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Syntheses and Some Properties of 9,2′:7′,9″-, 9,2′:9′,9″-, and 9,4′:9′,9″-Terfluorene

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Three kinds of terfluorene and 9,4′:9′,9″:4″,9‴-quaterfluorene were synthesized. The ^{1}H-NMR spectrum of 9′- and 9″-methine protons of 9,4′:9′,9″-terfluorene shows an AB spin pattern at room temperature, and that of 9,2′:9′,9″-terfluorene has an A_2 pattern. The π-π^* red shift of the UV spectra of some fulvalenes are in the order of 9,9′-bifluorenylidene, 4-(9-fluorenyl)-, and 4,4′-di(9-fluorenyl)-9,9′-bifluorenylidene. A homoconjugation effect was also observed in an alcohol series: 9-fluorenol, 4,9′-bifluoren-9-ol, and 9,4′:9′,9″-terfluoren-9′-ol.

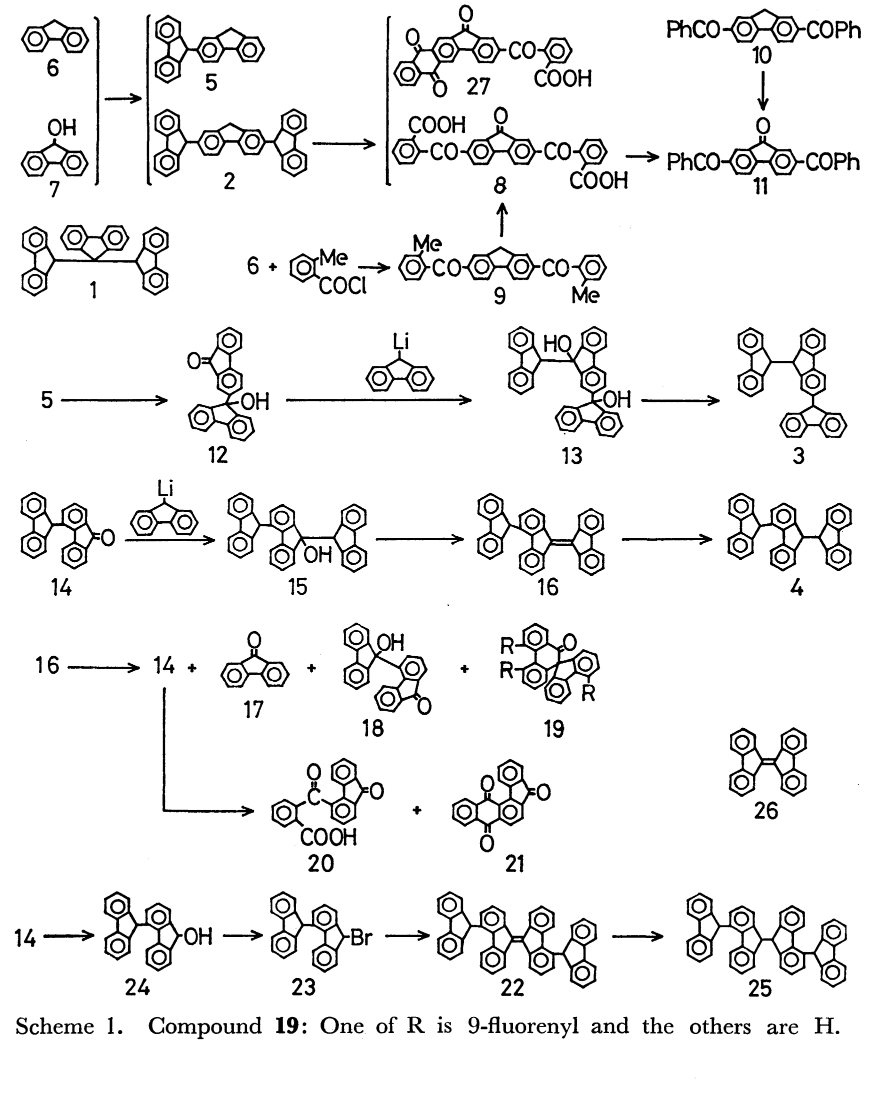
The synthesis and properties of the crowded molecule, 9,9′:9′,9″-terfluorene (**1**) have been reported in detail.[1] However, other types of terfluorenes have not been studied.

