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Syntheses and Spectral Properties of Several Branched-chain Polyphenyls containing 1,2,3-Trisubstituted Ring(s)[1]

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Nine polyphenyls, including six new compounds, 3′-phenyl-*o*-quaterphenyl (**3**), 2,6-diphenyl-*m*- (**4**), 2,6-diphenyl-*p*-terphenyl (**5**), 2,6,5′-triphenyl-*m*-terphenyl (**6**), 2′,2″-diphenyl-*m*-quaterphenyl (**8**), and 2′-(phenyl-d_5)-*m*-terphenyl (**9**), were synthesized by the Ullmann coupling reaction of aryl iodide(s) or by the Kharash-type coupling reaction of deuterated aryl Grignard reagent with aryl iodide catalyzed by bis(acetylacetonato)-nickel(II). Infrared studies of the polyphenyls showed that the range of 730—770 cm^{-1}, generally accepted as the position of the C–H out-of-plane bending bands of phenyl rings, should be widened slightly to 730—781 cm^{-1}. The high frequency bands were found to be correlated closely to the sterically overcrowded structure of terminal rings. Proton magnetic resonance spectral studies indicated that the characteristic spectral features of the polyphenyls containing 1,2,3-trisubstituted ring(s) were fully consistent with their conformational aspects deduced from stereomodels. Ultraviolet spectral data suggested that the most probable conformation of the highly crowded 3′,6″-diphenyl-*o*-quaterphenyl (**1**) is one in which the interplanar angles of the pivot bonds between the 1,2,3-trisubstituted ring and three benzene rings are rather smaller than those of the less crowded 2′-phenyl-*m*-terphenyl (**2**).

Keywords——Ullmann reaction; nickel-complex-catalyzed cross-coupling; quaterphenyl; deuterated quaterphenyl; quinquephenyl; sexiphenyl; polyphenyl; IR; UV; ^{1}H-NMR

In previous studies, a series of closely related linear polyphenyls up to octiphenyls has been synthesized in order to elucidate the relation between the structures and the physical properties of polyphenyls.[2] Spectral studies have shown that most of the linear polyphenyls studied displayed significant characteristics in their infrared (IR), ultraviolet (UV), and proton magnetic resonance (^{1}H-NMR) spectra.

The present work was undertaken to develop further the structure-property correlation study to polyphenyls of branched structure, wich might have different spectral behavior from linear polyphenyls. Thus, we synthesized seven branched-chain polyphenyls of symmetrical or unsymmetrical type (**1**—**6** and **8**), having one or two 1,2,3-trisubstituted benzene rings, and two other compounds (**7** and **9**) for comparison. The IR, UV, and ^{1}H-NMR spectra of the polyphenyls, including six new compounds (**3**—**6**, **8**, and **9**), were measured and their spectral characteristics, which originate from the number and conformation of the benzene rings in each molecule, are discussed.

For the syntheses of the polyphenyls (**1**—**8**), the Ullmann homo- or cross-coupling reaction of aryl iodides was employed.[2a—e,i] For that of **9** (a pentadeuterated analog of **2**), the Kharash-type Grignard cross-coupling reaction of phenyl-d_5-magnesium bromide (three-fold excess) and aryl iodide, in the presence of bis(acetylacetonato)nickel(II) as a catalyst, was used.[2f—h] Among the iodides used, iodobiphenyls (2- (**11**), 3- (**12**), and 4-iodobiphenyl (**13**)) were prepared as reported previously.[2a] The other key intermediates, iodoterphenyls (2′-iodo-*m*- (**14c**), 5′-iodo-*m*- (**15c**), and 3′-iodo-*o*-terphenyl (**16c**)) were obtained from the corresponding nitroterphenyls (2′-nitro-*m*- (**14a**), 5′-nitro-*m*- (**15a**), and 3′-nitro-*o*-terphenyl (**16a**)) *via* the corresponding aminoterphenyls (2′-amino-*m*- (**14b**), 5′-amino-*m*- (**15b**), and 3′-amino-*o*-terphenyl (**16b**)) in the usual manner.[2a] Iodobenzene (**10**) and bromobenzene-d_5 (**17**) are commercially available. For the Ullmann cross-coupling reaction, a mixture of the iodoter-

