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Syntheses and Spectral Properties of Several Branched-chain Polyphenyls containing 1,3,5-Trisubstituted Ring(s)¹⁾

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Six polyphenyls, including four new compounds, 5′,5′′-di(2-biphenylyl)-2,2′′′-diphenyl-*m*-quaterphenyl (**3**), 2,5′,2′′-triphenyl-*m*-terphenyl (**4**), 3,5-di(2-biphenylyl)-*o*-terphenyl (**5**), and 5′′-(3-biphenylyl)-*m*-quinquephenyl (**6**), were synthesized by the Ullmann coupling reaction of iodo compounds. Proton magnetic resonance spectral studies indicated that the characteristic spectral features of the polyphenyls containing 1,3,5-trisubstituted ring system(s) were fully compatible with their conformational aspects deduced from stereomodels. Ultraviolet spectral data indicated that the dihedral angle of the pivot bond of the branched ring in the polyphenyls in solution is very similar to that of biphenyl.

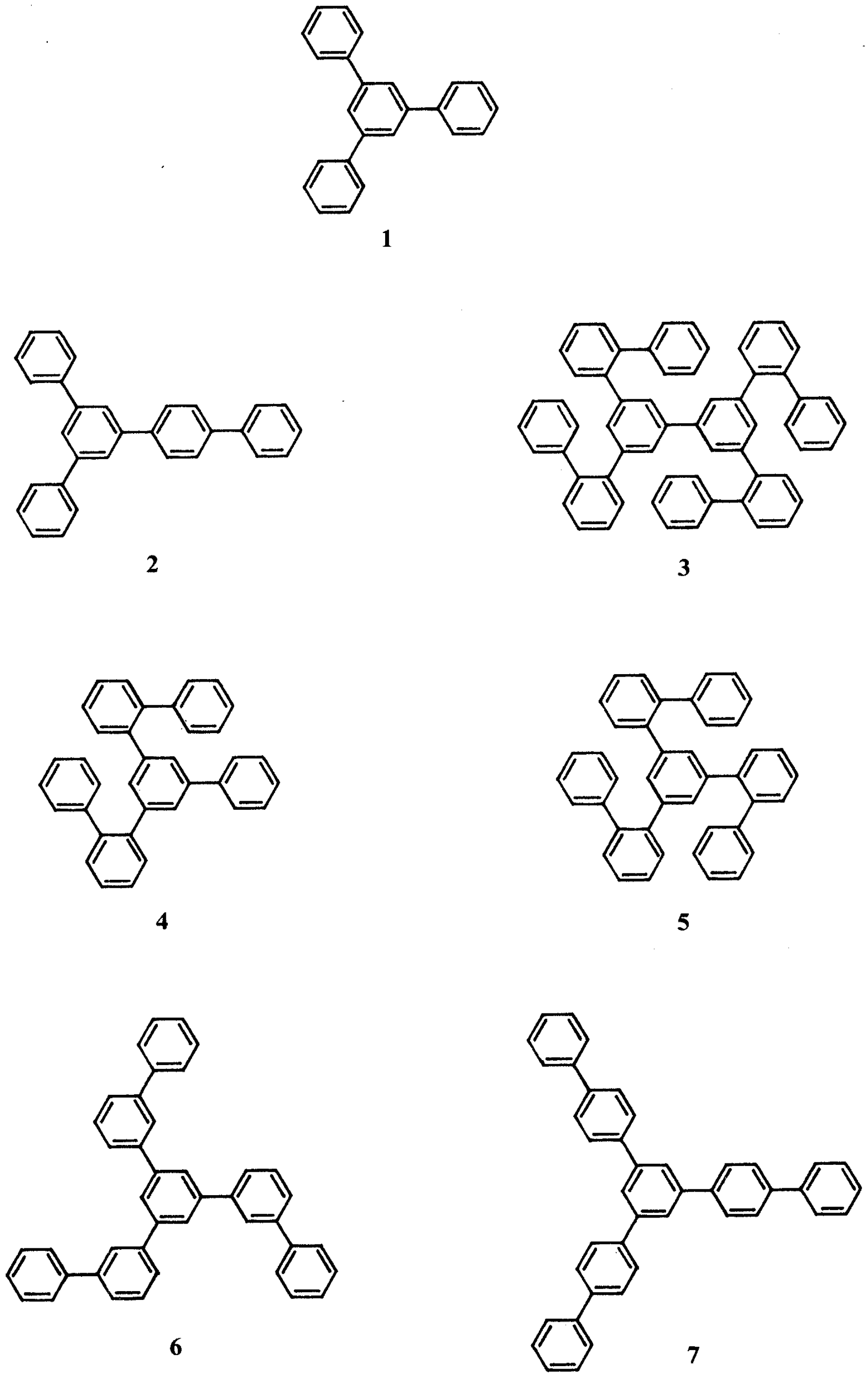
Keywords——Ullmann reaction; quinquephenyl; sexiphenyl; septiphenyl; decaphenyl; polyphenyl; IR; UV; ^{1}H-NMR