The present paper deals with the syntheses of 9,2′:7′,9″- (**2**), 9,2′:9′,9″- (**3**), and 9,4′:9′,9″-terfluorene (**4**) and also with the spectral properties of these terfluorenes in comparison with those of **1**.

Results and Discussion

Syntheses of Terfluorenes. A new terfluorene, **2** was obtained as one of by-products in the synthesis of 2,9′-bifluorene (**5**)[2] by condensation of fluorene (**6**) and 9-fluorenol (**7**). The oxidation of **2** with sodium dichromate afforded the corresponding dicarboxylic acid (**8**), which was identical with the compound obtained by oxidation of 2,7-di(*o*-toluoyl)fluorene (**9**). The oxidation of known 2,7-dibenzoylfluorene (**10**)[3] gave 2,7-dibenzoyl-9-fluorenone (**11**) derived from decarboxylation of the acid **8** (Scheme 1).

The reaction of 9-lithiofluorene with 9′-hydroxy-2,9′-bifluoren-9-one (**12**) yielded 9,2′:9′,9″-terfluorene-9,9′-diol (**13**), which was reduced to **3**. Also, the reaction of 9-lithiofluorene with 4,9′-bifluoren-9-one (**14**)[4] afforded 9,4′:9′,9″-terfluoren-9′-ol (**15**) and



Scheme 1. Compound **19**: One of R is 9-fluorenyl and the others are H.

TABLE 1. PROTON NMR SPECTRA OF SOME TERFLUORENES IN C_6D_6

Compd	Methine	Methylene	Aromatic
1	5.36(2H, s)		5.58—8.34(24H, m)
2	4.94(2H, s)	3.16(2H, s)	6.95—7.80(22H, m)
3	4.46(2H, s) 4.74(1H, s)		6.41(1H, s) 6.62—7.75(22H, m)
4	4.69(2H, q) 6.10(1H, s)		6.60—8.09(23H, m)

4-(9-fluorenyl)-9,9′-bifluorenylidene (**16**), and the latter was reduced to **4**.

Oxidative cleavage at the central 9—9′ carbon-carbon double bond on **16** gave **14**, 9-fluorenone (**17**), and 9′-hydroxy-4,9′-bifluoren-9-one (**18**),[4] and a compound (**19**) having a melting point of 332—333 °C. The structure of **19** has not been determined, but **19** should be formed through the pinacol-pinacolone rearrangement of 4-(9-fluorenyl)-9,9′-bifluorene-9,9′-diol. Further oxidation of **14** yielded the corresponding carboxylic acid **20** and an anthraquinone derivative, **21**. This suggests that the ring closure of **20** occurs at the 3-position to form **21**, but not the 5-position.

One of the quaterfluorenes, 4,4′-di(9-fluorenyl)-9,9′-bifluorenylidene (**22**), was obtained by condensation of 9-bromo-4,9′-bifluorene (**23**), which was prepared from alcohol **24**. Hydrogenation of **22** afforded hydrocarbon **25**.

Spectral Observation of Terfluorenes and Their Derivatives. Table 1 shows the ^{1}H-NMR spectral data of **2**, **3**, and **4** in comparison with that of **1**.[1] Methine protons of 9′- and 9″-positions on **3** appears at 4.46 ppm as an A_2 spin pattern. This finding suggests that the 9′- and 9″-protons of **3** are magnetically equivalent to each other, as in the case of 9,9′-bifluorene (4.61 ppm).[1] On the contrary, those of **4** are shown at 4.69 ppm as an AB quartet (J=3.6 Hz, $\Delta\nu$=6.2 Hz) at room temperature. The splitting of the methine protons may be caused by the dihedral angle between $H-C_{9'}-C_{9'}$ and $C_{9'}-C_{9''}-H$. This quartet of **4** is changed with elevation of the temperature and the spectrum at 134.5 °C was observed as an A_2 singlet.

