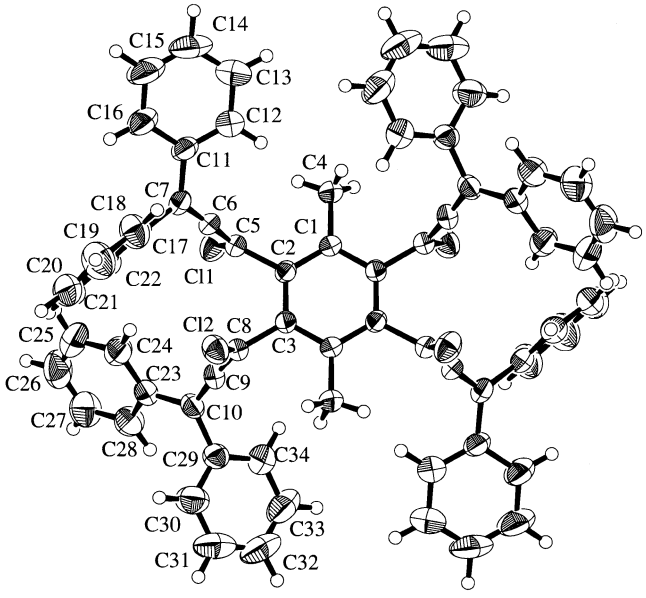

Figure 7. Molecular structure of **10a** in **11**.

(100 ml) was heated under reflux for 24 h. After filtration, the organic layer was evaporated to give, after recrystallization from toluene, **7** as colorless prisms (8.46 g, 41% yield). **7**. Mp: 220–222°C. IR (Nujol): 3302 cm^{-1}. ^{1}HNMR: δ 7.79–7.76 (m, Ar, 2H), 7.65–7.62 (m, Ar, 2H), 7.43–7.17 (brs, Ph, 20H), 3.29 (OH, 2H). UV ($CHCl_3$): λ_{max} (ϵ)=209 (11000), 212 (11000), 218 (12000), 229 (12000), 245 (52000), 272 nm (34000). Hydrobromic acid (4 ml, 48 wt% in water) was added slowly to an ice-cooled solution of 7 (1.0 g, 2.1 mmol) in THF–AcOH (1:2, 45 ml) and the reaction mixture was stirred for 2 h. The crude crystals formed was corrected by filtration, washed with water and air-dried. The crude crystals chromatographed on silica gel using toluene–hexane (1:1) as an eluent to give pure **2a** as yellow prisms (0.004 g, 0.3% yield). **2a**. Mp: 293–295°C. ^{1}HNMR: δ 8.37–8.34 (m, Ar, 2H), 7.74–7.71 (m, Ar, 2H), 7.44–7.00 (m, Ar, 18H). UV ($CHCl_3$): λ_{max} (ϵ)=209 (25000), 215 (26000), 232 (21000), 243 (54000), 274 (47000), 382 nm (3600). Anal. Calcd for $C_{36}H_{20}Br_2$: C, 70.61; H, 3.29. Found: C, 70.50; H, 3.34.

Hydriodic acid (4 ml, 57 wt% in water) was added slowly to an ice-cooled solution of **7** (1.0 g, 2.1 mmol) in THF–AcOH (1:2, 45 ml) and the reaction mixture was stirred for 2 h. The crude crystals formed was corrected by filtration, washed with water and air-dried. The crude crystals chromatographed on silica gel using toluene–hexane (1:1) as an eluent to give pure **2c** as colorless prisms (0.02 g, 1.4% yield). **2c**. Mp: 223–225°C. ^{1}HNMR: δ 8.20–8.16 (m, Ar, 2H), 7.71–7.67 (m, Ar, 2H), 7.7–6.99 (m, Ar, 18H). UV ($CHCl_3$): λ_{max} (ϵ)=234 (24000), 246 (110000), 286 (25000), 321 nm (11000). Anal. Calcd for $C_{36}H_{20}I_2$: C, 60.47; H, 3.55. Found: C, 60.41; H, 3.55.