In previous studies, a series of closely related polyphenyls having linear or branched structures have been synthesized to elucidate the relation between the structures and the physical properties of polyphenyls.²⁾ Spectral studies have shown that most of the polyphenyls studied displayed significant characteristics in the infrared (IR), ultraviolet (UV), and proton magnetic resonance (^{1}H-NMR) spectra. In particular, polyphenyls containing a 1,2,3-trisubstituted ring have interesting characteristics of ^{1}H-NMR and UV spectra, which might originate from the non-planar conformation of three contiguous benzene rings in their branched-chain systems.

The present work was undertaken to develop further the structure-property correlation study to branched-chain polyphenyls of 1,3,5-trisubstituted type, which may display different spectral behavior from those of 1,2,3-trisubstituted type. For the simplest compound of this type, 5′-phenyl-*m*-terphenyl (**1**), the dihedral angle between the planes of two adjacent benzene rings in the vapor phase has been reported as 46 ± 5°,³⁾ substantially identical with the value found for biphenyl.⁴⁾ However, the dihedral angles of the former in the crystalline state have been estimated as +34, −27, and +24°,⁵⁾ in striking contrast to biphenyl, which is known to be planar in the solid state.⁶⁾ Consequently, the conformation of **1** and those of branched-chain polyphenyls containing 1,3,5-trisubstituted ring(s) in solution are of much interest in comparison with that of biphenyl, for which the dihedral angle of approximately 20° was given by Suzuki.⁶⁾

We synthesized six branched-chain polyphenyls (up to decaphenyl) of closely related structures (**2**—**7**), having one or two 1,3,5-trisubstituted benzene rings to which phenyl or phenylene groups are linked in different modes to give sterically crowded or uncrowded geometry. The IR, UV, and ^{1}H-NMR spectra of the polyphenyls, including four new compounds (**3**—**6**), were measured and their spectral characteristics, which originate from the number and conformation of the benzene rings in each molecule, are discussed in the light of the results.

For the syntheses of the polyphenyls, the Ullmann homo- or cross-coupling reaction of iodo compounds was employed.[2,7-10] Among the iodo compounds used, iodobiphenyls (2- (**9**), 3- (**10**), and 4-iodobiphenyl (**11**))[7] and 5′-iodo-*m*-terphenyl (**14**)[2c] were prepared as reported previously. One of the key intermediates, 1,3,5-triiodobenzene (**12**), was prepared by direct iodination of aniline followed by deamination of the resultant 2,4,6-triiodoaniline. The other intermediate, 5′-iodo-2,2′′-diphenyl-*m*-terphenyl (**17**), was obtained *via* the Ullmann cross-coupling of 3,5-diiodo-1-nitrobenzene[2c] and **9** to give 5′-nitro-2,2′′-diphenyl-*m*-terphenyl (**15**), and the reduction of the latter to the corresponding amine (5′-amino-2,2′′-diphenyl-*m*-terphenyl (**16**)) followed by diazotization and iodine substitution. Iodobenzene



1

2

3

4

5

6

7

Chart 1

Table I. Syntheses of Branched-chain Polyphenyls containing 1,3,5-Trisubstituted Benzene Ring(s)

Reactants	Polyphenyl (Yield, %)	Other products
14+**11**	**2** (25)	**18**, **20**, **21**
17	**3** (35)	**22**
17+ **8**	**4** (35)	**18**
12+ **9**	**5** (22)	**19**, **22**
12+**10**	**6** (26)	**23**, **24**
12+**11**	**7** (20)	**21**, **25**

(**8**) is commercially available. For the Ullmann cross-coupling reaction, a mixture of the triiodo compound and aryl iodide or of two kinds of aryl iodides in molar ratios of 1 : 3 to 1 : 25 was used. Both homo- and cross-coupling of iodides were carried out at 250—280 °C (185—210 °C for the preparation of **4**) with copper powder, and the products were separated by column chromatography on alumina. The polyphenyls and by-products thus obtained are listed in Table I.

