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Syntheses and Spectral Characteristics of Seven Polyphenyls Containing Highly Branched *para*-Phenylene Ring(s)[1]

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Seven polyphenyls, including four new compounds, 2,2′,6′- (**2**) and 3,2′,6′-triphenyl-*p*-terphenyl (**3**), 3′,5′-diphenyl-*p*-quaterphenyl (**4**), and 2-phenyl-3′-(2-biphenylyl)-*p*-terphenyl (**7**), were synthesized by the Ullmann coupling reaction of aryl iodide(s) or by the Kharash-type coupling reaction of aryl Grignard reagent with an aryl iodide catalyzed by bis(acetylacetonato)-nickel(II). Infrared spectral studies of the polyphenyls showed that the range of 730—770 cm^{-1}, generally accepted as the position of the out-of-plane C–H bending bands of the phenyl ring, should be widened slightly to 730—786 cm^{-1}. The high frequency bands were confirmed to be correlated closely to the overcrowding by terminal rings in the complex structures. Proton magnetic resonance spectral studies indicated that the characteristic spectral features of the branched polyphenyls were fully consistent with their conformational aspects deduced from stereomodels. In the ultraviolet spectral studies the polyphenyls containing highly branched *p*-phenylene ring(s) showed intense K-bands or shoulders at locations very similar to those of the corresponding linear polyphenyls containing the same number of *p*-phenylene rings.

Keywords——Ullmann reaction; Ni-complex-catalyzed cross-coupling; quinquephenyl; sexiphenyl; octiphenyl; IR; UV; ^{1}H-NMR

In previous studies, a series of closely related quinque- to decaphenyls having linear and branched structures has been synthesized to elucidate the relationship between the structures and the physical properties of polyphenyls in which the π–π interaction of the benzene rings across the pivot bond is markedly affected by twisting of the bond.[2] Spectral studies have proved that the linear polyphenyls containing *p*-linkage(s) display characteristic absorptions or signals in their infrared (IR), ultraviolet (UV), and proton nuclear magnetic resonance (^{1}H-NMR) spectra.[2a,c,3]

This work was undertaken to investigate the spectral characteristics of polyphenyls containing highly branched *para*-phenylene ring(s). Thus, we synthesized five quinque- to octiphenyls (**1**—**5**) containing a highly branched 1,2,3,5-tetrasubstituted benzene ring(s) (1,2,3,5-C_6H_2), and two sexiphenyls (**6** and **7**) containing a 1,2,4-trisubstituted benzene ring (1,2,4-C_6H_3), for comparison. The IR, UV, and ^{1}H-NMR spectra of the polyphenyls, including four new compounds (**2**, **3**, **4**, and **7**), were measured and the structure–property correlations, especially the characteristics related to the presence of branched and over-crowded *p*-phenylene ring(s), where a restricted rotation of the pivot bonds might be present, are discussed.

For the syntheses of the polyphenyls (**1**—**6**), the Ullmann homo- or cross-coupling reaction of aryl iodo compounds was employed.[2–4] For the synthesis of **7**, the Kharash-type Grignard cross-coupling reaction of an arylmagnesium bromide and an aryl iodide, in the presence of bis(acetylacetonato)nickel(II) as a catalyst, was adopted.[5] Among the aryl halides used, iodobenzene (**8**) was commercially available; 2-bromo- (**9**),[4a] 2-iodo- (**10**), 3-iodo- (**11**), 4-iodo- (**12**),[3] and 2,5-diiodo-biphenyl (**13**)[6] were prepared as reported previously. The other

