Studies of Polyphenyls and Polyphenylenes. II.1) The Synthesis and Physical Properties of Polyphenyls Containing Para Linkage

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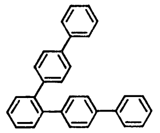
(Received January 28, 1980)

Twelve linear polyphenyls, including quinque- to octiphenyl, were synthesized by the Ullmann cross-coupling reaction of iodobiphenyl with diiodobenzene or iodoterphenyl. Ultraviolet spectral studies of the polyphenyls indicated that the positions of the K-bands above *ca.* 260 nm, regardless of the presence of *o*- or *m*-phenylene unit(s), may be considered to be an indication of the approximate number of consecutive *p*-phenylene units. Infrared studies also showed that the locations of strong or medium bands in the 815—850 cm^{-1} region may give the same information. The HMO calculations of the longest wavelength absorption bands of twenty-four polyphenyls were carried out. A comparison between the calculated and observed wavelengths gave rather good agreement, except in the cases of two compounds. The signals of the proton magnetic resonance spectra of eighteen polyphenyls were assigned tentatively. The correlations between the arrangement of the benzene rings and the spectral patterns are discussed.

In the previous paper, a series of closely related linear sexiphenyls have been synthesized to elucidate the relation between the structures and the physical properties of polyphenyls.1) Spectral studies have proved that the sexiphenyls having one or two *p*-phenylene rings displayed marked characteristics in both their infrared (IR) and ultraviolet (UV) absorption spectra.

In the present work, in order to investigate the spectral characteristics of a wide variety of polyphenyls, we synthesized twelve symmetrical and unsymmetrical linear polyphenyls (**1**—**12**), having one to four *p*-phenylene rings and not having them for comparison. The IR, UV, and proton magnetic resonance (^{1}H-NMR) spectra of the polyphenyls have been measured, and the relationship between the number and arrangement of the benzene rings and their physical properties, especially the characteristics due to the presence of *p*-linkage, has been discussed. In addition, we performed the HMO calculations of the longest wavelength absorption bands of the polyphenyls as well as of the closely related bi-, ter-, and quaterphenyls. The calculated results have been compared with the observed values.

For the synthesis of the polyphenyls, the Ullmann cross-coupling reaction of aryl halides has been used. Among the halides used, iodobiphenyls (2- (**13**), 3- (**14**), and 4-iodobiphenyl (**15**)) and iodoterphenyls (4-iodo-*o*- (**16**) and 4-iodo-*p*-terphenyl (**17**)) were prepared from commercial aminobiphenyls, aminonitrobenzene, and terphenyls. Diiodobenzenes (*o*- (**18**), *m*- (**19**), and *p*-diiodobenzene (**20**)) were commercially available. A mixture of iodobiphenyl and diiodobenzene in the molar ratio of 2 to 1 was subjected to the reaction at 230—275 °C with copper powder for the synthesis of symmetrical polyphenyls, while a mixture of an equimolar ratio of iodobiphenyl and iodoterphenyl was used for the synthesis of unsymmetrical ones. The polyphenyls and by-products thus obtained are given in Table 1.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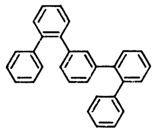
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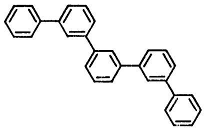
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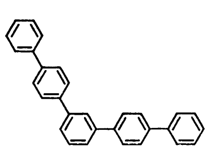
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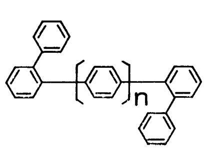
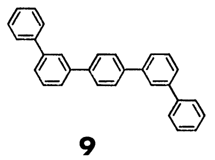

$n=1$: **5**
$n=2$: **6**
$n=3$: **7**
$n=4$: **8**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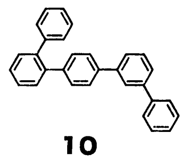
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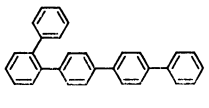
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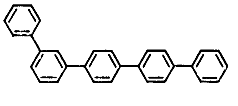
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The quinque-, septi-, and octiphenyl, thus prepared, showed IR spectral data consistent with their structure and gave acceptable results from elemental analysis and molecular weight determination. An alternative synthesis of eight quinquephenyls has been reported earlier by other workers (**1**,2) **2**,2) **3**,3) **4**,3b,4) **5**,3b) **9**,3b,5) **10**,2,6) **12**6)). Although the melting point of **2**7) does

TABLE 1. ULLMANN SYNTHESIS OF POLYPHENYLS

Iodide	Quinquephenyl (Yield/%)	Other products
15+**18**	**1**(16.4)	**21**, **27**
13+**19**	**2**(23.8)	**22**
14+**19**	**3**(8.1)	**26**
15+**19**	**4**(13.3)	**21**, **27**
13+**20**	**5**(13.9)	**22**, **6**, **7**, **8**
13+**16**	**5**(20.0)	**21**, **24**, **22**, **6**
14+**20**	**9**(13.1)	**21**, **26**
13+**18**	——	**21**, **22**, **23**
14+**16**	**10**(18.5)	**21**, **24**, **26**, **6**
15+**16**	**11**(24.7)	**21**, **24**, **27**, **6**
14+**17**	**12**(27.0)	**21**, **25**, **26**, **28**

not coincide with that of previous authors, those of the seven remaining quinquephenyls fall within 1—2 °C of those of the other authors.