The polyphenyls (**2**—**7**) showed IR spectral data consistent with their structures and gave acceptable results in elemental analyses and molecular weight determinations by mass spectroscopy (MS). While the melting point of **2** coincides (within 1 °C) with the reported value,[11] that of **7** falls between those given by other authors.[12,13] The yields of all the pure polyphenyls from quinque- to decaphenyl were 20—35%. In the cross-coupling reactions, the supposed routes of formation of the chief by-products isolated can be classified briefly into the following categories: A) hydrogenolytic deiodinations of starting aryl iodides (biphenyl (**18**) and *m*-terphenyl (**20**)); B) the homo-coupling of starting aryl iodides (**18**, *o*- (**19**), *p*- (**21**), and *m*-quaterphenyl (**23**)); C) the partial coupling of aryl iodides and triiodobenzene followed by the dehydrogenolytic deiodination of the intermediate iodoquinquephenyls (2,2′′-diphenyl-*m*-terphenyl (**22**), *m*-quinquephenyl (**24**), and 4,4′′-diphenyl-*m*-terphenyl (**25**)). In the homo-coupling reaction of **17**, a decaphenyl **3** (35%) and only one by-product **22** (40%) were isolated. The predominant formation of **22** by route A is presumably due to the sterically crowded structure of the starting iodide **17**.

The IR spectra of the polyphenyls were measured by the KBr-disk method. The characteristic bands (680—920 cm^{-1}) of six polyphenyls are listed in Table II; these bands are consistent with the kinds of benzene rings constituting each polyphenyl.

In all of the spectra, the C-H out-of-plane bending vibration bands of three free hydrogen atoms of the 1,3,5-trisubstituted benzene ring (1,3,5-C_6H_3) were observed in the range of 870—893 cm^{-1}. This range is within the region of 860—900 cm^{-1} proposed for the same bands of aromatic compounds by Bellamy,[14] but is slightly wider than that reported for five polyphenyls (874—886 cm^{-1}) by Sandroni and Geiss,[15] or that given for two polyphenyls (869—881 cm^{-1}) by Doss and Solomon.[16]

The spectrum of **7**, which has three isolated *p*-phenylene rings, displayed the C-H out-of-plane bending vibration bands of two adjacent hydrogen atoms of *p*-phenylene rings at 830 (m), 839 (m), and 847 (m) cm^{-1}, including rather lower frequency band as compared with that of *p*-terphenyl (840 (m) cm^{-1}).

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.

The spectra of **5** (δ 6.72), **6** (δ 7.90), and **7** (δ 7.89) display a sharp 3H singlet as a typical signal of an A_3 system, which can reasonably be assigned to the three free protons of 1,3,5-C_6H_3 by comparison with the corresponding proton signal of **1** (δ 7.78, 3H, s, C_6H_3; δ 7.34—

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

2	
693 s	$\gamma_{\text{C-C}}$
703 s	
728 w	
738 m	$\gamma_{\text{C-H}}$ (M)
753 s	
762 sh m	
766 m	
829 w	
843 m	$\gamma_{\text{C-H}}$ (*p*)
880 m	$\gamma_{\text{C-H}}$ (sym)
914 w	$\gamma_{\text{C-H}}$ (M)

3	
700 s	$\gamma_{\text{C-C}}$
716 s	
745 s	$\gamma_{\text{C-H}}$ (M, *o*)
756 s	
763 s	
767 s	
776 m	
782 m	$\gamma_{\text{C-H}}$ (*o*)
833 vw	
842 vw	
870 m	$\gamma_{\text{C-H}}$ (sym)
880 m	
911 w	$\gamma_{\text{C-H}}$ (M)
917 w	

4	
699 s	$\gamma_{\text{C-C}}$
715 m	
732 w	
747 s	$\gamma_{\text{C-H}}$ (M, *o*)
757 s	
765 s	
769 sh m	
779 m	$\gamma_{\text{C-H}}$ (*o*)
849 w	
876 w	$\gamma_{\text{C-H}}$ (sym)
887 m	
901 w	$\gamma_{\text{C-H}}$ (M)
913 w	
917 w	

5	
700 s	$\gamma_{\text{C-C}}$
715 m	
730 w	
742 s	$\gamma_{\text{C-H}}$ (M, *o*)
746 sh s	
759 s	
776 m	
835 w	
845 w	
873 w	$\gamma_{\text{C-H}}$ (sym)
893 m	
914 w	$\gamma_{\text{C-H}}$ (M)