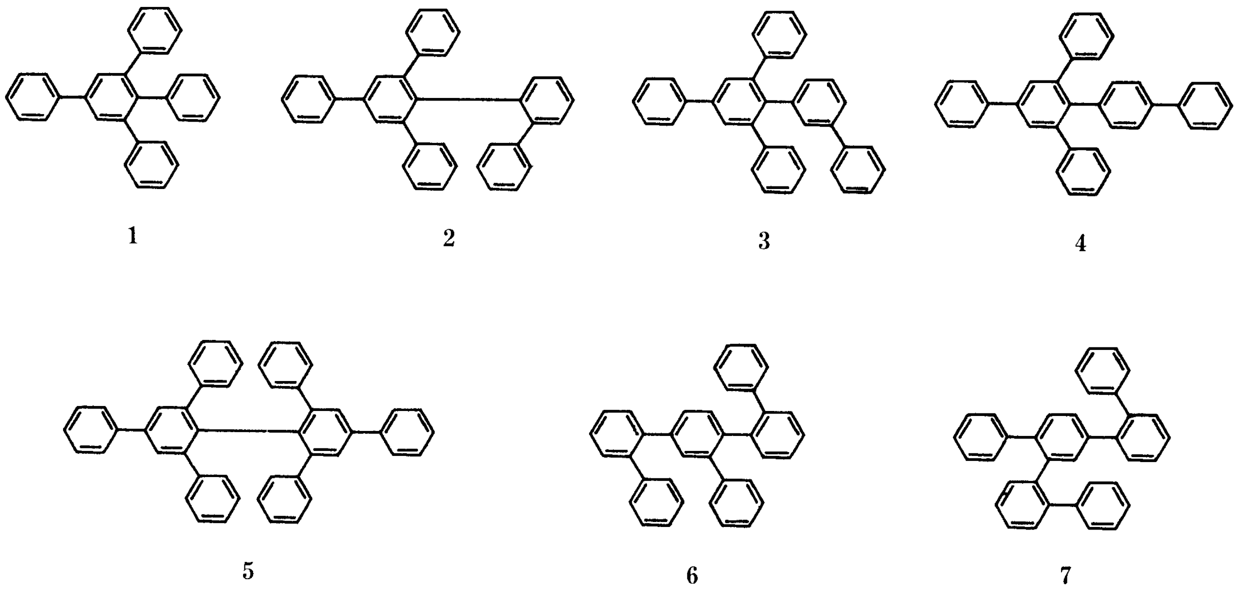

Chart 1

Table I. Syntheses of Branched-Chain Polyphenyls Containing *para*-Phenylene Ring(s)

Reactants	Procedure[a]	Polyphenyl (Yield, %)	Other products
14+ **8**	A	**1** (30)	Biphenyl (**17**)
14+**10**	A	**2** (27)	**17**, *o*-quaterphenyl (**18**)
14+**11**	A	**3** (10)	**17**, *m*-quaterphenyl (**19**), 5′-phenyl-*m*-terphenyl (**20**)
14+**12**	A	**4** (9)	**20**, *p*-quaterphenyl (**21**)
14	A	**5** (50)	**20**
13+**10**	A	**6** (36)	**17**, **18**, 2-phenyl-*m*-terphenyl (**22**)
9+**15**	B	**7** (78)	**17**, **18**

a) A: Ullmann reaction, B: Grignard reaction.

aryl halides, 2′-iodo-5′-phenyl-*m*-terphenyl (**14**) and 4′-iodo-*o*-quaterphenyl (**15**) were obtained from the corresponding nitroquaterphenyls *via* the corresponding amino compounds in the usual manner.[3] The Ullmann homo- and cross-coupling reactions of iodides were both carried out at 270—280 °C (185—210 °C for the preparation of **1**) in the presence of copper powder. The products of Ullmann coupling as well as of Kharash-type Grignard coupling were separated by column chromatography on alumina. The polyphenyls and by-products thus obtained are listed in Table I.

The structures of the polyphenyls (**1**—**7**) were supported by analytical results and spectral (IR and mass) data. The melting point of **6** coincided with that of an authentic sample,[7] though those of **1** and **5** were lower than the reported values by approximately 3 °C.[8,9]

In the IR spectra of the seven polyphenyls (**1**—**7**), the characteristic bands (680—920 $\mathrm{cm^{-1}}$) were confirmed to be consistent with the substitution patterns of the benzene rings constituting each polyphenyl (Table II). Among them, the spectra of **1**, **3**, **4**, and **5**, each of which has 1,2,3,5-C_6H_2, showed the strong or medium out-of-plane C–H bending vibration bands of five adjacent hydrogens on terminal rings in the 742—786 $\mathrm{cm^{-1}}$ region. Although

Table II. Positions and Tentative Assignments of Characteristic Bands in the IR Spectra (680—920 cm^{-1}) of Branched-Chain Quinque- to Octiphenyls[a)]