The methine proton on the 9-position of **4** appears at a lower field than that of the 9-position of **3** and than those of the 9- and 9″-positions of **2**. The rotation around the sp^3-sp^2 C–C single bond at 9—4′ positions of **4** may be hindered because of collisions between the adjacent hydrogen atoms on the 9- and 4′-fluorene planes. Therefore, the 9-methine proton of **4** could be situated on the deshielding zone of the 9′-fluorene plane, which shifts the signal to a lower field as in the case of the 4- or 5-proton of **6**[5] and also as in the cases of the 1,8,1′, and 8′-protons of **26**.[6] Actually, the 9′-methine proton of **14** has been observed at 5.89 ppm (CCl_4).[4]

Figure 1 shows the UV spectra of **1**,[7] **2**, **3**, **4**, and **25**. The spectra of **3** and **4** are very similar to that of **1**, but are somewhat different from that of **2**. Compound **2** has no 9—9′ C–C bond and the homoconjugation effect of **2** may be expected to be larger than

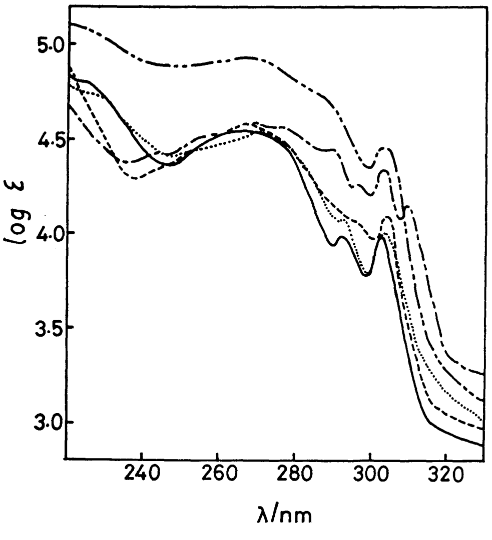


Fig. 1. UV spectra of **1** (——), **2** (———), **3** (----), **4** (······), and **25** (—·—·—).

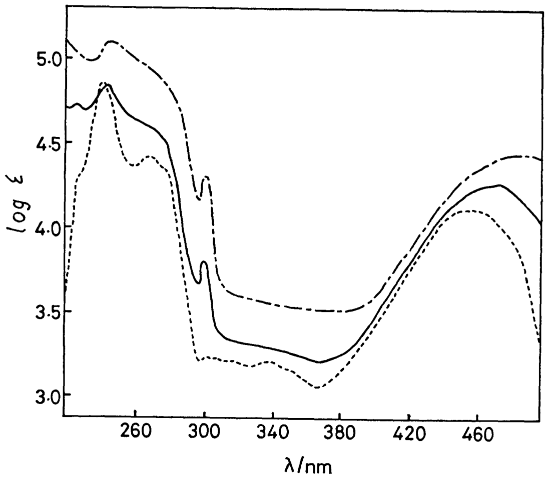


Fig. 2. UV and visible spectra of **16** (——), **22** (———), and **26** (----).