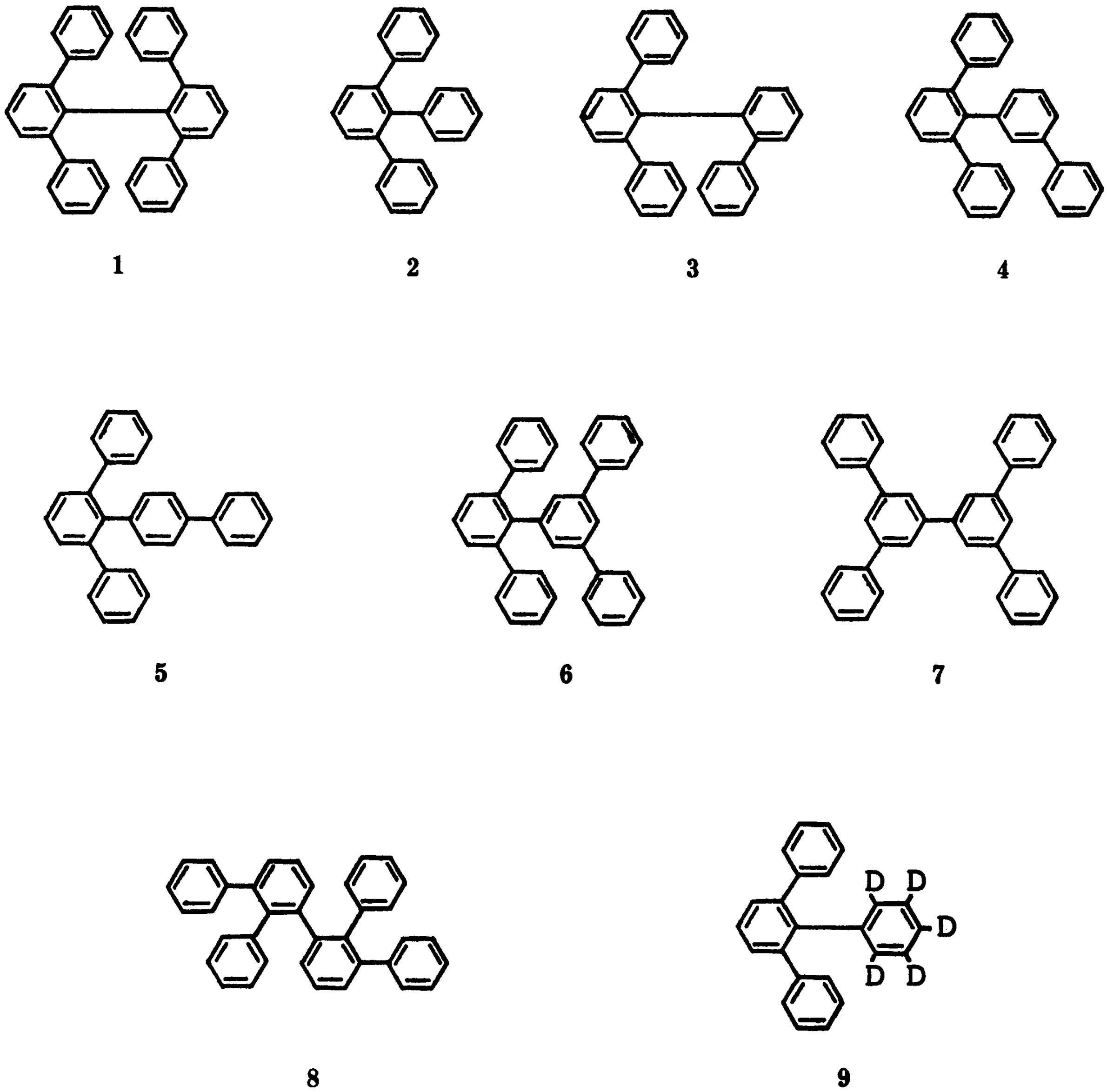


Chart 1

phenyl **14c** and a four- to eight-fold excess of a simpler iodide, **10**—**13**, or an equimolar mixture of two kinds of iodoterphenyls, **14c** and **15c**, was used. Both homo- and cross-coupling of iodides were carried out at 260—265°C (180—190°C for the preparation of **2**) 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 (**1**—**8**) showed IR spectral data consistent with their structures and gave acceptable results in elemental analyses and molecular weight determinations by mass spectroscopy. The melting points of **2** and **7** fell within 1—2°C of the reported values.[3,4] Further, the melting point of **1** coincided with that of an authentic sample prepared alternatively by us using the Kharash-type Grignard cross-coupling of *m*-terphenyl-2′-ylmagnesium iodide with 2′-iodo-*m*-terphenyl in the presence of bis(acetylacetonato)nickel(II).[2g] The high melting point of **1** (396°C), which is remarkable in comparison with those of other known sexiphenyls (except *p*-sexiphenyl, mp 465°C),[5,6] might be a result of the unique molecular shape. All the pure polyphenyls except **1** were obtained in yields of 19—64%. The very low yield of **1** probably arose from the difficulty in its isolation because of its low solubility. In all of the Ullmann coupling experiments except in the preparations of **2** and **3**, all of the reasonably

TABLE I. Syntheses of Branched-chain Polyphenyls containing 1,2,3-Trisubstituted Ring(s)

Reactants	Procedure[a]	Polyphenyl (Yield %)	Other product
14c	A	**1** (3)	*m*-Terphenyl (**19**)
14c+10	A	**2** (58)	Biphenyl (**18**), **1**
14c+11	A	**3** (39)	**18**, *o*-Quaterphenyl (**20**), **1**
14c+12	A	**4** (45)	**18**, **19**, *m*-Quaterphenyl (**23**), **1**
14c+13	A	**5** (39)	**18**, **19**, *p*-Quaterphenyl (**21**), **1**
14c+15c	A	**6** (19)	**19**, **7**, **1**
16c	A	**8** (64)	*o*-Terphenyl (**22**)
14c+17	B	**9** (35)	**19**, Biphenyl-d_{10} (**24**)

[a] A, Ullmann reaction; B, Grignard reaction.

expected by-products [a) the hydrogenolytic deiodination product(s) of starting iodide(s) and b) the homo-coupling products of the starting iodides (in the case of cross-coupling reactions)] were fully isolated.

The IR spectra of the polyphenyls were measured by the KBr-disk method. The characteristic bands (680—920 cm^{-1}) of six polyphenyls (**3**—**8**) are shown in Table II. These bands were consistent with the substitution patterns of the benzene rings constituting each polyphenyl.

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

3		**4**		**5**	
677 w		679 w		699 s	$\gamma_{\text{C-C}}$
698 s	$\gamma_{\text{C-C}}$	700 s	$\gamma_{\text{C-C}}$	731 m	
703 sh s		708 sh s		756 s	$\gamma_{\text{C-H}}(\mathrm{M})$
729 w		729 w		763 s	
742 s	$\gamma_{\text{C-H}}(\mathrm{M},o)$	754 s	$\gamma_{\text{C-H}}(\mathrm{M})$	771 s	
759 s		757 s		804 w	$\gamma_{\text{C-H}}(\mathrm{as})$
769 sh m		765 s		821 m	
777 m		796 m	$\gamma_{\text{C-H}}(m)$	840 m	$\gamma_{\text{C-H}}(p)$
782 m	$\gamma_{\text{C-H}}(o)$	810 m	$\gamma_{\text{C-H}}(\mathrm{as})$	852 m	
821 m	$\gamma_{\text{C-H}}(\mathrm{as})$	842 w		905 vw	$\gamma_{\text{C-H}}(\mathrm{M})$
836 w		899 m	$\gamma_{\text{C-H}}(m)$	917 vw	
842 w		907 vw	$\gamma_{\text{C-H}}(\mathrm{M})$		
910 w	$\gamma_{\text{C-H}}(\mathrm{M})$	916 vw			
917 w					