1	700 s	$\gamma_{\mathrm{C-C}}$
	706 sh, s	
	751 m	$\gamma_{\mathrm{C-H}}$ (M)
	765 s	
	775 s	
	794 w	
	887 m	$\gamma_{\mathrm{C-H}}$ (*sym*)
	916 w	$\gamma_{\mathrm{C-H}}$ (M)
2	693 s	$\gamma_{\mathrm{C-C}}$
	699 s	
	738 s	$\gamma_{\mathrm{C-H}}$ (M, *o*)
	751 m	
	755 s	
	763 s	
	767 m	
	773 m	
	781 m	$\gamma_{\mathrm{C-H}}$ (*o*)
	794 w	
	839 w	
	891 m	$\gamma_{\mathrm{C-H}}$ (*sym*)
	912 w	$\gamma_{\mathrm{C-H}}$ (M)
3	700 s	$\gamma_{\mathrm{C-C}}$
	712 sh, m	
	755 s	$\gamma_{\mathrm{C-H}}$ (M)
	770 m	
	781 m	
	794 w	$\gamma_{\mathrm{C-H}}$ (*m*)
	806 m	
	841 w	
	851 w	
	890 sh, m	$\gamma_{\mathrm{C-H}}$ (*m*, *sym*)
	893 m	
	903 w	$\gamma_{\mathrm{C-H}}$ (M)
4	698 s	$\gamma_{\mathrm{C-C}}$
	707 sh, m	
	731 m	
	758 s	$\gamma_{\mathrm{C-H}}$ (M)
	762 s	
	770 s	
	776 m	
	786 m	
	849 m	$\gamma_{\mathrm{C-H}}$ (*p*)
	890 m	$\gamma_{\mathrm{C-H}}$ (*sym*)
	903 vw	$\gamma_{\mathrm{C-H}}$ (M)
	917 w	
5	695 s	$\gamma_{\mathrm{C-C}}$
	742 s	$\gamma_{\mathrm{C-H}}$ (M)
	757 s	
	762 sh, s	
	768 s	
	783 m	
	799 w	
	837 w	
	883 w	$\gamma_{\mathrm{C-H}}$ (*sym*)
	887 m	
	895 m	
	909 w	$\gamma_{\mathrm{C-H}}$ (M)
6	698 s	$\gamma_{\mathrm{C-C}}$
	708 sh, m	
	730 sh, m	
	741 s	$\gamma_{\mathrm{C-H}}$ (M, *o*)
	757 s	
	766 m	
	780 s	$\gamma_{\mathrm{C-H}}$ (*o*)
	833 m	$\gamma_{\mathrm{C-H}}$ (*asym*)
	903 m	$\gamma_{\mathrm{C-H}}$ (*asym*)
	914 w	$\gamma_{\mathrm{C-H}}$ (M)
7	698 s	$\gamma_{\mathrm{C-C}}$
	701 s	
	734 s	$\gamma_{\mathrm{C-H}}$ (M, *o*)
	746 s	
	754 m	
	763 m	
	776 m	$\gamma_{\mathrm{C-H}}$ (*o*)
	779 sh, m	
	845 m	$\gamma_{\mathrm{C-H}}$ (*asym*)
	874 w	
	898 w	$\gamma_{\mathrm{C-H}}$ (*asym*)
	912 w	$\gamma_{\mathrm{C-H}}$ (M)

a) Measured by the KBr-disk method. Abbreviations: v, very; s, strong; m, medium; w, weak. $\gamma_{\mathrm{C-C}}$ and $\gamma_{\mathrm{C-H}}$ refer to vibrations which are primarily out-of-plane C–C, and out-of-plane C–H bending motions. M, *o*, *m*, *p*, *asym* and *sym* in parentheses refer to mono- and to *ortho*-, *meta*-, and *para*-substituted, and 1,2,4-tri- and 1,2,3,5-tetrasubstituted rings, respectively.

this region includes absorptions at rather higher frequencies than those noted by Bellamy (730—770 cm^{-1})[10)] and Sandroni and Geiss (742—762 cm^{-1}),[11)] the proposed assignments are reasonable because **1**, **4**, and **5** have neither three nor four adjacent ring hydrogens, which usually display absorptions in a similar region. Furthermore, analogous absorptions at higher frequencies than 770 cm^{-1} have been found in several branched-chain polyphenyls containing 1,2,3-[12)] or 1,2,4-trisubstituted ring(s).[2b,5b)]

The foregoing results on the C–H out-of-plane bending vibration bands of terminal ring hydrogens suggest a close correlation between the high frequency bands and the steric overcrowding caused by the terminal rings linked to the multiply substituted ring(s).