The yields of all the pure quinquephenyls except **3** (8.1%) were 13—27%, and in all of the coupling experiments an appreciable amount of quaterphenyls formed by the homo-coupling of the corresponding iodobiphenyl were isolated as by-products. Further, in the coupling reactions using **16** or **17** as one of the iodo compounds (**13**+**16**, **14**+**16**, **15**+**16**, and **14**+**17**) a significant amount of sexiphenyls were obtained. An attempted coupling of **13**+**20** gave **6** (9.8%), **7** (7.4%), and **8** (2.4%), in which two to four *p*-phenylene rings are present respectively, together with **5** (13.9%). A similar coupling of **14**+**20**, however, failed to give the analogous sexi-, septi, and octiphenyls except for quinquephenyl, **9**. In the case of **13**+**18**, no corresponding quinquephenyl was isolated, but biphenyl (**21**, 11.1%), *o*-quaterphenyl (**22**, 30.2%), and triphenylene (**23**, 23.9%) were obtained. The formation of **23** may be comparable to that of phenyltriphenylene in the Ullmann cross-coupling reaction of 2,2′-diiodobiphenyl with **14** or **15**;[1] it shows favorable cyclization by the apparent elimination of hydrogen iodide to form a triphenylene ring.

The IR spectra of the twelve polyphenyls (**1**—**12**) were measured by the KBr-disk method. Let us now discuss the most characteristic bands due to C–H out-of-plane deformation vibrations in the 675—920 cm^{-1} region.

In the spectra of **1**, **4**, **5**, **9**, and **10**, which have one or two isolated *p*-phenylene rings, the strong or medium C–H out-of-plane bending vibration bands of two adjacent hydrogen atoms of *p*-phenylene rings were observed in the range 835—850 cm^{-1}. In the cases of **11**, **12**, and **6**—**8**, in which two to four consecutive *p*-phenylene rings are present, the analogous intense bands were observed in the region 817—832 cm^{-1} (Table 2). These spectral data show that the position of strong or medium C–H bands observed in the 817—850 cm^{-1} range is shifted toward a lower wave number in accordance with the progression of *p*-phenylene rings. The shift of C–H band was considered to be quite analogous to that reported previously in the spectra of *p*-polyphenyls by Sandroni[9] and others.[10] The results also show that the position of the C–H band is nearly independent of whether the polyphenyls have *o*- or *m*-phenylene ring(s) or not.

On the basis of these results, the positions of strong or medium bands in the 815—850 cm^{-1} region of the polyphenyls, regardless of the presence of *o*- or *m*-phenylene unit(s) in them, may be considered to be an indication of the approximate number of consecutive *p*-phenylene units.

The UV spectra of the twelve polyphenyls were measured in a cyclohexane solution. The absorption curves are shown in Figs. 1—4. The longest wavelength absorption maxima above 220 nm of the polyphenyls, except the three new compounds (**7**, **8**, and **11**), coincide within 1—3 nm with those of other workers.[2,3b,5,6,8,11]

All of the polyphenyls displayed two groups of intense bands: one in the fairly narrow region of 192—207 nm with intensities approximately proportional to the number of ring units (ε 59300—129000) and another in the broad region of 230—315 nm with a high intensity. The former, whose band position was found to be independent of the structure, is considered to be the E-band, and the latter, whose band position was substantially affected by the nature and number of phenylene rings, is regarded as the K-band, as has been discussed in regard to the spectra of sexiphenyls.[1,12]

The spectrum of **3** displayed an intense K-band at substantially the same wavelength as the biphenyl

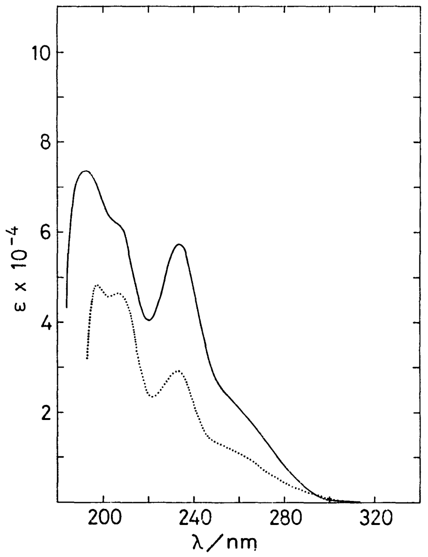
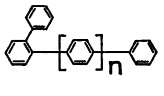
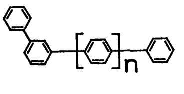
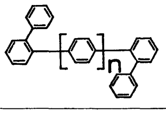
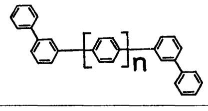
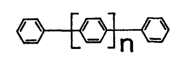


Fig. 1. UV spectra of terphenyl and quinquephenyl in cyclohexane.
——: 2,2″-Diphenyl-*m*-terphenyl (**2**), ……: *o*-terphenyl (**24**).

Table 2. IR spectra of polyphenyls containing para linkage (cm^{-1})

n						
1	841	845	841	848	842±5[a]	833—855[b]
2	826	829	832	826[d]	827±5[a]	826—833[b]
3	818[c]		823		819[a]	820[b]
4			817		814[a]	817[b]

a), b), c), and d) refer to Refs. 9, 10b, 13, and 1 respectively.