6		**7**		**8**	
698 s	$\gamma_{\text{C-C}}$	703 s	$\gamma_{\text{C-C}}$	700 s	$\gamma_{\text{C-C}}$
700 sh s		712 m		725 m	
713 m		759 s	$\gamma_{\text{C-H}}(\mathrm{M})$	742 s	$\gamma_{\text{C-H}}(\mathrm{M})$
753 s	$\gamma_{\text{C-H}}(\mathrm{M})$	763 sh s		750 sh m	
761 s		864 s	$\gamma_{\text{C-H}}(\mathrm{sym})$	760 s	
767 s		879 w		769 m	
808 m	$\gamma_{\text{C-H}}(\mathrm{as})$	887 w		781 m	
829 w		893 w		806 m	$\gamma_{\text{C-H}}(\mathrm{as})$
846 w		917 vw	$\gamma_{\text{C-H}}(\mathrm{M})$	818 w	
884 m	$\gamma_{\text{C-H}}(\mathrm{sym})$			842 w	
900 w	$\gamma_{\text{C-H}}(\mathrm{M})$			912 m	$\gamma_{\text{C-H}}(\mathrm{M})$
907 vw					

[a] v, very; s, strong; m, medium; w, weak; sh, sholder. $\gamma_{\text{C-C}}$ 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*, sym, and as in parentheses refer to mono- and to *ortho*-, *meta*-, and *para*-substituted, and 1,3,5- and 1,2,3-trisubstituted rings, respectively.

Table III. ^{1}H-NMR Spectral Data for Branched-chain Quater- to Sexiphenyls in $CDCl_3$[a]

1	6.57—7.35 (26H, m, all protons)
2	6.75—7.03 (5H, m, 2'-C_6H_5 7.07—7.14 (10H, m, 1'- and 3'-C_6H_5) 7.43 (3H, s, C_6H_3)
3	7.17—7.53 (3H, m, AB_2 system, C_6H_3) 6.61—7.14 (19H, m, other protons)
4	7.15 (10H, s, 2- and 6-C_6H_5) 7.47 (3H, s, C_6H_3) 6.71—7.33 (9H, m, *m*-$C_6H_4 \cdot C_6H_5$)
5	6.88 and 7.24 (4H, AA' BB'-q, *J*=8.4 Hz, $C_{2'}$, $C_{6'}$ and $C_{3'}$, $C_{5'}$H) 7.13 (10H, s, 2- and 6-C_6H_5) 7.46 (3H, s, C_6H_3) 7.22—7.58 (5H, m, *p*-$C_6H_4 \cdot C_6H_5$)
6	7.02 (2H, d, *J*=1.7 Hz, $C_{2'}$ and $C_{6'}$H) 7.20 (10H, s, 2- and 6-C_6H_5) 7.41 (1H, t, *J*=1.7 Hz, $C_{4'}$-H) 7.50 (3H, s, C_6H_3) 7.07—7.35 (10H, m, 3'- and 5'-C_6H_5)
7	7.36—7.79 (20H, m, C_6H_5) 7.80—7.91 (6H, m, AB_2 system, C_6H_3)
8	6.37—6.65 (4H, m, *o*- and *o'*-H of 2'- and 2''-C_6H_5) 7.27 (6H, s, C_6H_3) 6.71—7.14 (16H, m, other protons)
9	7.07—7.14 (10H, m, C_6H_5) 7.44 (3H, s, C_6H_3)

a) δ (ppm) from internal standard TMS.

A series of strong or medium bands of **1**, **2**, **5**, and **8** in the 742—781 cm^{-1} region should be assigned to C–H out-of-plane deformation vibrations of five adjacent hydrogens in the terminal rings. Although this region includes absorptions at rather higher frequencies than the 730—770 cm^{-1} region noted by Bellamy[7] and others,[8] the present assignments are supported by the following considerations.

1) Each of the following analogous polyphenyls, all of which have terminal rings of sterically overcrowded structure, shows strong or medium bands in the region up to 771—786 cm^{-1}: 2'-phenyl-*p*-terphenyl (756 s, 771 m, 781 m), 2',6'-diphenyl-*p*-terphenyl (751 m, 765 s, 775 s), 3',5'-diphenyl-*p*-quaterphenyl (758 s, 762 s, 770 s, 776 s, 786 m), and 3',5',2'',6''-tetraphenyl-*p*-quaterphenyl (742 s, 757 s, 768 s, 783 m).[9] Because the compounds have neither three nor four adjacent ring hydrogens, both of which generally reveal confusing absorptions in the similar region, the absorptions up to 786 cm^{-1} can reasonably be assigned to C–H out-of-plane deformation bands of the terminal rings.[10]

2) Each of the polyphenyls (**1**—**6** and **8**) shows the C–H out-of-plane deformation bands of three adjacent ring hydrogens in the range of slightly higher frequency, 804—821 cm^{-1}.[11]

The foregoing results on the C–H out-of-plane deformation bands of terminal ring hydrogens suggest a close correlation between the high frequency bands and the sterically overcrowded structure of terminal rings.