Whereas linear polyphenyls containing *p*-linkage(s) generally display the out-of-plane C–H bending vibration bands of two adjacent hydrogens in the 815—850 cm^{-1} region, the branched-chain polyphenyls containing 1,2,3,5-C_6H_2 (**1**—**5**) or 1,2,4-C_6H_3 (**6** and **7**) show exclusively or additionally the C–H bands of free hydrogen(s) in the 883—903 cm^{-1} region.[13)] The high frequency bands, therefore, are useful for identification of a branched structure having *p*-linkage(s).

The ^{1}H-NMR spectra of the polyphenyls were measured at 80 MHz in $CDCl_3$ solution, and the spectral data are summarized in Table III.

TABLE III. ¹H-NMR Spectral Data for Branched-Chain Quinque- to Octiphenyls in $CDCl_3$[a]

1	7.15 (10H, s, 2′- and 6′-C_6H_5) 7.68 (2H, s, C_6H_2) 6.82—7.26 (5H, m, 1′-C_6H_5) 7.34—7.78 (5H, m, 4′-C_6H_5)
2	7.56 (2H, s, C_6H_2) 7.32—7.76 (5H, m, 4′-C_6H_5) 6.62—7.19 (19H, m, other protons)
3	7.19 (10H, s, 2′- and 6′-C_6H_5) 7.71 (2H, s, C_6H_2) 7.34—7.79 (5H, m, 4′-C_6H_5) 6.84—7.28 (9H, m, other protons)
4	6.91 and 7.26 (4H, AA′BB′-q, $J=8.3\,Hz$, $C_{2''}$, $C_{6''}$- and $C_{3''}$, $C_{5''}$-H) 7.17 (10H, s, 3′- and 5′-C_6H_5) 7.69 (2H, s, C_6H_2) 7.34—7.79 (10H, m, other protons)
5	7.45 (4H, s, $C_6H_2 \cdot C_6H_2$) 6.63—7.20 (20H, m, 3′-, 5′-, 2″-, and 6″-C_6H_5) 7.30—7.78 (10H, m, 1′- and 4″-C_6H_5)
6	6.28—7.52 (26H, m, all protons)
7	7.43 (4H, s, 1′-C_6H_4) 6.41—7.49 (22H, m, other protons)

a) δ (ppm) from internal standard TMS.

The spectra of **1**, **3**, and **4** showed one apparent 10H singlet near δ 7.17, which is assigned to the protons of the phenyl rings at the 1- and 3-positions in the 1,2,3,5-C_6H_2 system, by comparison with the 10H singlet of phenyl protons of *o*-terphenyl (δ 7.17)[6] and 2,6-diphenyl-*p*-terphenyl (δ 7.13).[12] Analogous singlets were also found for protons of the phenyl ring(s) at the 1- and 2-positions in the 1,2-C_6H_4 and 1,2,4-C_6H_3 systems[2a,4c,6] and at the 1- and 3-positions in the 1,2,3-C_6H_3 system.[12] These results should provide an important clue to the structure of the substituted benzene ring adjacent to a phenyl ring.

A 5H (10H) multiplet in the range of δ 7.3—7.8 observed commonly in the spectra of **1**—**3** and **5** can be assigned to the protons of the phenyl ring(s) at the 5-position in the 1,2,3,5-C_6H_2 system, by comparison with the corresponding signal of 5′-phenyl-*m*-terphenyl (**20**) (δ 7.34—7.77, 15H, m, C_6H_5).[4c] In the case of **4**, however, a similar multiplet (δ 7.34—7.79) can be assigned to the protons of both terminal phenyl rings of the *p*-quaterphenyl unit by comparison with the corresponding signals of **20** and *p*-quaterphenyl (**21**) (δ 7.34—7.68, 10H, m, C_6H_5).[6]

The spectra of **1**, **3**, and **4** show a sharp 2H singlet near δ 7.7, which is assignable to the two protons of 1,2,3,5-C_6H_2 by comparison with the corresponding signal of **20** (δ 7.78, 2H, s, C_6H_3).[4c] Analogously, a similar 2H singlet in the spectra of **2** (δ 7.56) and **5** (δ 7.45) is assignable to the same two free protons. The slight high-field shifts of the signals in **2** (0.13 ppm) and **5** (0.24 ppm) as compared with those of **1**, **3**, and **4** are presumably due to the ring-current effects of the phenyl ring(s) (at the 2-, and 3′-, 5′-, 2″-, and 6″-positions, respectively) lying face-to-face to the tetrasubstituted benzene ring(s).[14]