6	
694 sh s	$\gamma_{\text{C-C}}$
701 s	
733 w	
756 s	$\gamma_{\text{C-H}}$ (M)
758 sh s	
779 w	
792 m	$\gamma_{\text{C-H}}$ (*m*)
797 m	
801 m	
870 m	$\gamma_{\text{C-H}}$ (*m*, sym)
876 m	
896 w	$\gamma_{\text{C-H}}$ (M, *m*)
908 w	

7	
687 s	$\gamma_{\text{C-C}}$
695 s	
717 w	
725 m	
737 m	$\gamma_{\text{C-H}}$ (M)
764 s	
769 s	
830 m	$\gamma_{\text{C-H}}$ (*p*)
839 m	
847 m	
889 w	$\gamma_{\text{C-H}}$ (sym)
909 w	$\gamma_{\text{C-H}}$ (M)

a) v, very; s, strong; m, medium; w, weak. $\gamma_{\text{C-C}}$ and $\gamma_{\text{C-H}}$ refer to vibrations which are primarily out-of-plane C-C, and out-of-plane C-H bending motions. M, *o*, *m*, *p*, and sym in parentheses refer to mono- and to *ortho*-, *meta*-, and *para*-substituted, and 1,3,5-trisubstituted rings, respectively.

7.77, 15H, m, C_6H_5).[17)] The remarkable high-field shift (1.1—1.2 ppm) of the 3H singlet of **5** as compared with the corresponding signal of the reference compound as well as those of **6** and **7** presumably reflects the ring current effects of terminal phenyl rings adjacent to *o*-phenylene rings.

In the spectrum of **3**, a 4H doublet (δ 6.65, $J = 1.6$ Hz) and a 2H triplet (δ 6.88, $J = 1.6$ Hz), which constitute a set of typical signals of an AB_2 system, can easily be assigned to the protons of the 2'-, 4'-, 2''-, and 6''-positions of $C_6H_3 \cdot C_6H_3$ and those of the 6'- and 4''-positions, respectively. The corresponding 6H signal of the reference compound, 5',5''-diphenyl-*m*-quaterphenyl,[2c)] appears as a multiplet of an AB_2 system at a rather low-field region (δ 7.80—7.91). The significant high-field shifts (1.0—1.2 ppm) obviously arise for the same reason as in the case of **5**.

In the spectrum of **2**, however, a 3H multiplet of an AB_2 system is observed in a rather narrow region of δ 7.81—7.87, and can be assigned to the three protons of 1,3,5-C_6H_3 by comparison with the spectrum of 5',5''-diphenyl-*m*-quaterphenyl mentioned above. The significant difference between the apparent signal patterns of the three protons of 1,3,5-C_6H_3 observed in the spectra of **2** and **3** may be explained as follows: the difference of chemical shifts between H_A and H_B of **3** ($C_6H_AH_{B_2} \cdot C_6H_AH_{B_2}$) should be large, as a result of the anisotropic effects of phenyl rings adjacent to *o*-phenylene rings, as compared with the corresponding difference in the case of **2**.

In **2** and **7**, which have one and three isolated *p*-phenylene rings, respectively, an apparent doublet of 4H (δ 7.74 and 7.76) and one of 12H (δ 7.77 and 7.79), respectively, are observed. These are assigned to the *p*-phenylene protons by comparison with the spectra of reference compounds, 3-phenyl-*p*-terphenyl (δ 7.71, 4H, s)[18] and 4,4′′-diphenyl-*m*-terphenyl (δ 7.73, 8H, s),[2a] respectively. Thus, the *p*-phenylene proton signals of **2** and **7** appear as apparent doublets in a narrow region at slightly lower field as compared with the corresponding singlets of the reference compounds. Such apparent differences may be accounted for by A) the deshielding effects due to the increased number of benzene ring(s);[19] and B) the slight difference between the chemical shifts of H_A and H_B of the *p*-phenylene rings of **2** and **7**, caused by A.

Although **4** showed a multiplet (δ 6.91—7.48) which is difficult to assign, the absence of the three-proton signal of 1,3,5-C_6H_3 in the regions up to δ 7.48 and down to δ 6.91 suggests a degree of high-field shift of the signal slightly less than that of **5** (δ 6.72, 3H, s) (*cf.* **1**: δ 7.78, 3H, s). The spectrum of **4**, therefore, serves as a basis for the proposed structure.

The foregoing results show that the ^{1}H-NMR spectra of the branched-chain polyphenyls studied here are consistent with their conformational aspects deduced from Dreiding stereomodels.