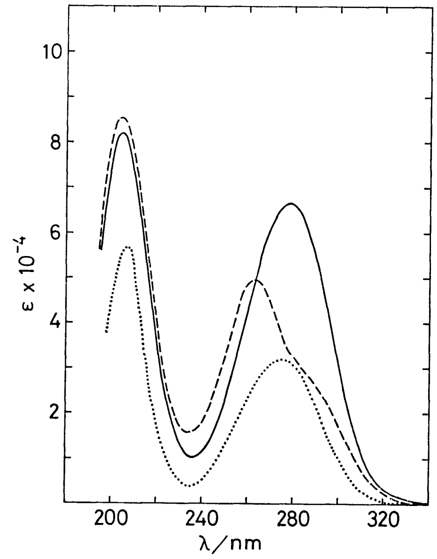


Fig. 2. UV spectra of terphenyl and quinquephenyls in cyclohexane.
——: 4,4″-Diphenyl-*m*-terphenyl (**4**), ----: 4,4″-diphenyl-*o*-terphenyl (**1**), ······: *p*-terphenyl (**25**).

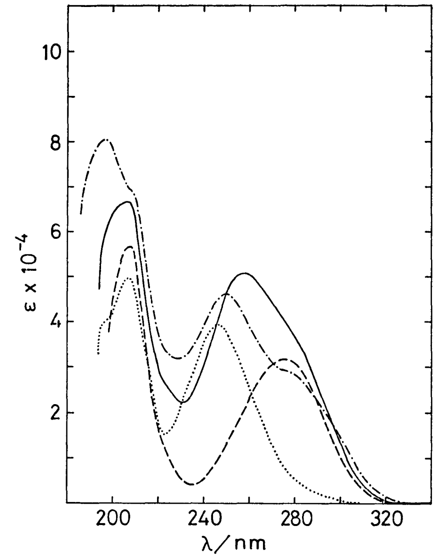


Fig. 3. UV spectra of terphenyls and quinquephenyls in cyclohexane.
——: 3,3″-Diphenyl-*p*-terphenyl (**9**), —·—·—: 2,3″-diphenyl-*p*-terphenyl (**10**), ----: *p*-terphenyl (**25**), ······: *m*-terphenyl.

band, but with an intensity about four times greater (Table 4). Also, the K-band (234 nm, 57700; 250 nm sh, 27000) of **2**, in which two *o*-terphenyl units hold a common *m*-phenylene ring, appeared at the similar wavelength with an intensity about two times that of *o*-terphenyl (**24**) (233 nm, 29100; 251 nm sh, 13300) (Fig. 1). In the cases of **4** and **1**, in each of which two isolated *p*-phenylene rings are present, the spectrum of the former revealed a strong K-band (280 nm, 66500) at a similar wavelength with an intensity about two times that of *p*-terphenyl (**25**) (277 nm, 31600), while the spectrum of the latter displayed a discernible shoulder near 280 nm, together with a intense K-band at about 260 nm (264 nm, 49800; 284 nm sh, 30600). The differences of the spectra might reflect the difficult extension of the two conjugated systems of *p*-terphenyl separated by *m*-phenylene ring in the former, and the reduced π-π interaction across the pivot bonds between *o*-phenylene ring and its nearest neighbors in the latter (Fig. 2). In the cases of **10** and **9**, which each have one *p*-terphenyl unit, the spectra (250 nm, 46200; 275 nm sh, 29300) (258 nm, 50800; 280 nm sh, 38200) displayed only a discernible shoulder near 280 nm together with a prominent K-band at 250 nm or at 258 nm respectively (Fig. 3).

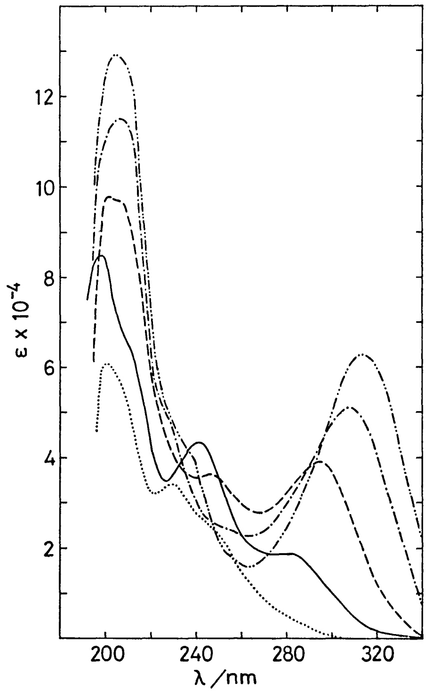
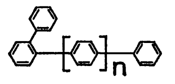
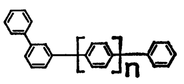
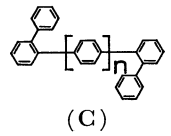
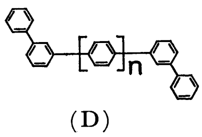
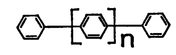


Fig. 4. UV spectra of related quater-, quinque-, sexi-, septi-, and octiphenyl in cyclohexane.
··—··: 2,2′′′′′-Diphenyl-*p*-sexiphenyl (**8**), —·—·—: 2,2′′′′-diphenyl-*p*-quinquephenyl (**7**), ----: 2,2‴-diphenyl-*p*-quaterphenyl (**6**), ——: 2,2″-diphenyl-*p*-terphenyl (**5**), ······: *o*-quaterphenyl (**22**).