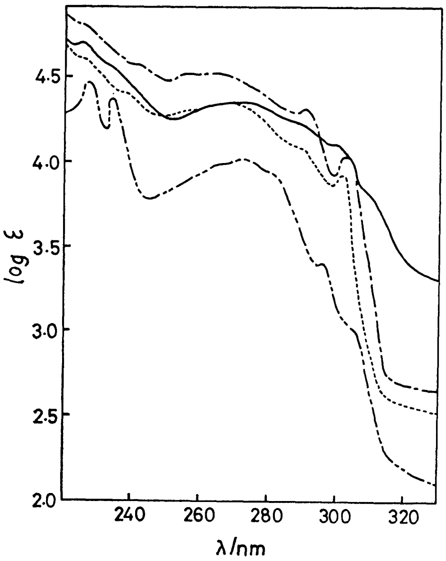


Fig. 3. UV spectra of **7** (———), **13** (——), **15** (—·—·—), and **24** (----).

that of the other terfluorenes. The spectrum of **25** suggests that the increase of absorbance is brought about by the substitution of the 9-fluorenyl group to the 4″-position of **4**, despite the fact that the coplanarity may be prevented at this position.

The UV and visible spectra of fulvalenes, **16**, **22**, and **26**[8–10] are given in Fig. 2. The π-π^* red shift and an increase of absorbance due to the central 9—9′ double bond are observed in the order of the increase of fluorene moiety: **26** (λ_{max} 455 nm, log ε 4.11); **16** (477 nm, 4.24); **22** (490 nm, 4.44). An additive property by the homoconjugation effect may also be postulated in an alcohol series, **7**, **13**, **15**, and **24**, as shown in Fig. 3.

Experimental

All the melting points are uncorrected. The UV, IR, ^{1}H-NMR, and MS spectra were obtained with a ORD/UV-5 apparatus (JASCO) in cyclohexane (scanning speed 0.76 s/nm), an IR-G spectrophotometer (JASCO) as KBr-pellets, a JNM-C60HL spectrometer (60 MHz) (JEOL), using TMS as an internal reference at 21 °C, and a RMU-6E apparatus (Hitachi) by means of a direct-inlet system, respectively.

*9,2′:7′,9″-Terfluorene (**2**).* A mixture of **6** (2.0 g) and **7** (4.0 g) in acetic acid (30 ml) was refluxed with concd sulfuric acid (0.15 ml) for 5 h. After being poured into cold water, the precipitate was collected and recrystallized from pyridine to give 0.10 g (2%) of **2**: mp 299—300 °C; NMR (C_5D_5N) δ=3.64 (2H, s), 5.27 (2H, s), and 7.15—8.10 (22H, m); MS, *m/e*, 494 (M^+), 329, and 165. Found: C, 94.54; H, 5.23%. Calcd for $C_{39}H_{26}$: C, 94.70; H, 5.30%.

The mother liquor was evaporated to dryness and the residue was recrystallized from benzene to afford 1.22 g (34%) of **5**: mp 225—226 °C (lit,[2] mp 225—226 °C).

*Structural Proof of **2**.* *a) Oxidation of **2***: An acetic acid (950 ml) solution of **2** (494 mg) was refluxed with sodium dichromate (19.0 g) for 3.5 h. Upon evaporation to dryness, the residue was extracted with aqueous alkaline and the extract was neutralized with dilute hydrochloric acid. The precipitate was collected and recrystallized from acetic acid to yield 73 mg (15%) of 2,7-bis(*o*-carboxybenzoyl)-9-fluorenone (**8**): mp 299—300 °C (dec); IR, 3420 (OH), 1715, and 1680 cm^{-1} (C=O); MS, *m/e*, 476 (M^+), 432, 388, 355, 311, and 283. Found: C, 73.23; H, 3.49%. Calcd for $C_{29}H_{16}O_7$: C, 73.11; H, 3.39%.

Additionally, 3 mg (1%) of *o*-[6,11,13-trioxo-13*H*-indeno-[1,2-*b*]anthracen-2-ylcarbonyl]benzoic acid (**27**) was isolated from the mother liquor: mp 340 °C (dec); IR, 3430 (OH), 1710, and 1670 cm^{-1} (C=O); MS, *m/e*, 458 (M^+), 414, 337, and 208. Found: C, 76.29: H, 2.70%. Calcd for $C_{29}H_{14}O_6$: C, 75.98; H, 3.08%.