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 **2** (δ 7.43), **4** (δ 7.47), **5** (δ 7.46), and **6** (δ 7.50) show one 3H singlet near δ 7.46, which can be assigned to the three adjacent protons of the 1,2,3-trisubstituted ring by comparison with the three-proton signal of **9** (δ 7.44), which is a deuterated analog of **2**. Besides, the chemical shift of one 3H singlet corresponds to that of the *o*-phenylene proton signal in *o*-terphenyl (δ 7.40, s)[2f] and in 2-phenyl-*p*-terphenyl (δ 7.44, s).[2f] The appearance of a 3H singlet near δ 7.46 in each of the spectra (for **2** and **4**—**6**) is consistent with the hypothesis that the three contiguous benzene rings of the 1-, 2-, and 3-positions lie face to face with each other, giving an important clue to their highly non-planar structures.

In the spectrum of **8**, however, a similar 6H singlet is observed at slightly higher field (δ 7.27) as compared with those of **2** and **4**—**6**; the shift presumably reflects ring current effects caused by the presence of the 2′- and 2″-phenyl rings. Further, in the case of **3**, a 3H AB_2 multiplet in the range of δ 7.17—7.53 is attributable to be affected by the unequal anisotropic effects of the phenyl ring at the 2″-position. Analogously, compound **1**, which contains the structure of **3**, also shows not a singlet but a multiplet of 6H.

An apparent 10H singlet near δ 7.15 in each of **4** (δ 7.15), **5** (δ 7.13), and **6** (δ 7.20) is assignable to the protons of two phenyl rings at the 1- and 3-positions in the 1,2,3-trisubstituted ring system, by comparison with the singlet of phenyl protons of *o*-terphenyl (δ 7.16).[2f)] In the spectra of **1**, **2**,[12)] **3**, and **9**, however, no apparent singlet of phenyl protons is observed.

An apparent 4H AA′BB′-q pattern of **5** (δ 6.88 and 7.24, J=8.4 Hz), assignable to the *p*-phenylene protons at the $C_{2'}$, $C_{6'}$- and $C_{3'}$,$C_{5'}$-positions, is observed at higher field as compared with the chemical shift of the *p*-phenylene protons in *p*-terphenyl (δ 7.68).[2f)] The magnitude of the high-field shifts (0.80 ppm for *o*,*o*′-H, 0.44 ppm for *m*,*m*′-H) are about twice those of the *p*-phenylene protons of 2-phenyl-*p*-terphenyl (0.47 ppm for *o*,*o*′-H, 0.22 ppm for *m*,*m*′-H).[2f)] In addition, the high-field shifts in both compounds undoubtedly reflect the ring current effects caused by the presence of phenyl ring(s) adjacent to the di- or trisubstituted ring, and hence provide information regarding their non-planar structures.

In the case of **6**, the high-field shifts (*ca.* 0.8 ppm) of $C_{2'}$– and $C_{6'}$–H (δ 7.02, d, J=1.7 Hz) as compared with the chemical shift of C_2–, C_4–, and C_6–H (δ 7.78, s) of 1,3,5-triphenylbenzene[9)] probably reflect the ring current effects caused by the presence of two phenyl rings at the 2- and 6-positions. In addition, the chemical shift of $C_{4'}$–H (δ 7.41, t, J=1.7 Hz) also suggests

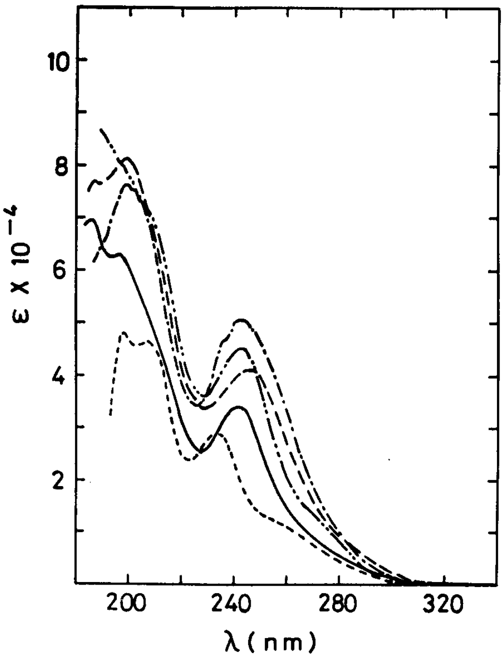


Fig. 1. UV Spectra of Terphenyl, Quaterphenyl, Quinquephenyls, and Sexiphenyl in Cyclohexane

————, 2′-phenyl-*m*-terphenyl (**2**);
– – – – –, 3′-phenyl-*o*-quaterphenyl (**3**);
—·—·—, 2,6-diphenyl-*m*-terphenyl (**4**);
— — — —, 2′,2″-diphenyl-*m*-quaterphenyl (**8**);
··········, *o*-terphenyl.

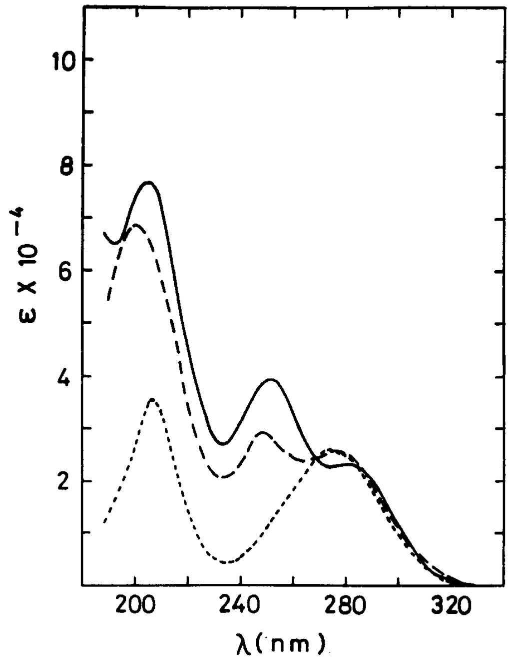
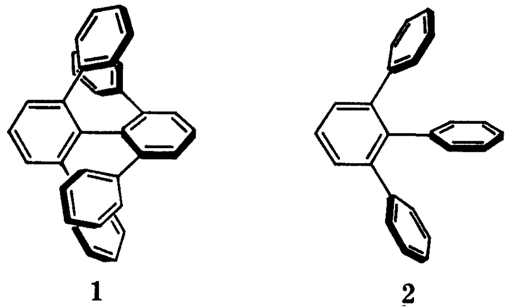


Fig. 2. UV Spectra of Terphenyl, Quaterphenyl and Quinquephenyl in Cyclohexane

————, 2,6-diphenyl-*p*-terphenyl (**5**);
– – – – –, 2-phenyl-*p*-terphenyl;
··········, *p*-terphenyl.