Then, the spectra of the series of four polyphenyls **5**—**8** (series C), in which both terminals of one or two to four consecutive *p*-phenylene units are linked by *o*-phenylene rings, showed a remarkable bathochromic shift and an increase in intensity of the characteristic K-bands with an increase in the number of consecutive *p*-phenylene rings (Fig. 4). An analogous shift and increase in intensity of the K-band were also observed in the spectra of series B, A, and D, in which one or both terminals of one or more *p*-phenylene units are linked by *m*- or *o*-phenylene ring(s), as shown in Table 3. Such a characteristic shift and increase in intensity of K-band are compatible with the observation in the spectra of four *p*-polyphenyls (series E) by Gillam and Hey.[12a)]

The foregoing results in the spectra of the polyphenyls show that the K-band above *ca.* 260 nm suggest the presence of *p*-phenylene unit(s), and that the positions

Table 3. UV spectra of polyphenyls containing para linkage in cyclohexane (λ_{max}/nm (ε))

n	 (A)	 (B)	 (C)	 (D)	 (E)
1	278 (25100)	268 (38400)	280 (18500)	280^{sh} (38200)	277 (31600)
2	295 (42100)	296 (47500)	297 (38900)	296 (51900)[b]	294 (44000)
3	307 (57000)[a]		307 (51000)		310 (62000)[c,d]
4			315 (62900)		317.5 (>75600)[c,d]

a), b), and c) refer to Refs. 13, 1, and 12a respectively. d) In chloroform.

Table 4. Calculated and observed longest wavelength absorption bands of the polyphenyls and related compounds

Compound	Calcd trans. energy β[a]	Absorption band Calcd λ_{max}/nm	Obsd λ_{max}/nm	Obsd ε
21	−1.4392	233	248	18500
25	−1.2254	273	277	31600
27	−1.1176	300	294	44400
ϕpppϕ[b]	−1.0550	318	310	62000[c]
ϕmϕ	−1.3564	247	247	39100
26	−1.3222	253	248	62700
3	−1.3048	257	249	83200
24	−1.4810	226	251 sh	13300
22	−1.4192	236	245 sh	25600
ϕoooϕ	−1.3834	242	237	46200[d]
ϕpoϕ	−1.2308	272	278	25100
ϕpmϕ	−1.2090	277	268	38400
ϕmoϕ	−1.3492	248	251 sh	32400[d]
1	−1.1418	293	284 sh	30600
2	−1.3440	249	250 sh	27000
4	−1.1702	286	280	66500
5	−1.2354	271	280	18500
7	−1.0676	314	307	51000
8	−1.0246	327	315	62900
ϕmomϕ	−1.2922	259	249 sh	48300[d]
9	−1.1956	280	280 sh	38200
10	−1.2150	276	275 sh	29300
11	−1.1254	298	295	41200
12	−1.1116	301	296	47500

a) For β, −3.70 eV was used as the mean value calculated from the absorption bands of the biphenyl and the first four *p*-polyphenyls. b) ϕ, p, m, and o refer to phenyl, *p*-, *m*-, and *o*-phenylene rings. c) And d) refer to Refs. 12a and 13.

of the bands may be an indication of the approximate number of continuous *p*-phenylene units.

A comparison between the calculated and observed longest wavelength bands of the polyphenyls and closely related compounds is given in Table 4. Here the HMO calculations were performed by assuming tentatively the dihedral angle of the pivot bond as follows: 50° for phenyl–*o*- and *o*–*o*-phenylene linkages, 35° for *o*–*p*- and *m*–*p*-phenylene linkages, and 20° for the other linkages. The table shows rather good agreement between calculated and observed wavelengths except in the cases of **21** and **24**. The results may also be confirmed by the approximate linear relation of the wave numbers of the longest wavelength absorption bands to the calculated longest wavelength transition energies, as shown in Fig. 5.

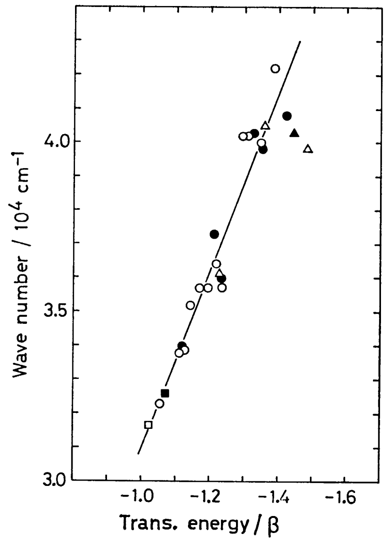


Fig. 5. Plots of wave numbers of longest wavelength absorption bands *vs.* calculated longest wavelength transition energies of the polyphenyls and related compounds.

▲: Biphenyl, △: terphenyls, ●: quaterphenyls, ○: quinquephenyls, ■: septiphenyl, □: octiphenyl.

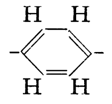
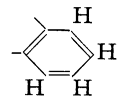
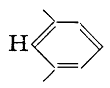
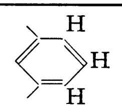
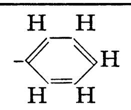
The ^{1}H-NMR spectra of the polyphenyls and closely related compounds were measured at 80 MHz in a $CDCl_3$ solution. The chemical shifts from tetramethylsilane are summarized in Table 5.

The spectra of **1**, **5**—**8**, **10**, and **11** show one singlet peak near δ 7.44; this is assigned to the resonances of protons on one or two *o*-phenylene rings by comparison with the *o*-phenylene proton signal of **24** (δ 7.41, 4H, s, *o*-C_6H_4).

The most down field multiplet peaks (δ 7.75—7.93) found commonly in the spectra of **3**, **4**, **9**, **10**, **12**, and *m*-quaterphenyl (**26**) may be assigned to the resonances of one isolated *m*-phenylene proton by comparing with the signals of *m*-terphenyl and 1,3-di(phenyl-d_5)benzene[13] (δ 7.78—7.83, 1H, m, *m*-C_6H).