*b) Synthesis and Oxidation of 2,7-Di(o-toluoyl)fluorene (**9**)*: The Friedel-Crafts reaction of **6** (1.66 g) and *o*-toluoyl chloride (3.90 g) was carried out at 120 °C in nitrobenzene (55 ml) during a period of 4 h in the presence of anhydrous aluminum chloride (3.33 g) to give 2.34 g (58%) of **9**: mp 175—176 °C (recrystallized from ethyl acetate); IR, 1650 cm^{-1} (C=O); NMR ($CDCl_3$) δ=2.36 (6H, s), 3.99 (2H, s), and 7.22—8.08 (14 H, m). Found: C, 86.65; H, 5.34%. Calcd for $C_{29}H_{22}O_2$: C, 86.54; H, 5.51%.

A solution of **9** (2.00 g) in pyridine (60 ml) was stirred with potassium permanganate (7.20 g) for 6.5 h at room temperature. The reaction mixture yielded 1.88 g (91%) of 2,7-di(*o*-toluoyl)-9-fluorenone: mp 197—199 °C; IR, 1718, 1663, and 1650 cm^{-1} (C=O); NMR ($CDCl_3$) δ=2.36 (6H, s) and 7.20—8.30 (14H, m); MS, *m/e*, 416 (M^+) and 401. Found: C, 83.44; H, 4.56%. Calcd for $C_{29}H_{20}O_3$: C, 83.63; H, 4.84%.

The foregoing fluorenone (827 mg) in benzene (80 ml) was refluxed with *N*-bromosuccinimide (2.12 g) for 1.5 h. Upon cooling, the reaction mixture was washed with water and evaporated to dryness. The residue was dissolved in acetic acid (40 ml) containing sodium dichromate (5.96 g) and refluxed for 3 h to yield 220 mg (25%) of **8**, which was identical in all respects with that obtained in a).

*c) 2,7-Dibenzoyl-9-fluorenone (**11**)*: A solution of **10** (480 mg) in pyridine (20 ml) was stirred with potassium permanganate (300 mg) at room temperature for 22 h giving 420 mg (84%) of **11**: mp 227—228 °C (recrystallized from ethyl acetate); IR, 1716 and 1648 cm^{-1} (C=O); MS, *m/e*, 388 (M^+) and 311. Found: C, 83.44; H, 4.54%. Calcd for $C_{27}H_{16}O_3$: C, 83.49; H, 4.15%.

*d) Decarboxylation of **8***: The foregoing dicarboxylic acid **8** (210 mg) was dissolved in quinoline (30 ml) and the solution was refluxed with copper bronze (200 mg) for 16 h. After cooling, the reaction mixture was filtered, then the filtrate was added to dilute hydrochloric acid and extracted with benzene. The extract was dried and chromatographed on an alumina column; 58 mg (34%) of **11** was obtained from the yellow band on the column. The compound was identical in all respects with that obtained in method c).

*Oxidation of 2,9′-Bifluorene (**5**).* Hydrocarbon **5** (3.00 g) in pyridine (150 ml) was stirred at 15—25 °C for 4 h in the presence of Triton B (40%, 0.5 ml) with gentle introduction of oxygen. The reaction mixture gave 2.83g (87%) of **12**: mp 184—185 °C; IR, 3550 (OH) and 1708 cm^{-1} (C=O); NMR ($CDCl_3$) δ=2.58 (1H, s) and 7.05—7.74 (15H, m); MS, *m/e*, 360 (M^+), 344, 315, and 180. Found: C, 86.67; H, 4.74%. Calcd for $C_{26}H_{16}O_2$: C, 86.65; H, 4.47%.