3.1.3. Preparation of 10a. The tetraallene **10a** was prepared by the previously reported method[1]. Recrystallization of **10a** from THF–toluene gave a 1:2 inclusion complex (**11**) as colorless prisms. **11**. Mp: not clear. IR (Nujol): 1946 cm^{-1}. Anal. Calcd for $C_{82}H_{62}Cl_4$: C, 82.82; H, 5.26. Found: C, 82.52; H, 5.31.

3.1.4. Preparation of 10b. A mixture of **4b** (15.0 g, 63 mmol), 1,2,4,5-tetrabromo-*p*-xylene (5 g, 12 mmol), CuI (0.1 g), $[(Ph_3P)_2PdCl_2]$ (0.8 g), PPh_3 (0.6 g), and NEt_3 (300 ml) was heated under reflux for 24 h. After filtration, the organic layer was evaporated to give, after recrystallization from toluene, tetrakis(3-hydroxy-3,3-di-*p*-tolyl-1-propynyl)-*p*-xylene (**9b**) as colorless prisms (7.75 g, 58% yield). **9b**. Mp: 263–265°C. IR (Nujol): 3507 m^{-1}(OH). ^{1}HNMR: δ 2.30 (s, Me, 24H), 2.60 (s, Me, 6H), 3.02 (s, OH, 4H), 7.0–7.46 (m, Ar, 32H). Anal. Calcd for $C_{76}H_{66}O_4$: C, 87.49; H, 6.38. Found: C, 87.35; H, 6.38. After a solution of **9b** (1.0 g, 0.97 mmol), pyridine (0.64 ml), and $SOCl_2$ (0.72 ml) in THF (50 ml) had been stirred at room temperature for 1 h, the solution was extracted with ether. The ether solution was worked up by the usual method to give **10b** as colorless needles (1.05 g, 98% yield). **10b**. Mp: not clear. IR (Nujol): 1943 m^{-1}(C=C=C). ^{1}H NMR: δ 2.35 (s, Me, 24H), 2.51 (s, Me, 6H), 7.14–7.47 (m, Ar, 32H). Anal. Calcd for $C_{82}H_{62}Cl_4$: C, 81.71; H, 5.59. Found: C, 81.68; H, 5.91.

3.1.5. Preparation of 10c. A mixture of **4c** (15.5 g, 63 mmol), 1,2,4,5-tetrabromo-*p*-xylene (5 g, 12 mmol), CuI (0.1 g), $[(Ph_3P)_2PdCl_2]$ (0.8 g), PPh_3 (0.6 g), and NEt_3 (300 ml) was heated under reflux for 24 h. After filtration, the organic layer was evaporated to give, after recrystallization from toluene, tetrakis(3-hydroxy-3,3-di-*p*-fluorophenyl-1-propynyl)-*p*-xylene (**9c**) as 1:2 toluene complex (colorless prisms, 6.80 g, 50% yield). **9c**. Mp: 178–180°C. IR (Nujol): 3275 cm^{-1} (OH). ^{1}HNMR: δ 2.42 (s, Me, 6H), 3.67 (s, OH, 4H), 6.88–7.50 (m, Ar, 32H). Anal. Calcd for $C_{82}H_{58}F_8O_4$: C, 75.97; H, 3.94. Found: C, 75.24; H, 4.22. After a solution of **9c** (1.0 g, 0.93 mmol), pyridine (0.6 ml), and $SOCl_2$ (0.69 ml) in THF (50 ml) had been stirred at room temperature for 1 h, the solution was extracted with ether. The ether solution was worked up by the usual method to give **10c** as colorless prisms (0.96 g, 90% yield). **10c**. Mp: not clear. IR (Nujol): 1948 cm^{-1} (C=C=C). ^{1}HNMR: δ 2.43 (s, Me, 6H), 7.00–7.39 (m, Ar, 32H). Anal. Calcd for $C_{68}H_{38}Cl_4F_8$: C, 71.09; H, 3.33. Found: C, 70.91; H, 3.28.