1 **2**

Chart 2

the presence of ring current effects caused by the same phenyl rings.

The foregoing results indicate that the characteristic ^{1}H-NMR spectral features of the branched-chain polyphenyls studied are fully compatible with their conformational aspects deduced from Dreiding stereomodels.

The UV spectra of the polyphenyls (**1**—**8**) 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 185—205 nm and the K-band in the broad region of 240—280 nm.

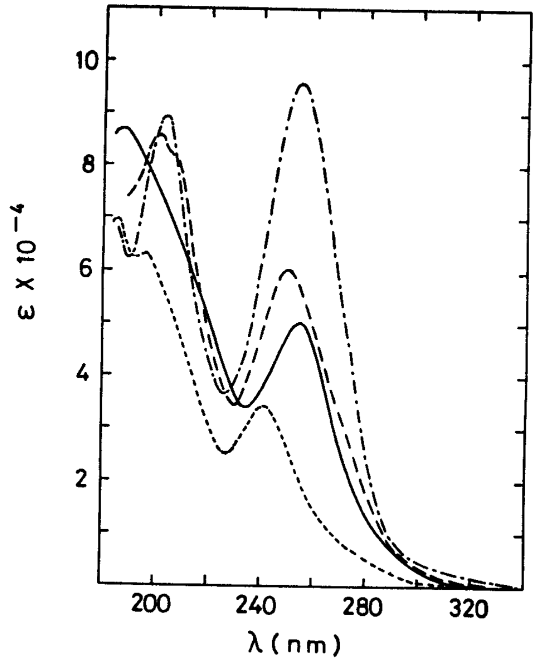


Fig. 3. UV Spectra of Quaterphenyl and Sexipheyls in Cyclohexane

———, 3′,6″-diphenyl-*o*-quaterphenyl (**1**);
--------, 2,6,5′-triphenyl-*m*-terphenyl (**6**);
—·—·—, 5′,5″-diphenyl-*m*-quaterphenyl (**7**);
··········, 2′-phenyl-*m*-terphenyl (**2**).

In the spectrum of **2**, the simplest member of the polyphenyls (**1**—**6** and **8**) containing 1,2,3-trisubstituted ring(s), the K-band (242 nm, $\varepsilon=33800$) appeared at shorter wavelength as compared with that of *o*-terphenyl (251 (sh) nm, $\varepsilon=13300$).[2b,13] As pointed out by Buza and Polaczkowa,[14] the hypsochromic shift of the K-band in the spectrum of **2** suggests a greater restriction of π-π interaction, due to the steric interference of three contiguous benzene rings.

In the cases of **3** (245, 40700), **4** (243, 51700), and **8** (243, 45800), the K-band wavelengths were obviously very similar to that of **2** (242, 33800) (Fig. 1), suggesting that the interplanar angles of the pivot bonds between the 1,2,3-trisubstituted ring and three benzene rings of each compound are rather similar to those of **2** (Chart 2).

The K-band of **5** at 281 nm (23300) might be due to the π-π transition in the *p*-terphenyl unit, on the basis of a comparison with those of *p*-terphenyl (276, 25500) and 2-phenyl-*p*-terphenyl (249, 29100; 278, 25100).[2f] Further the spectrum of **5** displayed one more maximum (251, 40100) at longer wavelength than that of **2** (242, 33800) (Fig. 2). Analogous K-band shifts were also observed in the spectra of **1** (254, 50100) and **6** (250, 61000). These bathochromic shifts are compatible with a reduction of nonplanarity in the conformation of the three contiguous benzene rings in the branched-chain systems (Fig. 3). In addition, it should be emphasized that the spectrum of **1**, which probably has the most crowded conformation, displayed the K-band at the longest wavelength among those of the polyphenyls (except **5**) and moreover at rather longer wavelength than that of *m*-terphenyl (247, 36100),[2d] which corresponds to the molecular halves of **1**. In other words, the data suggest that the most probable conformation of highly crowded **1** in solution is one in which the interplanar angles of the pivot bonds between the 1,2,3-trisubstituted ring and three benzene rings are rather smaller than those of the less crowded **2**. This conformation of **1** appears to minimize steric hindrance in the highly crowded system (Chart 2).

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 (**10**) was a commercial product, and was distilled before use. 2- (**11**), 3- (**12**), and 4-Iodobiphenyl (**13**)[2a)] and 1,3-dibromo-2-nitrobenzene[2d)] were prepared as reported previously. Bromobenzene-d_5 (**17**) was obtained commercially and used without further purification (isotopic purity: 99 atom%, Merck).

2′-Nitro-*m*-terphenyl (14a)——A mixture of 1,3-dibromo-2-nitrobenzene (3.7 g, 13.2 mmol) and **10** (32.6 g, 160 mmol) in a reaction tube (ϕ3.5 × 20 cm) was heated in an oil bath at 185—190°C, and then copper powder (56.0 g, 880 mg-atom) was added to the mixture in portions under stirring over a 3-h period, after which the mixture was heated at 210—220°C for an additional hour. After cooling, the reaction product was extracted with hot benzene, then the solvent was distilled off. The residue (18.3 g) was dissolved in cyclohexane and chromatographed on alumina with the same solvent as the eluent. The eluate was concentrated and the residue was crystallized from ethanol to provide biphenyl (**18**) (colorless leaves; mp 69.7°C; 5.6 g). Subsequent elutions with cyclohexane–benzene (4: 1, v/v) mixture (C–B (4: 1)) and C–B (3: 2) afforded **14a** as pale yellow needles from ethanol; mp 126.4°C; yield, 2.6 g (72%). *Anal.* Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.40; H, 4.91; N, 4.93.