In addition, an apparent 4H AA′BB′-q pattern of **4** (δ 6.91 and 7.26, $J=8.3\,Hz$), assignable to the *p*-phenylene protons at the $C_{2''}$, $C_{6''}$- and $C_{3''}$, $C_{5''}$-positions, is observed quite analogously with the corresponding signals of 2,6-diphenyl-*p*-terphenyl (δ 6.88 and 7.24, $J=8.4\,Hz$)[12] and 2-phenyl-*p*-terphenyl (δ 7.21 and 7.46, $J=8.6\,Hz$).[2a] The high-field shift of the *p*-phenylene proton signals of **4** as compared with that of **21** (δ 7.71, 8H, s; *cf.* *p*-terphenyl: δ 7.68, 4H, s)[2a] probably reflects the ring-current effects caused by the 3′- and 5′-phenyl rings.

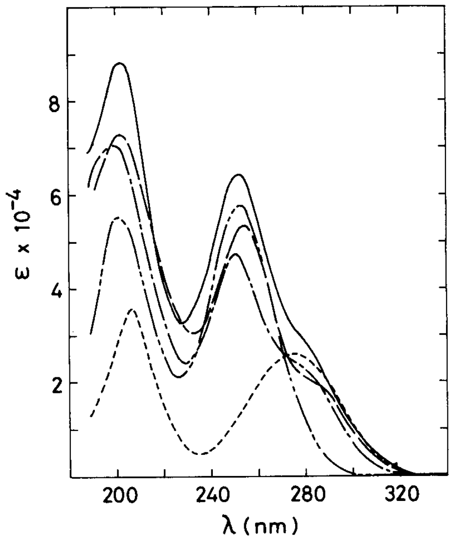

Fig. 1. UV Spectra of Ter-, Quater-, Quinque-, and Sexiphenyls in Cyclohexane

——, 3,2′,6′-triphenyl-*p*-terphenyl (**3**); - - - -, 2,2′,6′-triphenyl-*p*-terphenyl (**2**); - -- - --, 2′,6′-diphenyl-*p*-terphenyl (**1**); – – – –, 5′-phenyl-*m*-terphenyl (**20**): ------, *p*-terphenyl.

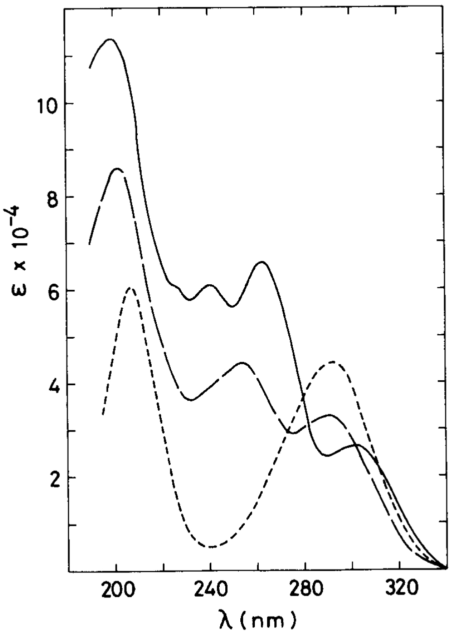

Fig. 2. UV Spectra of Quater-, Sexi-, and Octiphenyl in Cyclohexane

——, 3′,5′,2′′,6′′-tetraphenyl-*p*-quaterphenyl (**5**); – – – –, 3′,5′-diphenyl-*p*-quaterphenyl (**4**); ------, *p*-quaterphenyl (**21**).

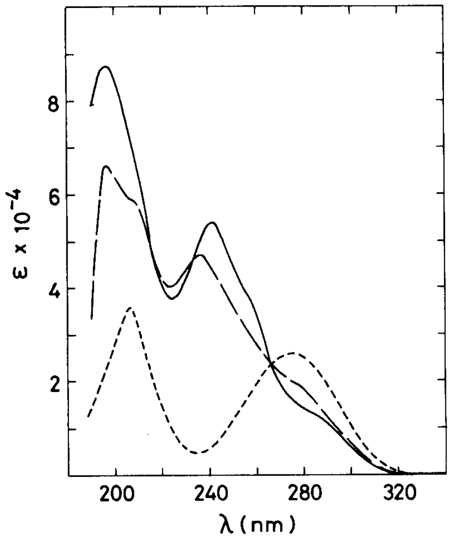

Fig. 3. UV Spectra of Ter- and Sexiphenyls in Cyclohexane

——, 2,2′,2′′-triphenyl-*p*-terphenyl (**6**); – – – –, 2-phenyl-3′-(2-biphenylyl)-*p*-terphenyl (**7**); ------, *p*-terphenyl.