*9,2′: 9′,9″-Terfluorene-9,9′-diol (**13**).* Alcohol **12** (720 mg) in xylene (60 ml) was allowed to react with 9-lithiofluorene (prepared from 1.32 g of **6**) under reflux for 1 h to afford 231 mg (22%) of **13**: mp 195—197 °C (dec) from benzene–cyclohexane (1:1); IR, 3580 and 3450 cm^{-1} (OH); NMR ($CDCl_3$) δ=2.34 (1H, s), 2.46 (1H, s), 4.70 (1H, s), and 6.85—7.67 (23H, m); MS, *m/e*, 526 (M^+), 509, 494, and 492. Found: C, 89.23; H, 4.72%. Calcd for $C_{39}H_{26}O_2$: C, 88.95; H, 4.98%.

*9,2′: 9′,9″-Terfluorene (**3**).* Diol **13** (100 mg) was reduced with hydroiodic acid (57%, 3 ml) and red phosphorus (3 g) in acetic acid (50 ml) under reflux for 20 h, giving 65 mg (69%) of **3**: mp 214.5—216.5 °C (dec); NMR (C_5D_5N) δ=4.94 (2H, s), 5.01 (1H, s), 6.70 (1H, s), and 6.96—8.03 (22H, m); MS, *m/e*, 494 (M^+), 329, and 165. Found: C, 95.00; H, 5.12%. Calcd for $C_{39}H_{26}$: C, 94.70; H, 5.30%.

*9,4′: 9′,9″-Terfluoren-9′-ol (**15**).* To a 9-lithiofluorene solution (prepared from 1.66 g of **6** in xylene), **14** (1.73 g) in xylene (100 ml) was added for 10 min at room temperature and then the reaction mixture was stirred at 70 °C for an additional 1 h to yield 1.82 g (72%) of **15**: mp 233—235 °C (dec); IR, 3550 cm^{-1} (OH); NMR ($CDCl_3$) δ=2.57 (1H, s), 4.81 (1H, s), 5.58 (1H, s), and 6.44—8.12 (23H, m); MS, *m/e*, 510 (M^+), 494, 492, 347, and 329. Found: C, 91.95; H, 5.19%. Calcd for $C_{39}H_{26}O$: C, 91.74; H, 5.13%.

Under different conditions, the reaction mixture was refluxed for 1 h; 0.23 g (9%) of **15** and 1.52 g (62%) of **16** were isolated: mp of **16**, 272—274 °C (dec) from ethyl acetate; NMR ($CDCl_3$) δ=6.14 (1H, s) and 6.33—8.61

(23H, m); MS, *m/e*, 492 (M^+) and 330. Found: C, 94.91; H, 5.22%. Calcd for $C_{39}H_{24}$: C, 95.09; H, 4.91%.

*9,4′: 9′,9″-Terfluorene (**4**).* A solution of **16** (1.00 g) in benzene–ethanol (50 ml and 30 ml) was shaken with Raney nickel (W-7, 1.5 g) for 2 h at room temperature under an atmosphere of hydrogen. The reaction mixture was filtered, the filtrate was concentrated to a small volume, and 0.84 g (84%) of **4** crystallized out: mp 253—254 °C (dec); NMR (C_5D_5N) δ=5.06 (2H, q, J=3.6 Hz, $\Delta\nu$= 5.3 Hz), 6.28 (1H, s), and 6.59—8.39 (23H, m); MS, *m/e*, 494 (M^+) and 329. Found: C, 94.98; H, 5.41%. Calcd for $C_{39}H_{26}$: C, 94.70; H, 5.30%.

*Oxidation of **16**.* A mixture of **16** (980 mg) and sodium dichromate (2.40 g) in acetic acid (150 ml) was refluxed for 1 h; **17** (170 mg, 47%, mp 82—84 °C), **14** (100 mg, 15%, mp 216—218 °C, lit,[4] mp 216.5—218.0 °C), and **18** (110 mg, 15%, mp 207.5—209.0 °C, lit,[4] mp 207.5—209.0 °C) were isolated by means of alumina-column chromatography.