Among the spectra of the eleven polyphenyls containing *p*-linkage(s), those of **4**, **9**, **12**, and *p*-quater-

Table 5. ^{1}H-NMR spectral data of **1**—**12**, **21**, **22**, and **24**—**27** in CDCl$_3$[a)]

Compound					
21	—	—	—	—	7.16—7.70(10H, m)
25	7.68(4H, s)	—	—	—	7.33—7.71(10H, m)
27	7.71(8H, s)	—	—	—	7.34—7.68(10H, m)
26	—	—	7.81—7.88(2H, m)	7.32—7.74(16H, m)	
24	—	7.41(4H, s)	—	—	7.17(10H, s)
22	—	7.12—7.43(8H, m)	—	—	6.51—7.08(10H, m)
1	7.26 and 7.48(8H, AA'BB'-q, J=8.6 Hz, C_2, C_6-H and C_3, C_5-H)	7.47(4H, s)	—	—	7.32—7.66(10H, m)
2	—	6.78—7.48(22H, m)			
3	—	—	7.84—7.93(3H, m)	7.32—7.75(19H, m)	
4	7.73(8H, s)	—	7.87—7.93(1H, m)	7.33—7.68(13H, m)	
5	6.97(4H, s)	7.40(8H, s)	—	—	7.12—7.21(10H, m)
6	7.18 and 7.44(8H, AA'BB'-q, J=8.3 Hz, $C_{2'}$, $C_{6'}$-H and $C_{3'}$, $C_{5'}$-H)	7.43(8H, s)	—	—	7.20(10H, s)
7	7.21 and 7.50(8H, AA'BB'-q, J=8.8 Hz, $C_{2'}$, $C_{6'}$-H and $C_{3'}$, $C_{5'}$-H) 7.64(4H, s, middle)	7.45(8H, s)	—	—	7.21(10H, s)
8	7.23 and 7.51(8H, AA'BB'-q, J=8.7 Hz, $C_{2'}$, $C_{6'}$-H and $C_{3'}$, $C_{5'}$-H) 7.69(8H, s, inner)	7.45(8H, s)	—	—	7.22(10H, s)
9	7.75(4H, s)	—	7.84—7.89(2H, m)	7.33—7.71(16H, m)	
10	7.23 and 7.51(4H, AA'BB'-q, J=8.7 Hz, $C_{2'}$, $C_{6'}$-H and $C_{3'}$, $C_{5'}$-H)	7.45(4H, s)	7.75—7.82(1H, m)	7.21(5H, s, o-$C_6H_4 \cdot C_6\underline{H}_5$) 7.33—7.71(8H, m, m-$C_6\underline{H}_3 \cdot C_6\underline{H}_5$)	
11	7.23 and 7.50(4H, AA'BB'-q, J=8.7 Hz, $C_{2'}$, $C_{6'}$-H and $C_{3'}$, $C_{5'}$-H) 7.66(4H, s, p-$C_6\underline{H}_4 \cdot C_6H_5$)	7.45(4H, s)	—	—	7.21(5H, s, o-$C_6H_4 \cdot C_6\underline{H}_5$) 7.33—7.71(5H, m, p-$C_6H_4 \cdot C_6\underline{H}_5$)
12	7.72(4H, s, p-$C_6\underline{H}_4 \cdot C_6H_5$) 7.75(4H, s, p-$C_6\underline{H}_4 \cdot p$-$C_6H_4 \cdot C_6H_5$)	—	7.84—7.90(1H, m)	7.33—7.67(13H, m)	

a) δ(ppm) from internal standard TMS.

phenyl (**27**) display one or two singlet peaks near δ 7.73. These are assigned to the resonances of *p*-phenylene protons by comparison with the *p*-phenylene proton signal of **25** (δ 7.68, 4H, s, *p*-$\mathrm{C_6H_4}$). On the other hand, those of **1**, **6**, and **10** reveal an apparent AA'BB'-q pattern near δ 7.22 and 7.48, which may be assigned to the resonances of the *p*-phenylene protons from analogy with the spectra of *p*-phenylene protons of 2,4'-diphenylbiphenyl and 2,4'-di(phenyl-d_5)biphenyl[13] (δ 7.21 and 7.46, 4H, AA'BB'-q, J=8.6 Hz, 2'-, 6'-H and 3'-, 5'-H). Furthermore, those of **7**, **8**, and **11** show one singlet peak near δ 7.66 in addition to an apparent AA'BB'-q pattern near δ 7.22 and 7.50, and both peak and pattern are assigned to the resonances of the protons on the different types of *p*-phenylene rings. In the case of **5**, however, the resonances of the *p*-phenylene protons are observed as a singlet peak at a rather higher field (δ 6.97) as compared with those of **25**. The marked high field shift possibly reflects the ring current effect of both terminal phenyl groups. The foregoing results suggest that the two types of *p*-phenylene proton signal, a singlet peak and an AA'BB'-q pattern, are related closely with the kinds of the two groups adjacent to the *p*-phenylene ring. The correlation may be generalized as follows: 1) In the cases of polyphenyls, in which the *p*-phenylene ring is linked by two identical groups (phenyl or phenylenes) or by two different groups (phenyl or phenylenes except *o*-phenylene), the resonances of *p*-phenylene protons are generally observed as a singlet peak. 2) The resonances of *p*-phenylene protons of polyphenyls, in which the *p*-phenylene ring is linked by two different groups (phenyl or phenylenes), of which one is an *o*-phenylene ring, are generally observed as an AA'BB'-q pattern.