3.1.6. Preparation of 10d. A mixture of **4d** (17.6 g, 64 mmol), 1,2,4,5-tetrabromo-*p*-xylene (5 g, 12 mmol),

CuI (0.1 g), [$(Ph_3P)_2PdCl_2$] (0.8 g), PPh_3 (0.6 g), and NEt_3 (300 ml) was heated under reflux for 24 h. After filtration, the organic layer was evaporated to give, after recrystallization from THF, tetrakis(3-hydroxy-3,3-di-*p*-chlorophenyl-1-propynyl)-*p*-xylene (**9d**) as colorless prisms (9.5 g, 62% yield). **9d**. Mp: >300°C. IR (Nujol): 3232 cm^{-1} (OH). ^{1}HNMR: δ 2.46 (s, Me, 6H), 3.67 (s, OH, 4H), 7.2–7.45 (m, Ar, 32H). Anal. Calcd for $C_{68}H_{43}Cl_8O_4$: C, 67.68; H, 3.51. Found: C, 67.54; H, 3.58. After a solution of **9d** (1.0 g, 0.83 mmol), pyridine (0.6 ml), and $SOCl_2$ (0.72 ml) in THF (50 ml) had been stirred at room temperature for 1 h, the solution was extracted with ether. The ether solution was worked up by the usual method to give **10d** as colorless needles (0.96 g, 90% yield). **10d**. Mp: not clear. IR (Nujol): 1942 cm^{-1}(C=C=C). ^{1}HNMR: δ 2.40 (s, Me, 6H), 7.26–7.48 (m, Ar, 32H). Anal. Calcd for $C_{68}H_{38}Cl_{12}$: C, 63.78; H, 2.99. Found: C, 63.96; H, 3.27.

3.1.7. Preparation of 3a. Compound **11** (0.5 g) was heated in the crystalline state at 180°C on a hot plate for 30 min to give **3a**[1] (0.42 g, 100% yield) as yellow prisms. **3a**. Mp: >300°C. ^{1}HNMR: δ 3.31 (s, Me, 6H), 7.0 (brs, Ph, 40H). UV ($CHCl_3$): λ_{max} (ϵ)=237 (81000), 297 (53000), 398 (2200), 425 (2900), 451 nm (3100). Recrystallization of **3a** from toluene gave a 1:2 inclusion complex (**12**) of **3a** and toluene as yellow prisms. Anal. Calcd for $C_{82}H_{62}Cl_4$: C, 82.82; H, 5.26. Found: C, 82.91; H, 5.34.

3.1.8. Preparation of 3b. Compound **10b** (0.2 g) was heated in the crystalline state at 180°C on a hot plate for 30 min to give **3b** (0.2 g, 100% yield) as yellow prisms. **3b**. Mp: >300°C. ^{1}HNMR: δ 2.22 (s, Me, 24H), 3.28 (s, Me, 6H), 6.80 (d, J=9 Hz, Ar, 16H), 6.90 (d, J=9 Hz, Ar, 16H). UV ($CHCl_3$): λ_{max} (ϵ)=361 (45000), 397 (9800), 424 (10000), 451 nm (9300). Anal. Calcd for $C_{76}H_{62}Cl_4$: C, 81.71; H, 5.59. Found: C, 81.57; H, 5.97.

3.1.9. Preparation of 3c. Compound **10c** (0.2 g) was heated in the crystalline state at 180°C on a hot plate for 30 min to give **3c** (0.2 g, 100% yield) as yellow prisms. **3c**. Mp: >300°C. ^{1}HNMR: δ 3.29 (s, Me, 6H), 6.7 (m, Ar, 16H), 6.9 (m, Ar, 16H). UV ($CHCl_3$): λ_{max} (ϵ)=245 (32000), 303 (51000), 375 (3000), 402 (5500), 426 (5500), 452 nm (5500). Anal. Calcd for $C_{68}H_{38}Cl_4F_8$: C, 71.09; H, 3.33. Found: C, 71.12; H, 3.51.

3.1.10. Preparation of 3d. Compound **10d** (0.2 g) was heated in the crystalline state at 180°C on a hot plate for 30 min to give **3d** (0.2 g, 100% yield) as yellow prisms. **3d**. Mp: >300°C. ^{1}HNMR: δ 3.28 (s, Me, 6H), 6.90 (d, J=6 Hz, Ar, 16H), 7.05 (d, J=6 Hz, Ar, 16H). UV ($CHCl_3$): λ_{max} (ϵ)=281 (51000), 376 (6700), 402 (7500), 427 (9500), 453 nm (9400). Anal. Calcd for $C_{68}H_{38}Cl_{12}$: C, 63.78; H, 2.99. Found: C, 63.90; H, 3.18.