The UV spectra of the polyphenyls 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 190—210 nm and the K-band in the broad region of 230—285 nm.

The K-bands of **2** (263 nm, $\varepsilon = 52300$; 280 nm (infl), $\varepsilon = 40600$) and **7** (285 nm, $\varepsilon = 89900$), both of which have isolated *p*-phenylene ring(s), appeared at wavelengths similar to those of the corresponding reference compounds, 3-phenyl-*p*-terphenyl (268, 38400; 275 (infl), 36100)[18] and 4,4′′-diphenyl-*m*-terphenyl (280, 66500)[2a] (Fig. 1). These results indicate that an intense K-band above *ca.* 260 nm in the spectra of branched-chain polyphenyls may be

TABLE III. ^{1}H-NMR Spectral Data for Branched-chain Quinque- to Decaphenyl in $CDCl_3$[a]

2	7.74 and 7.76 (4H, apparent d, *p*-C_6H_4) 7.81—7.87 (3H, m, C_2, C_4, and C_6–H) 7.33—7.78 (15H, m, C_6H_5)
3	6.65 (4H, d, $J = 1.6$ Hz, $C_{2'}$, $C_{4'}$, $C_{2''}$, and $C_{6''}$–H) 6.88 (2H, t, $J = 1.6$ Hz, $C_{6'}$ and $C_{4''}$–H) 6.95—7.46 (36H, m, other protons)
4	6.91—7.48 (26H, m, all protons)
5	6.72 (3H, s, C_2, C_4, and C_6–H) 6.75—7.40 (27H, m, other protons)
6	7.90 (3H, s, $C_{2''}$, $C_{4''}$, and $C_{6''}$–H) 7.85—7.98 (3H, m, *m*-$\underline{H}C_6H_3 \cdot C_6H_5$) 7.32—7.79 (24H, m, other protons)
7	7.77 and 7.79 (12H, apparent d, *p*-C_6H_4) 7.89 (3H, s, C_2, C_4, and C_6–H) 7.25—7.72 (15H, m, C_6H_5)

[a] δ (ppm) from internal standard TMS.

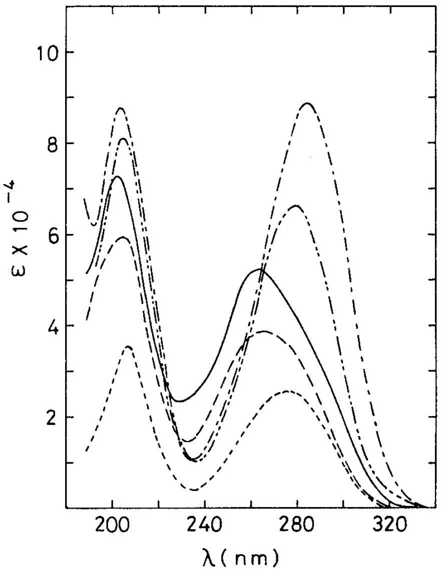


Fig. 1. UV Spectra of Terphenyl, Quaterphenyl, Quinquephenyls, and Septiphenyl in Cyclohexane

——, 3,5-diphenyl-*p*-terphenyl (**2**); – – – –, 3-phenyl-*p*-terphenyl; –·–·–·–, 3,5-di(4-biphenylyl)-*p*-terphenyl (**7**); –·–·–, 4,4′′-diphenyl-*m*-terphenyl; ------, *p*-terphenyl.

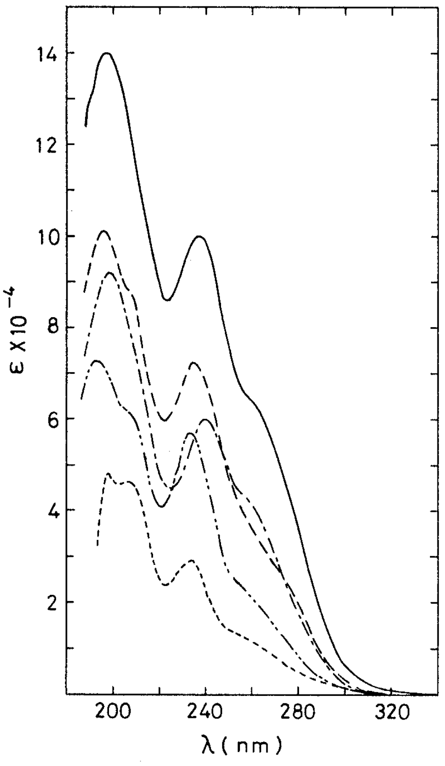


Fig. 2. UV Spectra of Terphenyl, Quinquephenyl, Sexiphenyl, Septiphenyl, and Decaphenyl in Cyclohexane