The spectra of **6**—**8**, **10**, and **11** reveal one singlet peak near δ 7.21. This is assigned to the resonances of protons of phenyl group(s) adjacent to *o*-phenylene ring(s), by comparison with the phenyl proton signal of **24** (δ 7.17, 10H, s, $\mathrm{C_6H_5}$). However, the phenyl proton signals of **10** and **11**, each of which has a phenyl group linked by a *m*- or *p*-phenylene group, respectively, and those of **1**, **3**, **4**, **9**, **12**, and **25**—**27** are observed as multiplet peaks in the region δ 7.32—7.75. Among them, the multiplet peaks in the δ 7.32—7.75 region of **3**, **4**, **9**, **10**, **12**, and **26**, all of which have *m*-phenylene ring(s), are assigned to the resonances not only of phenyl protons but also of three adjacent *m*-phenylene protons, from analogy with the spectra of *m*-terphenyl (δ 7.78—7.83, 1H, m, *m*-$\mathrm{C_6H}$; δ 7.27—7.72, 13H, m, *m*-$\mathrm{C_6H_3}$ and $\mathrm{C_6H_5}$) and 1,3-di(phenyl-d_5)benzene[13] (δ 7.78—7.83, 1H, m, *m*-$\mathrm{C_6H}$; δ 7.51—7.61, 3H, m, *m*-$\mathrm{C_6H_3}$).

The spectrum of **22** shows multiplet peaks of 10H at a rather higher field (δ 6.51—7.08). These are assigned to the resonances of protons on two terminal phenyl rings. That of **2** displays multiplet peaks (δ 6.78—7.48, 22H, m) which are quite difficult to assign.

Experimental

Low melting points were determined with a Mettler FP-51 apparatus; for those above 300 °C, a Shimadzu DSC-30M differential scanning calorimeter was employed. The UV spectra were measured on a Shimadzu QV-50 and a Hitachi EPS-2 spectrophotometer, the IR spectra on a Leitz III-G spectrophotometer, and ^{1}H-NMR spectra on a Varian CFT-20 spectrometer at 80 MHz, using TMS as an internal standard. The molecular weights were determined with a Mechrolab 301A vapor-pressure osmometer and a Hitachi RMU-6E mass spectrometer.

2- (**13**), 3- (**14**), and 4-Iodobiphenyl (**15**) were prepared as reported previously.[1]

o- (**18**), *m*- (**19**), and *p*-Diiodobenzene (**20**) were commercially available and purified before use.

*4-Iodo-*o*-terphenyl (**16**).* Commercially available *o*-terphenyl was subjected to nitration[14] to give 4-nitro-*o*-terphenyl (mp 117.3 °C), which was reduced with activated iron in hot benzene[15] to prepare 4-amino-*o*-terphenyl (mp 117.4 °C). Then the amine was converted to **16** in the usual manner. Colorless plates; mp 117.6 °C (lit,[16] mp 116—116.5 °C). (Found: C, 60.51; H, 3.81%).

*4-Iodo-*p*-terphenyl (**17**).* 4-Iodo-*p*-terphenyl was prepared by the direct iodination[17] of *p*-terphenyl. Colorless needles; mp 246.5 °C (lit,[18] mp 246—247 °C). (Found: C, 60.67; H, 3.66%).

*Preparation of 4,4''-Diphenyl-*o*-terphenyl (**1**).* A mixture of **15** (8.40 g, 30.0 mmol) and **18** (4.95 g, 15.0 mmol) in a reaction tube (ϕ2.5×20 cm) was heated in an oil bath at 230—240 °C, and then copper powder (19.1 g, 300 mg-atom) was added under stirring in portions over a one hour period, after which the mixture was heated at 245 °C for an additional hour. After cooling, the reaction product was extracted with hot benzene followed by hot xylene, then the solvents were distilled off. The benzene extract (5.34 g) was treated with 60 ml of a cyclohexane–benzene (5:1 v/v) mixture (C–B(5:1)) to separate the product into soluble and insoluble parts. Recrystallization of the latter together with the xylene extract (1.09 g) from benzene provided *p*-quaterphenyl (**27**) (colorless plates; mp 319 °C (lit,[19] mp 317.7—318.7 °C); yield, 1471 mg). The former was dissolved in the C–B (5:1) and then subjected to chromatography on alumina with the same solvent as the eluent, to provide biphenyl (**21**) (colorless leaves from ethanol; mp 69.4 °C; yield, 1405 mg) and **1**. The properties of the latter are as follows.

1: Colorless needles from ethanol; mp 184.5 °C (lit,[2] mp 182—184 °C); yield, 939 mg (16.4%). IR: 675 m; 700 s ($\gamma_{\mathrm{C-C}}$); 715 w, 727 m, 737 m, 757 s ($\gamma_{\mathrm{C-H}}$, M, *o*); 773 s ($\gamma_{\mathrm{C-H}}$, *o*); 837 s, 842 cm^{-1} s ($\gamma_{\mathrm{C-H}}$, *p*).[20] UV: $\lambda_{\max}$ (ε) 204 (85300), 264 (49800), 284 nm (sh) (30600). Found: C, 94.34; H, 5.76%; mol wt, 382. Calcd for $\mathrm{C_{30}H_{22}}$: C, 94.20; H, 5.80%; mol wt, 382.