3.1.11. Crystal data for 1b. $C_{36}H_{24}Br_2$, M=616.39, monoclinic, $P2_1/n$ (No. 14), a=9.000 (4), b=17.027 (4), c=17.680 (4) Å, β=96.29 (3)°, V=2692 (1) Å^3, Z=4, D_c=1.52 g cm^{-3}, μ(MoKα)=30.43 cm^{-1}. The final R indices: $R(F)$=0.040 based on 2919 reflections ($I>2\sigma(I)$), $wR(F^2)$=0.122 based on 6173 observed reflections (all data) and 368 parameters, GOF=1.05.

3.1.12. Crystal data for 1c. $C_{36}H_{24}I_2$, M=710.39, monoclinic, $P2_1/c$ (No. 14), a=16.332 (3), b=9.217 (5), c=19.212 (2) Å, β=94.45 (1)°, V=2883 (1) Å^3, Z=4, D_c=1.64 g cm^{-3}, μ(MoKα)=22.05 cm^{-1}. The final R indices: $R(F)$=0.040 based on 3648 reflections ($I>2\sigma(I)$, $wR(F^2)$=0.089 based on 6614 observed reflections (all data) and 343 parameters, GOF=1.35.

3.1.13. Crystal data for 2b. $C_{40}H_{28}I_2O_2$, M=794.47, triclinic, $P_{\bar{1}}$ (No. 2), a=12.647 (3), b=13.121 (2), c=10.853 (2) Å, α=93.29 (2)°, β=114.47 (2)°, γ=83.10 (2)°, V=1627.3 (6) Å^3, Z=2, D_c=1.62 g cm^{-3}, μ(MoKα)=19.67 cm^{-1}. The final R indices: $R(F)$=0.033 based on 4853 reflections ($I>2\sigma(I)$, $wR(F^2)$=0.105 based on 7465 observed reflections (all data) and 374 parameters, GOF=1.15.

3.1.14. Crystal data for 11. $C_{82}H_{62}Cl_4$, M=1189.20, triclinic, $P_{\bar{1}}$ (No. 2), a=12.180 (3), b=14.293 (2), c=10.628 (2) Å, α=110.10 (1)°, β=110.25 (2)°, γ=84.69 (2)° V=1629.5 (6) Å^3, Z=1, D_c=1.21 g cm^{-3}, $D_{m=}$1.19 g cm^{-3}, μ(MoKα)=2.26 cm^{-1}. The final R indices: $R(F)$=0.052 based on 4245 reflections ($I>2\sigma(I)$, $wR(F^2)$=0.166 based on 7491 observed reflections (all data) and 365 parameters, GOF=1.34.

3.1.15. Crystal data for 12. $C_{82}H_{62}Cl_4$, M=1189.20, triclinic, $P_{\bar{1}}$ (No. 2), a=17.949 (5), b=21.057 (2), c=9.038 (2) Å, α=94.20 (2)°, β=98.70 (2)°, γ=69.46 (2)°V=3161 (1) Å^3, Z=2, D_c=1.25 g cm^{-3}, μ(MoKα)=2.33 cm^{-1}. The final R indices: $R(F)$=0.093 based on 7467 reflections ($I>2\sigma(I)$), $wR(F^2)$=0.245 based on 14538 observed reflections (all data) and 675 parameters, GOF=3.16.

The diffraction data for all crystals were collected on a Rigaku AFC-7R four-circle diffractometer with graphite monochromated MoKα radiation (λ=0.71073 Å) to 2θ=55°. Non-hydrogen atoms except for solvated toluene molecules for **11** and **12** were refined anisotropically and hydrogen atoms were included but not refined. The solvated toluene molecules were found to be disordered: They were refined isotropically being located on two disordered positions for **11**, but the disorder is so serious for **12** that the molecules were treated as rigid groups. Though the quality of the analysis for **12** is not entirely satisfied because of the disorder, the molecular structure would give useful information. Full crystallographic detail excluding structure factor tables have been deposited at the Cambridge Crystallographic Data Center (CCDC). All calculations were performed using the teXsan crystallographic software package.[7]

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