——, 5′,5″-di-(2-biphenylyl)-2,2‴-diphenyl-*m*-quaterphenyl (**3**); – – – –, 3,5-di(2-biphenylyl)-*o*-terphenyl (**5**); —·—·—·—, 2,5′,2″-triphenyl-*m*-terphenyl (**4**); ------, 2, 2″-diphenyl-*m*-terphenyl; -----, *o*-terphenyl.

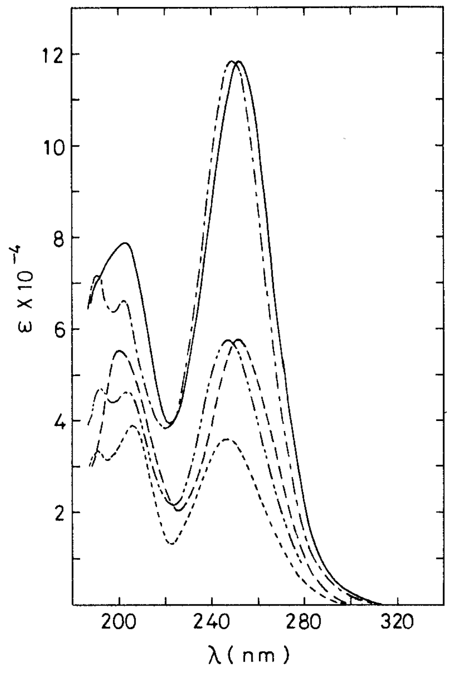


Fig. 3. UV Spectra of Terphenyl, Quaterphenyls, and Septiphenyls in Cyclohexane

——, 5″-(3-biphenylyl)-*m*-quinquephenyl (**6**); —·—·—·—, *m*-septiphenyl; – – – –, 5′-phenyl-*m*-terphenyl (**1**); ------, *m*-quaterphenyl; -----, *m*-terphenyl.

considered to be an indication of the presence of one or more *p*-phenylene units, as in the case of linear polyphenyls.[2a,b,7,9)]

In the cases of **5** and **3**, in which three and four isolated *o*-phenylene rings, respectively, are present, each of the spectra revealed an intense K-band with a shoulder (**5**: 235, 72800; 254 (sh), 41700; **3**: 237, 100900; 254 (sh), 68800) at similar wavelengths but with intensities about three and four times, respectively, greater than those of *o*-terphenyl (233, 29100; 251 (sh), 13300) (Fig. 2).

Analogously, the absorption curve of **4** (K-band: 240, 60300; 254 (sh), 44800), which has two isolated *o*-phenylene rings, was observed to be related closely with that of *o*-terphenyl (Fig. 2).

Finally, the spectrum of **6** displayed an intense K-band (252, 119700) at a slightly longer wavelength with an intensity substantially the same as that of a linear isomer, *m*-septiphenyl (249, 118200)[2b)] (Fig. 3). This close relationship between the spectra of two isomers was also observed for **1** (252, 57800)[17)] and the isomeric *m*-quaterphenyl (248, 57400),[2b)] and for 5′,5″-diphenyl-*m*-quaterphenyl (253, 96500)[2c)] and the isomeric *m*-sexiphenyl (249, 95200).[2b)] These results suggest that the π-π interactions across the pivot bonds of the 1,3,5-C_6H_3 ring in **6**, **1**, and 5′,5″-diphenyl-*m*-quaterphenyl are rather similar to those of *m*-linkages in their isomeric *m*-polyphenyls. In the linear *m*-polyphenyls, it is known that the UV spectra reveal the K-band at substantially the same wavelength as that of the K-band of biphenyl with an intensity, which is approximately proportional to the maximum number of separate biphenyl groupings possible (or to the number of pivot bonds).[2b,20)] This suggests that the twisting of the pivot bond of *m*-polyphenyls in solution is very similar to that of biphenyl.

The foregoing discussion led us to the conclusion that the dihedral angle of the pivot bond of 1,3,5-C_6H_3 in the branched-chain polyphenyls in solution is very similar to that of biphenyl, *ca.* 20°.

Experimental

The melting points were determined with a Mettler FP-51 or FP-52 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 MS were recorded on a Hitachi RMU-6E mass spectrometer.