*Preparation of 2,2''-Diphenyl-*m*-terphenyl (**2**).* A mixture of **13** (8.40 g) and **19** (4.95 g) was treated with copper powder (19.1 g) at 260—270 °C for 1 h, and the mixture was heated at 275 °C for a further 1 h. The hot benzene extract of the product (6.10 g) was chromatographed on alumina with C–B (5:1) to give *o*-quaterphenyl (**22**) (colorless cubes from ethanol; mp 118.0 °C (lit,[21] mp 118 °C); 2509 mg) and **2**.

2: Colorless prisms from ethanol; mp 164.2 °C (lit,[8] mp 155.5—156.6 °C); 1362 mg (23.8%). IR: 695 s, 704 s, 711 s ($\gamma_{\mathrm{C-C}}$); 728 w; 745 s, 749 s, 755 sh s, 764 s ($\gamma_{\mathrm{C-H}}$, M, *o*); 779 m, 783 m ($\gamma_{\mathrm{C-H}}$, *o*); 803 m ($\gamma_{\mathrm{C-H}}$, *m*); 846 w, 879 w; 908 cm^{-1} m ($\gamma_{\mathrm{C-H}}$, *m*). UV: $\lambda_{\max}$ (ε) 192 (73800), 204 (sh) (63400), 234 (57700), 250 nm (sh) (27000). Found: C, 94.35; H, 5.95%; mol wt, 382. Calcd for $\mathrm{C_{30}H_{22}}$: C, 94.20; H, 5.80%; mol wt, 382.

Preparation of m-*Quinquephenyl* (***3***). A mixture of **14** and **19** was heated with copper powder as has been described in the preparation of **1**. The hot benzene extract of the product (5.80 g) was subjected to distillation *in vacuo*, then the distillate was chromatographed on alumina with C–B (5:2) to afford *m*-quaterphenyl (**26**) (colorless plates from ethanol; mp 87.1 °C (lit,[22] mp 85.5—86 °C); 992 mg) and **3**.

3: Colorless needles from ethanol; mp 114.0 °C (lit,[3a] mp 114—115 °C; lit,[3b] mp 115.3—115.6 °C); 462 mg (8.1%). IR: 699 s, 707 sh m ($\gamma_{\text{C-C}}$); 729 w; 750 s ($\gamma_{\text{C-H}}$, M); 779 s, 791 w, 807 w, 810 sh w ($\gamma_{\text{C-H}}$, *m*); 884 sh m, 888 m, 899 vw, 908 cm^{-1} vw ($\gamma_{\text{C-H}}$, *m*). UV: λ_{max} (ε) 196 (59300), 205 (60400), 249 nm (83200). Found: C, 93.93; H, 6.07%; mol wt, 382. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80%; mol wt, 382.

*Preparation of 4,4″-Diphenyl-*m*-terphenyl* (***4***). A mixture of **15** and **19** was treated with copper powder under conditions similar to those used in the preparation of **2**. The product was extracted with hot benzene followed by hot toluene. The benzene extract (4.41 g) was treated with 50 ml of the C–B (5:2) to separate soluble [B_1] (2.50 g) and insoluble [B_2] (1.91 g) parts. The toluene extract (1.64 g) was treated as described above to separate soluble [T_1] (0.33 g) and insoluble [T_2] (1.58 g) parts. The soluble [B_1] was chromatographed on alumina with the C–B (5:2) to give **21** (378 mg). The [B_2] and [T_1] parts were combined and chromatographed with C–B (1:1) to give **4**. Crystallization of the insoluble [T_2] from benzene afforded **27** (1523 mg).

4: Colorless prisms from benzene; mp 269.7 °C (lit,[4] mp 264—266 °C; lit,[3b] mp 273.4—273.8 °C); 764 mg (13.3 %). IR: 690 s, 698 sh s ($\gamma_{\text{C-C}}$); 725 m, 732 w; 759 s ($\gamma_{\text{C-H}}$, M); 796 s ($\gamma_{\text{C-H}}$, *m*); 826 w; 845 s, 849 s ($\gamma_{\text{C-H}}$, *p*); 893 w, 910 cm^{-1} w ($\gamma_{\text{C-H}}$, *m*). UV: λ_{max} (ε) 205 (82100), 280 nm (66500). Found: C, 94.17; H, 5.76%; mol wt, 386. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80%; mol wt, 382.

*Preparation of 2,2″-Diphenyl-*p*-terphenyl* (***5***). *Procedure A*: A mixture of **13** (8.40 g) and **20** (5.00 g) was treated with copper powder (19.1 g) at 250—260 °C for 1 h, and then at 265 °C for another hour. The hot benzene extract (6.19 g) was digested with 60 ml of the C–B (5:2) to remove insoluble material. The soluble part (6.00 g), after removal of the solvent, was subjected to chromatography on alumina with cyclohexane to afford **22** (2526 mg). Subsequent progressive elutions with C–B(5:1), then with C–B(5:2) and C–B(5:3), and finally with C–B(1:1), provided **5**, 2,2‴-diphenyl-*p*-quaterphenyl (**6**) and 2,2⁗-diphenyl-*p*-quinquephenyl (**7**), and 2,2'''''-diphenyl-*p*-sexiphenyl (**8**) respectively.

5: Colorless needles from ethanol; mp 185.8 °C (lit,[3b] mp 185.6—185.8 °C); 798 mg (13.9%). IR: 678 w; 700 s ($\gamma_{\text{C-C}}$); 744 s, 755 s, 763 m ($\gamma_{\text{C-H}}$, M, *o*); 778 m, 781 m ($\gamma_{\text{C-H}}$, *o*); 841 s, 848 m ($\gamma_{\text{C-H}}$, *p*); 877 cm^{-1} w. UV: λ_{max} (ε) 198 (85000), 242 (43200), 280 nm (18500). Found: C, 94.36; H, 6.06%; mol wt, 382 (M^+). Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80%; mol wt, 382.