In addition, 80 mg (8%) of **19** was obtained: mp 332—333 °C; IR, 1682 cm^{-1} (C=O); MS, *m/e*, 508 (M^+). Found: C, 92.28; H, 4.80%. Calcd for $C_{39}H_{24}O$: C, 92.10; H, 4.76%.

*Oxidation of 4,9′-Bifluoren-9-one (**14**).* A mixture of **14** (1.03 g) and sodium dichromate (19.6 g) in acetic acid (50 ml) was refluxed for 3.5 h to afford 530 mg (54%) of *o*-(9-oxofluoren-4-ylcarbonyl)benzoic acid (**20**): mp 210—212 °C; IR, 3070 (OH), 1722, and 1688 cm^{-1} (C=O); MS, *m/e*, 328 (M^+) and 207. Found: C, 76.83; H, 3.34%. Calcd for $C_{21}H_{12}O_4$: C, 76.82; H, 3.68%.

Additionally, 50 mg (5%) of 8*H*-indeno[1,2-*a*]anthracene-5,8,13-trione (**21**) was isolated: mp 321—323 °C (dec); IR, 1714 and 1687 cm^{-1} (C=O); MS, *m/e*, 310 (M^+), 282, and 254. Found: C, 80.98; H, 3.17%. Calcd for $C_{21}H_{10}O_3$: C, 81.28; H, 3.25%.

*9-Bromo-4,9′-bifluorene (**23**).* *a)*: A solution of **14** (500 mg) in benzene–ethanol (30 ml and 10 ml) was shaken at room temperature for 2.5 h in the presence of Raney nickel (W-7, 0.5 g) under an atmosphere of hydrogen to give 460 mg (92%) of 4,9′-bifluoren-9-ol (**24**): mp 195—196 °C; IR, 3385 cm^{-1} (OH); NMR (C_6D_6) δ=1.46 (1H, d, J=9.00 Hz), 5.40 (1H, d), 5.97 (1H, s), and 6.65—7.97 (15H, m); MS, *m/e*, 346 (M^+), 181, and 165. Found: C, 90.25; H, 5.37%. Calcd for $C_{26}H_{18}O$: C, 90.14; H, 5.24%.

The foregoing **24** (300 mg) was treated with hydrogen bromide in acetic acid to yield 310 mg (87%) of **23**: mp 192—193 °C (dec); NMR (C_6D_6) δ=5.70 (1H, s), 5.85 (1H, s), and 6.56—7.93 (15H, m); MS, *m/e*, 410, 408 (M^+), and 330. Found: C, 76.55; H, 3.98%. Calcd for $C_{26}H_{17}Br$: C, 76.29; H, 4.19%.

b): A mixture of 4,9′-bifluorene[7] (1.98 g) and *N*-bromosuccinimide (1.16 g) in benzene (75 ml) was refluxed for 6 h to give 1.75 g (72%) of **23**, which was identical in all respects with that obtained in a).

*Formation of 4,4′-Di(9-fluorenyl)-9,9′-bifluorenylidene (**22**).* A solution of **23** (1.10 g) in acetone (170 ml) was treated with potassium hydroxide (0.20 g) in methanol (10 ml) at −15 °C to afford 136 mg (15%) of **22**: mp 290—291 °C (dec); NMR (C_5D_5N) δ=6.28 (2H, s) and 6.53—8.63 (30H, m) (measured at 53 °C). Found: C, 94.91; H, 5.00%. Calcd for $C_{52}H_{32}$: C, 95.09; H, 4.91%.

*Reduction of **22**.* Olefin **22** (100 mg) in benzene (120 ml) was shaken for 3 h at room temperature with Raney nickel (W-4, 0.5 g) under an atmosphere of hydrogen, giving 71 mg (71%) of 9,4′:-9′,9″:4″,9‴-quaterfluorene (**25**): mp 292—293 °C (dec). Found: C, 94.52; H, 5.20%. Calcd for $C_{52}H_{34}$: C, 94.80; H, 5.20%.

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