Iodobenzene (**8**) was obtained commercially and distilled before use. 2- (**9**), 3- (**10**), and 4-Iodobiphenyl (**11**),[7] 3,5-diiodo-1-nitrobenzene (**13**),[2c] and 5′-iodo-*m*-terphenyl (**14**)[2c] were prepared as reported previously. 1,3,5-Triiodobenzene (**12**) (mp 181.4—182.5 °C (lit.[21] mp 182—184 °C)) was prepared by direct iodination of aniline followed by deamination of the resultant triiodoaniline. Yield, 54% (based on aniline).

5′-Nitro-2,2″-diphenyl-*m*-terphenyl (15)——A solution of **13** (3.75 g) and **9** (16.8 g) in dimethylformamide (DMF) (46 ml) was brought to reflux. Copper powder (20.3 g) was added in four portions at intervals of 5 h with stirring, after which the mixture was refluxed for 10 h. The hot reaction mixture was filtered, and the solid material was washed several times with hot DMF and benzene. The filtrates were combined and washed with 10% hydrochloric acid and water. After removal of the solvents *in vacuo*, the residual oil (12.0 g) was dissolved in a cyclohexane–benzene (4 : 1, v/v) mixture (C–B (4 : 1)) and subjected to chromatography on alumina with the same solvent as the eluent to give biphenyl (**18**) (colorless leaves from ethanol; mp 69.9 °C; 4.7 g) and *o*-quaterphenyl (**19**) (colorless cubes from ethanol; mp 117.8 °C (lit.[22] mp 118 °C); 1.6 g). Subsequent elution with C–B (3 : 2) provided 3-nitro-*o*-terphenyl (pale yellow rhombs from ethanol; mp 87.3 °C (lit.[23] mp 88—89.5 °C); 0.6 g) and **15** as pale yellow needles from ethanol; mp 160.8 °C; 0.44 g (10%). *Anal.* Calcd for $C_{30}H_{21}NO_2$: C, 84.29; H, 4.95; N, 3.28. Found: C, 84.26; H, 4.88; N, 3.44.

5′-Amino-2,2″-diphenyl-*m*-terphenyl (16)——A solution of **15** (3.0 g) in hot benzene (100 ml) was treated with activated iron (30.0 g) by a method similar to that of Hazlet and Dornfeld.[24] After filtration, the solvent of the filtrate was distilled off, then the residual solid was crystallized from benzene to yield **16** as colorless cubes; mp 241.7 °C; 2.0 g (72%). *Anal.* Calcd for $C_{30}H_{23}N$: C, 90.65; H, 5.83; N, 3.52. Found: C, 90.80; H, 5.65; N, 3.48.

5′-Iodo-2,2″-diphenyl-*m*-terphenyl (17)——Isoamyl nitrite (1.1 g) was added to a solution of **16** (2.0 g) and concentrated sulfuric acid (1.4 ml) in dioxane (70 ml) at 10—15 °C, then the mixture was stirred at the same temperature for 2 h. The resulting cold suspension of diazonium salt was added to a cold solution of potassium iodide (1.5 g) in water (2 ml) with stirring, and the mixture was stirred at 0 °C for 1 h, at 50 °C for 1 h, and at 80 °C for 0.5 h, then cooled. The insoluble solid formed by addition of water was extracted with benzene, and the organic layer was washed successively with water, sodium thiosulfate solution, sodium hydroxide solution, and then water. After removal of the solvent, the residue (2.80 g) was subjected to chromatography on alumina with C–B (9 : 1) to give **17** as colorless cubes from ethanol; mp 150.3 °C; 1.18 g (46%). *Anal.* Calcd for $C_{30}H_{21}I$: C, 70.87; H, 4.16. Found: C, 71.06; H, 4.44.

General Procedure for the Preparation of Polyphenyls——The iodide (**17**) or a mixture of two kinds of iodides in a reaction tube (ϕ 2.0 × 20 cm) was heated in an oil bath at 250—275 °C (185—210 °C for the preparation of **4**), and then copper powder was added in portions with stirring over a 2-h period, after which the mixture was heated at 255—280 °C for an additional hour. After cooling, the reaction product was extracted with hot benzene, then the solvent was distilled off. The benzene extract was subjected to chromatography on alumina using cyclohexane, C–B mixtures, and benzene successively as eluents to afford the polyphenyl and by-products.