The foregoing results indicate that the characteristic ^{1}H-NMR spectral features of the branched-chain polyphenyls can be reasonably interpreted on the basis of conformational considerations using Dreiding stereomodels.

The UV spectra of the polyphenyls (**1**—**7**) were measured in cyclohexane solution. The absorption curves are shown in Figs. 1—3. All of the polyphenyls displayed the E-band in the fairly narrow region of 195—210 nm and the K-band in the broad region of 235—300 nm.

The spectra of **1**, **2**, and **3**, each of which contains a branched *p*-terphenyl unit of 1,2,3,5-C_6H_2 type, all displayed a prominent K-band at about 252 nm (**1**: 250 nm, $\varepsilon = 47500$; **2**: 254, 53400; **3**: 252, 64300) together with a shoulder near 275 nm (**1**: 270 sh, 26200; **2**: 276 sh, 21800; **3**: 275 sh, 31700). The prominent band is very similar to that in the spectrum of **20** (252, 57800),[4c)] which has a structural unit in common with **1**, **2**, and **3**. The shoulder was also rather similar in both location and intensity with those of *p*-terphenyl (276, 25500) (Fig. 1).

Further, the spectra of **4** and **5**, in which a branched *p*-quaterphenyl unit of 1,2,3,5-C_6H_2 type is present, showed an intense K-band with multiple absorption maxima (**4**: 254, 44000; 291, 32400. **5**: 240, 61100; 262, 65800; 301, 26700). Among them, the longest wavelength bands of **4** and **5** were similar in location to, but slightly weaker in intensity than, that of **21** (294, 44400)[6] (Fig. 2). These data suggest the presence of conjugation over the *p*-quaterphenyl unit, even in a highly branched and sterically overcrowded structure. In the cases of **6** and **7**, which each have a branched *p*-terphenyl unit of 1,2,4-C_6H_3 type, the spectra showed a shoulder of the K-band at 281 nm (13900) and at 277 nm (19300), respectively, similar in location to, but slightly weaker in intensity than, that of *p*-terphenyl (276, 25500) (Fig. 3). In other words, branched polyphenyls containing branched *p*-phenylene ring(s) (1,2,3,5-C_6H_2 or 1,2,4-C_6H_3) show intense K-bands or shoulders at locations similar to those of corresponding linear polyphenyls containing the same number of *p*-phenylene ring(s).

In a series of previous UV spectral studies, we confirmed that linear polyphenyls containing *p*-linkage(s) showed K-bands above *ca.* 260 nm as the longest wavelength band, and the band position could be used as an indication of the approximate number of consecutive *p*-phenylene units.[2a,3]

On the basis of the foregoing results, the generalization for linear polyphenyls containing *p*-linkage(s) was found to be applicable even to polyphenyls containing highly branched *p*-phenylene rings.

Experimental

The melting points were determined with a Mettler FP-51 apparatus, except for those above 300 °C, which were determined with a Shimadzu DSC-30M differential scanning calorimeter. The UV spectra were measured on a Shimadzu MPS-50L spectrophotometer, the IR spectra on a Leitz III-G spectrophotometer, and the ^{1}H-NMR spectra on a Varian CFT-20 spectrometer at 80 MHz, using tetramethylsilane (TMS) as an internal standard. The mass spectra (MS) were recorded on a Hitachi RMU-6E mass spectrometer.

Iodobenzene (**8**) was obtained commercially and purified before use. 2-Bromobiphenyl (**9**),[4a] 2- (**10**), 3- (**11**), and 4-iodobiphenyl (**12**)[3] and 2,5-diiodobiphenyl (**13**)[6] were prepared as reported previously.

2′-Iodo-5′-phenyl-*m*-terphenyl (14)——Commercially available 2′-nitro-5′-phenyl-*m*-terphenyl was reduced with activated iron in hot benzene[16] to prepare 2′-amino-5′-phenyl-*m*-terphenyl (mp 122.8 °C). The amine was converted into **14** in the usual manner. Colorless needles from ethanol; mp 97.5 °C; 3.6 g (41%). *Anal.* Calcd for $C_{24}H_{17}I$: C, 66.68; H, 3.96. Found: C, 66.54; H, 4.01.