2′-Amino-*m*-terphenyl (14b)——A solution of **14a** (7.0 g) in hot benzene (300 ml) was treated with activated iron by a method similar to that of Hazlet and Dornfeld.[15)] After filtration, hydrogen chloride was passed into the filtrate, then the precipitate formed was collected, washed with benzene, and dried. The amine salt was treated in the usual manner with aqueous alkali to yield the free amine (**14b**) as colorless plates from petroleum benzin; mp 78.5°C; yield, 5.9 g (95%). *Anal.* Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.15; H, 6.10; N, 5.82.

2′-Iodo-*m*-terphenyl (14c)——A suspension of **14b** (4.9 g, 20 mmol) in concentrated sulfuric acid (1.8 ml) and water (30 ml) was diazotized with sodium nitrite (2.5 g) in water (5 ml) at 0—5°C with stirring for 4 h. The cold suspension of diazonium salt thus formed was added to a cold solution of potassium iodide (4.0 g) in water (4 ml) with stirring, and the mixture was stirred at the same temperature for 1 h, then heated at 40°C for 1 h and at 70°C for 0.5 h, then cooled. The benzene extract of the product was washed with water, sodium thiosulfate solution, water, 3% sodium hydroxide solution, and then water. After removal of the solvent, the residue (7.7 g) was chromatographed on alumina with C–B (9: 1) and C–B (4: 1) to provide **14c** as colorless needles from ethanol; mp 114.5°C (lit.[16)] mp 114.4°C); 5.7 g (80%). *Anal.* Calcd for $C_{18}H_{13}I$: C, 60.69; H, 3.68. Found: C, 60.90; H, 3.77.

5′-Nitro-*m*-terphenyl (15a)——2,6-Diiodo-*p*-nitroaniline, mp 244.7°C (lit.[17)] mp 243—245°C) was prepared by direct iodination of *p*-nitroaniline;[17)] yield, 44%.

2,6-Diiodo-*p*-nitroaniline (39.0 g) was dissolved in concentrated sulfuric acid (400 ml) and water (200 ml) under heating with stirring. The solution was cooled to 0—5°C, then sodium nitrite (10.0 g) in water (100 ml) was added at 0—5°C, and the mixture was stirred at the same temperature for 2 h. The cold suspension of diazonium salt thus formed was added in portions to a suspension of Gattermann copper in dioxane (freshly prepared from copper sulfate (99.8 g)), and the resulting mixture was stirred at room temperature for 1 h then heated at 80°C for 0.5 h. After cooling, the copper powder was filtered off, then water was added to the filtrate to give an insoluble solid. The benzene extract of the solid was crystallized from ethanol to afford 3,5-diiodo-1-nitrobenzene as pale yellow needles; mp 103.5°C; 16.7 g (45%).

A mixture of 3,5-diiodo-1-nitrobenzene (3.8 g, 10 mmol) and **10** (24.5 g, 120 mmol) was treated with copper powder (41.3 g, 650 mg-atom) under conditions similar to those used in the preparation of **14a.** The hot benzene extract (8.8 g) was subjected to chromatography on alumina with C–B (9: 1) to provide **18** (4.7 g). Subsequent elution with C–B (5: 1) gave **15a** as pale yellow needles from ethanol; mp 106.2°C; 0.68 g (24%). *Anal.* Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.60; H, 4.58; N, 5.04.

5′-Amino-*m*-terphenyl (15b)——A benzene solution of **15a** (5.5 g) was reduced and the amine formed was separated as the hydrochloride as described for **14b**. **15b**·HCl: White powder; mp 101.7°C; 5.4 g (96%).

5′-Iodo-*m*-terphenyl (15c)——A suspension of **15b**·HCl (5.6 g) in concentrated sulfuric acid (1.9 ml) and water (34 ml) was diazotized with sodium nitrite (2.7 g) in water (5.4 ml), and the solution was treated with a solution of potassium iodide (4.4 g) in water (4.4 ml) as described for the preparation of **14c**. The benzene extract (7.0 g) was subjected to chromatography on alumina with C–B (9: 1) and C–B (4: 1) to give **15c** as colorless plates from ethanol; mp 99.5°C; 4.4 g (62%). *Anal.* Calcd for $C_{18}H_{13}I$: C, 60.69; H, 3.68. Found: C, 60.94; H, 3.53.

3′-Nitro-*o*-terphenyl (16a)——2-Amino-3-nitrobiphenyl, mp 54.2°C (lit.[18)] mp 44—45°C) was prepared by acetylation of 2-aminobiphenyl[19)] followed by nitration[18)] and hydrolysis of the product; yield, 15% (based on 2-aminobiphenyl).

A suspension of 2-amino-3-nitrobiphenyl (21.4 g) in concentrated sulfuric acid (100 ml) was diazotized with sodium nitrite (7.5 g) in ice (250 g) at 0—5°C with stirring for 2.5 h. After removal of the insoluble solid by filtration, the cold filtrate was added in portions to a solution of potassium iodide (20.0 g) in water with stirring. The chloroform extract was distilled *in vacuo* to give a yellow solid (bp 176—179°C/4 mmHg), which provided 2-iodo-3-nitrobiphenyl as pale yellow needles from ethanol; mp 90.1°C (lit.[18] mp 90—91°C); 22.9 g (71%). *Anal.* Calcd for $C_{12}H_8INO_2$: C, 44.33; H, 2.48; N, 4.31. Found: C, 44.16; H, 2.60; N, 4.07.