3,5-Diphenyl-*p*-terphenyl (**2**): A mixture of **14** (1.07 g) and **11** (2.52 g) was heated with copper powder (7.0 g). The eluate with C–B (4 : 1) provided **18** (34 mg) and *m*-terphenyl (**20**) (colorless needles from ethanol; mp 86.7 °C; 13 mg). The eluates with C–B (4 : 1) and C–B (1 : 1), and with benzene afforded **2** and *p*-quaterphenyl (**21**) (colorless plates from benzene; mp 317 °C (lit.[25] mp 317.7—318.7 °C); 108 mg), respectively. **2**: Colorless needles from ethanol; mp 134.1 °C (lit.[26] mp 134—135 °C); 290 mg (25%). UV $\lambda_{\text{max}}^{\text{cyclohexane}}$ nm (ε): 202 (73100), 263 (52300), 280 (infl) (40600).

5′,5″-Di(2-biphenylyl)-2,2‴-diphenyl-*m*-quaterphenyl (**3**): The iodoquinquephenyl (**17**) (0.51 g) was treated with copper powder (0.51 g). The eluate with C–B (4 : 1) afforded 2,2″-diphenyl-*m*-terphenyl (**22**) (colorless prisms from ethanol; mp 165.0 °C (lit.[11] mp 155.5—156.6 °C, lit.[2a] mp 164.2 °C); 155 mg) and **3**. **3**: Colorless prisms from C–B (4 : 1); mp 243.1 °C; 135 mg (35%). UV $\lambda_{\text{max}}^{\text{cyclohexane}}$ nm (ε): 197 (140800), 237 (100900), 254 (sh) (68800). *Anal.* Calcd for $C_{60}H_{42}$: C, 94.45; H, 5.55. Found: C, 94.25; H, 5.69. MS *m/e*: 762 (M^+).

2,5′,2″-Triphenyl-*m*-terphenyl (**4**): A mixture of **17** (0.51 g) and **8** (5.10 g) was heated with copper powder (8.3 g). The eluates with cyclohexane and C–B (9 : 1) provided **18** (930 mg) and **4**. **4**: Colorless needles from ethanol; mp

171.6 °C; 160 mg (35%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 198 (92800), 240 (60300), 254 (sh) (44800). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 93.98; H, 5.68. MS *m/e*: 458 (M^+).

3,5-Di(2-biphenylyl)-*o*-terphenyl (**5**): A mixture of **12** (4.56 g) and **9** (25.20 g) was heated with copper powder (38.1 g). The eluate with cyclohexane gave **19** (6250 mg). The eluate with C–B (5 : 1) afforded **22** (232 mg) and **5**. **5**: Colorless cubes from cyclohexane; mp 217.0 °C; 1180 mg (22%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 196 (101900), 207 (sh) (87100), 235 (72500), 254 (sh) (41700). *Anal.* Calcd for $C_{42}H_{30}$: C, 94.34; H, 5.66. Found: C, 94.07; H, 5.39. MS *m/e*: 534 (M^+).

5′′-(3-Biphenylyl)-*m*-quinquephenyl (**6**): A mixture of **12** (4.56 g) and **10** (25.20 g) was treated with copper powder (38.1 g). The eluate with cyclohexane gave *m*-quaterphenyl (**23**) (colorless plates from ethanol; mp 86.8 °C (lit.[27] mp 85.5—86 °C); 5140 mg). The eluates with C–B (4 : 1) and with C–B (7 : 3) provided *m*-quinquephenyl (**24**) (colorless needles from ethanol; mp 114.2 °C (lit.[28] mp 114—115 °C); 53 mg) and **6**, respectively. **6**: Colorless needles from ethanol; mp 143.1 °C; 1388 mg (26%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 204 (80000), 252 (119700). *Anal.* Calcd for $C_{42}H_{30}$: C, 94.34; H, 5.66. Found: C, 94.36; H, 5.79. MS *m/e*: 534 (M^+).

3,5-Di(4-biphenylyl)-*p*-terphenyl (**7**): A mixture of **12** (4.56 g) and **11** (25.20 g) was heated with copper powder. The eluate with benzene afforded **7**, 4,4′′-diphenyl-*m*-terphenyl (**25**) (colorless prisms from benzene; mp 271.0 °C (lit.[29] mp 264—266 °C, lit.[30] mp 273.4—273.8 °C); 960 mg) and **21** (2480 mg). **7**: Colorless needles from benzene; mp 236.7 °C (lit.[13] mp 230.5—231 °C, lit.[12] mp 241 °C); 1075 mg (20%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 204 (89300), 285 (89900).

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References and Notes

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