4′-Iodo-*o*-quaterphenyl (15)——Fuming nitric acid ($d = 1.50$, 32 ml) was added in portions to a solution of *o*-quaterphenyl (30.6 g) in acetic acid (230 ml) at 75—80 °C, with stirring for 2 h. After being stirred at the same temperature for 3 h, the mixture was added in portions to water (500 ml) with stirring. The benzene-insoluble part of the product formed was collected, dried *in vacuo*, and then crystallized from benzene to provide 4,4‴-dinitro-*o*-quaterphenyl (mp 286.0 °C (lit.[17] mp 290 °C); 1.2 g). The organic layer was washed with sodium hydroxide solution, and the solvent was distilled off. The residual oil thus obtained was subjected to chromatography on alumina. Fractional crystallizations of the eluates with a cyclohexane–benzene (9 : 1, v/v) mixture (C–B (9 : 1)), C–B (4 : 1), and C–B (3 : 2) afforded 4′-nitro-*o*-quaterphenyl (**16**) and 4-nitro-*o*-quaterphenyl (mp 136.2 °C (lit.[4b] mp 135.5—137 °C); 1.7 g). **16**: Pale yellow plates from ethanol; mp 146.1 °C; 3.5 g (10%). *Anal.* Calcd for $C_{24}H_{17}NO_2$: C, 82.03; H, 4.88; N, 3.99. Found: C, 82.29; H, 4.84; N, 3.94.

The nitro compound **16** (3.5 g) was reduced with activated iron in hot benzene[16] to give 4′-amino-*o*-quaterphenyl; colorless needles from ethanol; mp 145.6 °C; 3.1 g (97%). The amine was then converted into **15** in the usual manner. Colorless leaves from ethanol; mp 155.6 °C; 1.7 g (39%). *Anal.* Calcd for $C_{24}H_{17}I$: C, 66.68; H, 3.96. Found: C, 66.98; H, 3.78.

General Procedure for the Preparation of Polyphenyls (1—6)——A mixture of two kinds of starting iodides (one kind for the preparation of **5**) was introduced into a reaction tube (i.d. 2.0 × 20 cm), which was heated in an oil bath at 270—275 °C (185—190 °C for the preparation of **1**). Copper powder was then added in portions with stirring over a 2-h period, after which the mixture was heated at 275—280 °C (190—210 °C for the preparation of **1**) for an additional hour. After cooling of the reaction mixture, the product was extracted with hot benzene, then the solvent was distilled off. The extract was subjected to chromatography on alumina using cyclohexane, C–B mixture, and benzene successively as eluents to afford each polyphenyl and by-products.

2′,6′-Diphenyl-*p*-terphenyl (**1**): A mixture of **14** (1.30 g, 3.0 mmol) and **8** (6.12 g, 30.0 mmol) was heated with copper powder (15.2 g, 240 mg-atom). The eluate with cyclohexane provided biphenyl (**17**) (colorless leaves from ethanol; mp 69.4 °C; 631 mg) and **1**. **1**: Colorless needles from ethanol; mp 223.1 °C (lit.[8] mp 224—226 °C); 346 mg (30%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 199 (71200), 250 (47500), 270 (sh) (26200). *Anal.* Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.08; H, 5.79. MS *m/e*: 382 (M^+).

2,2′,6′-Triphenyl-*p*-terphenyl (**2**): A mixture of **14** (4.32 g, 10.0 mmol) and **10** (11.20 g, 40.0 mmol) was heated with copper powder (25.4 g, 400 mg-atom). The eluate with cyclohexane afforded **17** (91 mg), *o*-quaterphenyl (**18**) (colorless cubes from ethanol; mp 118.6 °C (lit.[18] mp 118 °C); 2800 mg), and **2**. **2**: Colorless needles from ethanol; mp 214.6 °C; 1241 mg (27%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 201 (72900), 254 (53400), 276 (sh) (21800). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 93.99; H, 5.64. MS *m/e*: 458 (M^+).