A mixture of 2-iodo-3-nitrobiphenyl (7.5 g, 23 mmol) and **10** (25.0 g, 123 mmol) was heated with copper powder (43.9 g, 690 mg-atom) as described for **14a**. The hot benzene extract (16.4 g) was treated with C–B (4: 1) (200 ml), and the insoluble solid was filtered off. The filtrate was chromatographed on alumina with the same solvent as the eluent to afford **18** (9.9 g) and **16a** as pale yellow leaves from ethanol; mp 116.3°C; 2.6 g (41%). *Anal.* Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.29; H, 4.57; N, 5.11.

3′-Amino-*o*-terphenyl (16b)——A solution of **16a** (3.5 g) in benzene was reduced in the same manner as described above to give **16b** as pale yellow needles from ethanol; mp 97.7°C; 2.6 g (84%). *Anal.* Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.33; H, 6.02; N, 5.70.

3′-Iodo-*o*-terphenyl (16c)——A suspension of **16b** (2.6 g) in sulfuric acid (1.4 ml) and water (16 ml) was worked up in the usual manner. The crude product (4.3 g) was purified by chromatography on alumina with C–B (4: 1) to provide **16c** as colorless needles from ethanol; mp 112.2°C; 2.1 g (56%). *Anal.* Calcd for $C_{18}H_{13}I$: C, 60.69; H, 3.68. Found: C, 60.81; H, 3.53.

Preparation of 3′,6″-Diphenyl-*o*-quaterphenyl (**1**)——The iodoterphenyl **14c** (1.07 g, 3.0 mmol) in a reaction tube (ϕ1.5 × 20 cm) was heated in an oil bath at 260—265°C, and then copper powder (1.6 g, 25 mg-atom) was added in portions under stirring over a 2-h period, after which the mixture was heated at 265—270°C for 1 h. After cooling, the reaction product was extracted with hot benzene, then the solvent was distilled off. The benzene extract thus obtained (0.60 g) was chromatographed on alumina with cyclohexane followed by C–B (19: 1) to separate *m*-terphenyl (**19**) (colorless needles from ethanol; mp 86.3°C; yield, 205 mg). Subsequent elutions with C–B (9: 1) and C–B (4: 1) gave **1**. The properties of **1** are as follows.

1: Colorless cubes from benzene; mp 396°C (lit.[2g] mp 396°C); yield, 22 mg (3.2%). IR (KBr) cm^{-1}: 677 w; 697 s (γ_{C-C}); 711 m; 745 s, 760 s, 776 m (γ_{C-H}, M); 812 m (γ_{C-H}, as); 828 w, 838 w; 905 w, 916 w (γ_{C-H}, M). UV $\lambda_{max}^{cyclohexane}$ nm (ε): 188 (87100), 254 (50100). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.12; H, 5.52. MS *m/e*: 458 (M^+).

Preparation of 2′-Phenyl-*m*-terphenyl (**2**)——A mixture of **14c** (1.07 g, 3.0 mmol) and **10** (5.06 g, 25.0 mmol) was heated with copper powder (14.0 g, 220 mg-atom) at 180—190°C for 2 h, then at 190—220°C for 1 h. The hot benzene extract of the product (2.91 g) was subjected to chromatography on alumina with cyclohexane to give **18** (884 mg). Subsequent elutions with C–B (19: 1), then C–B (9: 1), C–B (4: 1), and C–B (3: 2) afforded **2** and **1** (32 mg).

2: Colorless needles from ethanol; mp 158.4°C (lit.[2g,3] mp 156—157°C); 530 mg (57.6%). IR (KBr) cm^{-1}: 679 w; 701 s (γ_{C-C}); 745 s, 755 s, 761 s, 768 s, 775 s (γ_{C-H}, M); 808 w, 818 m (γ_{C-H}, as); 848 w, 854 w; 908 vw, 918 w (γ_{C-H}, M). UV $\lambda_{max}^{cyclohexane}$ nm (ε): 186 (69000), 196 (62600), 242 (33800) (lit.[14] UV λ_{max}^{EtOH} nm (ε): 239 (33600)). *Anal.* Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 93.90; H, 6.00. MS *m/e*: 306 (M^+).

Preparation of 3′-Phenyl-*o*-quaterphenyl (**3**)——A mixture of **14c** (1.07 g, 3.0 mmol) and **11** (3.47 g, 12.4 mmol) was treated with copper powder (7.9 g, 124 mg-atom) at 260—265°C for 2 h, then at 265—270°C for 1 h. The hot benzene extract of the product (3.18 g) was chromatographed on alumina with cyclohexane to provide **18** (37 mg). Successive elutions with cyclohexane, then with C–B (9: 1), and finally with C–B (9: 1), C–B (4: 1), and C–B (3: 2) afforded *o*-quaterphenyl (**20**) (colorless cubes from ethanol; mp 118.0°C (lit.[20] mp 118°C); 1302 mg), **3**, and **1** (29 mg), respectively.

3: Colorless needles from benzene–ethanol; mp 188.8°C; 446 mg (38.8%). UV $\lambda_{max}^{cyclohexane}$ nm (ε): 187 (76700), 198 (80500), 245 (40700). *Anal.* Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 93.95; H 6.09. MS *m/e* 382 (M^+).

Preparation of 2,6-Diphenyl-*m*-terphenyl (**4**)——A mixture of **14c** (1.07 g) and **12** (3.47 g) was treated as described for the preparation of **3**. The hot benzene extract of the product (2.96 g) was chromatographed on alumina with C–B (19: 1) to give **18** (186 mg) and **19** (19 mg). Subsequent elutions with C–B (9: 1) and C–B (4: 1), and then with C–B (4: 1) provided **4** and *m*-quaterphenyl (**23**) (colorless needles from ethanol; mp 87.0°C (lit.[21] mp 85.5—86°C); 1283 mg), and **1** (28 mg), respectively.