3,2′,6′-Triphenyl-*p*-terphenyl (**3**): A mixture of **14** (3.02 g) and **11** (7.84 g) was heated with copper powder (18.5 g). The eluate with cyclohexane provided **17** (63 mg). The eluate with C–B (9 : 1) afforded 5′-phenyl-*m*-terphenyl (**20**) (colorless needles from ethanol; mp 173.2 °C (lit.[19] mp 171—172 °C); 189 mg), *m*-quaterphenyl (**19**) (colorless plates from ethanol; mp 85.5 °C (lit.[20] mp 85.5—86 °C); 498 mg), and **3**. **3**: Colorless needles from ethanol; mp 161.0 °C; 314 mg (10%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 202 (88900), 252 (64300), 275 (sh) (31700). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 93.98; H, 5.65. MS *m/e*: 458 (M^+).

3′,5′-Diphenyl-*p*-quaterphenyl (**4**): A mixture of **14** (3.02 g) and **12** (7.84 g) was treated with copper powder. The eluates with C–B (9 : 1), with C–B (9 : 1) and C–B (3 : 2), and with C–B (3 : 2) provided **20** (505 mg), **4**, and *p*-quaterphenyl (**21**) (colorless plates from benzene; mp 318 °C (lit.[21] mp 317.7—318.7 °C); 394 mg), respectively. **4**: Colorless needles from ethanol–benzene (2 : 1); mp 247.0 °C; 298 mg (9%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 202 (86600), 254 (44000), 291 (32400). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.31; H, 5.86. MS *m/e*: 458 (M^+).

3′,5′,2″,6″-Tetraphenyl-*p*-quaterphenyl (**5**): The iodoquaterphenyl (**14**) (1.73 g) was heated with copper powder (2.5 g). The eluate with C–B (5 : 1) afforded **20** (7 mg) and **5**. **5**: Colorless needles from benzene–ethanol; mp 345 °C (lit.[9] mp 348 °C); 610 mg (50%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 199 (113700), 225 (sh) (60700), 240 (61100), 262 (65800), 301 (26700). *Anal.* Calcd for $C_{48}H_{34}$: C, 94.39; H, 5.61. Found: C, 94.13; H, 5.48. MS *m/e*: 610 (M^+).

2,2′,2″-Triphenyl-*p*-terphenyl (**6**): A mixture of **13** (2.84 g) and **10** (7.84 g) was heated with copper powder (18.0 g). The eluate with cyclohexane provided **17** (53 mg) and **18** (2830 mg). The eluate with C–B (4 : 1) gave 2-phenyl-*m*-terphenyl (**22**) (colorless prisms from ethanol; mp 91.4 °C (lit.[6] mp 91.4 °C); 98 mg) and **6**. **6**: Colorless needles from ethanol; mp 164.7 °C (lit.[5b] mp 165.1 °C); 1147 mg (36%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 196 (87400), 241 (54400), 281 (sh) (13900). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.41; H, 5.88. MS *m/e*: 458 (M^+).

Preparation of 2-Phenyl-3′-(2-biphenylyl)-*p*-terphenyl (7)——An ethereal solution of 2-biphenylylmagnesium bromide was prepared from **9** (0.93 g, 4.0 mmol), magnesium turnings (0.10 g, 4.1 mg-atom), and absolute ether (20 ml) under a nitrogen atmosphere in the usual manner. A solution of **15** (0.87 g, 2.0 mmol) and bis(acetylacetonato)nickel(II) (10 mg, 0.04 mmol) in benzene (20 ml) was added to the Grignard reagent obtained above all at once. The whole was stirred for 1 h at 0 °C, then refluxed for 3 h. The reaction mixture was hydrolyzed with dilute hydrochloric acid and then extracted with benzene. The organic layer was separated, washed successively with dilute hydrochloric acid, sodium carbonate solution, sodium thiosulfate solution, and finally with water, then dried. After the removal of the solvent, the residue (1.35 g) was chromatographed on alumina with C–B (9 : 1) to give **17** (315 mg), **18** (105 mg), and **7**.

7: Colorless needles from ethanol–benzene; mp 216.0 °C; 720 mg (78%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 197 (66300), 210 (58700), 236 (47300) 277 (sh) (19300). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.56; H, 6.02. MS *m/e*: 458 (M^+).

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References and Notes

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14) The face-to-face arrangement of two benzene rings has been found in the following compounds: 1,8-diarylnaphthalenes (Ref. 15*a*), cyclophanes (Ref. 15*b*), cage compounds (Ref. 15*c*), and polyphenylenes (Ref. 15*d*).

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