4: Colorless prisms from ethanol; mp 148.4°C; 512 mg (44.5%). UV $\lambda_{max}^{cyclohexane}$ nm (ε): 199 (77400), 201 (sh) (76000), 237 (sh) (48000), 243 (51700). *Anal.* Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.19; H, 5.94. MS *m/e*: 382 (M^+).

Preparation of 2,6-Diphenyl-*p*-terphenyl (**5**)——A mixture of **14c** (0.90 g, 2.5 mmol) and **13** (2.80 g, 10.0 mmol) was worked up as described for **3**. The hot benzene-soluble part of the product (1.45 g) was subjected to chromatography on alumina with C–B (19: 1) to afford **18** (70 mg) and **19** (20 mg). Subsequent elutions with C–B (9: 1) and C–B (4: 1), and then with benzene provided **5** and **1** (20 mg), and *p*-quaterphenyl (**21**) (colorless plates from benzene; mp 319°C (lit.[22] mp 317.7—318.7°C); 210 mg), respectively.

5: Colorless cubes from cyclohexane; mp 175.3°C; 380 mg (39.3%). UV $\lambda_{max}^{cyclohexane}$ nm (ε): 205 (77500), 251 (40100), 281 (23300). *Anal.* Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.22; H, 5.89. MS *m/e*: 382 (M^+).

Preparation of 2,6,5′-Triphenyl-*m*-terphenyl (6)——A mixture of **14c** (2.85 g, 8.0 mmol) and **15c** (2.85 g, 8.0 mmol) was heated with copper powder (8.0 g, 126 mg-atom) as described for **3**. The hot benzene extract of the product (4.38 g) was chromatographed on alumina with C–B (19: 1) to give **19** (809 mg), **1** (31 mg), and **6**. Subsequent elutions with C–B (9: 1) and C–B (4: 1) afforded 5′,5″-diphenyl-*m*-quaterphenyl (**7**).

6: Colorless prisms from ethanol–benzene; mp 256.6°C; 692 mg (18.9%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 201 (87100), 204 (sh) (84000), 250 (61000). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.39; H, 5.42. MS *m/e*: 458 (M^+).

7: Colorless needles from ethanol–benzene; mp 231.6°C (lit.[4] mp 231—232°C); 987 mg (53.8%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 203 (90000), 253 (96500). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.42; H, 5.56. MS *m/e*: 458 (M^+).

Preparation of 2′,2″-Diphenyl-*m*-quaterphenyl (8)——The iodoterphenyl **16c** (2.00 g, 5.6 mmol) was treated with copper powder (2.9 g) under conditions similar to those used for the preparation of **3**. The hot benzene extract of the product (1.30 g) was subjected to chromatography on alumina with cyclohexane to provide *o*-terphenyl (**22**) (colorless needles from ethanol; mp 56.4°C; 416 mg) and **8**.

8: Colorless prisms from ethanol–benzene (19: 1); mp 194.5°C, 823 mg (63.8%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 243 (45800). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 93.99; H, 5.66. MS *m/e*: 458 (M^+).

Preparation of 2′-(Phenyl-d_5)-*m*-terphenyl (9)——An ethereal solution of phenyl-d_5-magnesium bromide was prepared from bromobenzene-d_5 (**17**) (1.94 g, 12.0 mmol), magnesium turnings (0.29 g, 12.0 mg-atom), and absolute ether (15 ml) under nitrogen in the usual manner. To the Grignard reagent thus prepared, a solution of **14c** (1.42 g, 4.0 mmol) and bis(acetylacetonato)nickel(II) (11 mg, 0.04 mmol) in benzene (20 ml) was added all at once. The mixture was refluxed with stirring for 3 h, then hydrolyzed with dilute hydrochloric acid. The product was extracted with benzene. The organic layer was separated, washed with water, and dried. After the removal of the solvent, the residue was chromatographed on alumina with cyclohexane to give biphenyl-d_{10} (**24**). Subsequent elution with C–B (9: 1) afforded **19** (325 mg) and **9**.

9: Colorless needles from ethanol; mp 158.4°C; 429 mg (34.6%). *Anal.* Calcd for $C_{24}H_{13}D_5$: C, 92.56; H and D, 7.44. Found: C, 92.53; H and D, 7.32. MS *m/e*: 311 (M^+).

24: Colorless leaves from methanol; mp 68.5°C (lit.[23] mp 69—70°C); 134 mg. *Anal.* Calcd for $C_{12}D_{10}$: C, 87.81; D, 12.19. Found: C, 87.74; D, 12.30. MS *m/e*: 164 (M^+).

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References and Notes

1) This paper forms Part X of "Studies of Polyphenyls and Polyphenylenes." The preceding paper, Part IX: ref. 2*i*.

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10) Additional examples have been reported in refs. 2*c* and 2*h*.

11) While Bellamy (ref. 7) and Silverstein (ref. 8*a*) have noted the region of the same bands to be 750—810 and 760—820 cm^{-1}, respectively, we have already confirmed that these bands in the isolated and two consecutive *m*-phenylene rings of linear polyphenyls are generally found in the regions of 790—810 and 780—800 cm^{-1}, respectively (*cf.* refs. 2*a*—*e*, *h*, *i*).

12) The spectrum of **2**, measured on a spectrometer at 60 MHz, shows a sharp 10H singlet assignable to the protons of the 1′- and 3′-phenyl rings.

13) The dihedral angles in the *o*-terphenyl molecule in solution have been calculated as 43° by Suzuki. H. Suzuki, *Bull. Chem. Soc. Jpn.*, 33, 109 (1960); *cf.* J. Dale, *Acta Chem. Scand.*, **11**, 650 (1957).
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