6: Colorless leaves from benzene–ethanol; mp 236.1 °C; 670 mg (9.8%); identified by mixed-melting-point method and identical IR and UV spectra to those from the authentic sample.[1]

7: Colorless leaves from ethanol–benzene; mp 256.6 °C; 589 mg (7.4%). IR: 683 w; 706 s ($\gamma_{\text{C-C}}$); 720 m, 734 w; 747 s, 763 s ($\gamma_{\text{C-H}}$, M, *o*); 785 m ($\gamma_{\text{C-H}}$, *o*); 823 s, 830 cm^{-1} sh m ($\gamma_{\text{C-H}}$, *p*). UV: λ_{max} (ε) 206 (115800), 230 (sh) (45800), 307 nm (51000). Found: C, 94.06; H, 5.83%; mol wt, 534 (M^+). Calcd for $C_{42}H_{30}$: C, 94.34; H, 5.66%; mol wt, 534.

8: Colorless leaves from benzene; mp 309 °C; 218 mg (2.4%). IR: 684 w; 706 s ($\gamma_{\text{C-C}}$); 729 w; 743 s, 747 s, 764 s ($\gamma_{\text{C-H}}$, M, *o*); 786 m ($\gamma_{\text{C-H}}$, *o*); 817 s ($\gamma_{\text{C-H}}$, *p*); 854 cm^{-1} w. UV: λ_{max} (ε) 203 (129600), 234 (sh) (41100), 315 nm (62900). Found: C, 94.09; H, 5.55%; mol wt, 610 (M^+). Calcd for $C_{48}H_{34}$: C, 94.39; H, 5.61%; mol wt, 610.

Procedure B: A mixture of **13** (2.80 g, 10.0 mmol) and **16** (3.56 g, 10.0 mmol) was treated with copper powder (6.35 g, 100 mg·atom) at 260—265 °C for 1.5 h, and then at 270 °C for an additional hour. The hot benzene extract (3.82 g) was chromatographed as above with cyclohexane to yield **21** (40 mg) and *o*-terphenyl (**24**) (colorless needles from ethanol; mp 56.7 °C; 184 mg). Subsequent progressive elutions with C–B(9:1), then C–B(9:1) and C–B(4:1), and finally with C–B(4:1) and C–B(1:1) provided **22** (600 mg), **5** (765 mg, 20.0%), and **6** (570 mg, 12.5%) respectively.

*Preparation of 3,3″-Diphenyl-*p*-terphenyl* (***9***). A mixture of **14** and **20** was heated with copper powder, as has been described for the preparation of **1**. The hot benzene extract (5.50 g) was separated into soluble and insoluble parts in 150 ml of C–B(1:1). Chromatography of the former (2.90 g) with the same solvent and of the latter (2.60 g) with benzene on alumina afforded **21** (250 mg) and **26** (1600 mg), and **26** (40 mg) and **9** respectively.

9: Colorless plates from benzene; mp 235.7 °C (lit,[5] mp 235—236 °C; lit,[3b] mp 236.1—236.3 °C); 750 mg (13.1%). IR: 686 w; 699 s ($\gamma_{\text{C-C}}$); 754 s, 760 s ($\gamma_{\text{C-H}}$, M); 790 s, 798 m ($\gamma_{\text{C-H}}$, *m*); 848 m, 855 w ($\gamma_{\text{C-H}}$, *p*); 890 cm^{-1} m ($\gamma_{\text{C-H}}$, *m*). UV: λ_{max} (ε) 207 (66800), 258 (50800), 280 nm (sh) (38200). Found: C, 93.93; H, 5.94%; mol wt, 381. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80%; mol wt, 382.

*Reaction of **13** and **18***. A mixture of **13** and **18** was treated under conditions similar to those used in the preparation of **2**. The hot benzene extract (6.40 g) was subjected to chromatography on alumina with cyclohexane to provide **21** (512 mg). Subsequent elution with C–B(5:1) gave **22** (1389 mg) and triphenylene (**23**).

23: Colorless needles from cyclohexane; mp 198.6 °C (lit,[23] mp 197—198 °C); 829 mg (23.9%). Found: C, 94.78; H, 5.25%; mol wt, 221. Calcd for $C_{18}H_{12}$: C, 94.70; H, 5.30%; mol wt, 228.

*Preparation of 2,3″-Diphenyl-*p*-terphenyl* (***10***). A mixture of **14** (2.80 g) and **16** (3.56 g) was heated as has been described in the preparation of **5** (Procedure B). The hot benzene extract (3.77 g) was chromatographed on alumina with cyclohexane to give **21** (30 mg). Subsequent elutions with C–B(9:1), then C–B(9:1) and C–B(4:1), and finally with C–B(4:1) and C–B(1:1) afforded **24** (280 mg) and **26** (270 mg), **10**, and **6** (950 mg, 20.7%) respectively.

10: Colorless plates from ethanol; mp 120.0 °C (lit,[6] mp 120.1—120.5 °C; lit,[2] mp 119.5—120.0 °C); 705 mg (18.5%). IR: 684 w, 689 w; 701 s, 704 sh s ($\gamma_{\text{C-C}}$); 736 m; 746 s, 751 sh s, 765 w ($\gamma_{\text{C-H}}$, M, *o*); 779 m ($\gamma_{\text{C-H}}$, *o*); 797 m, 812 vw ($\gamma_{\text{C-H}}$, *m*); 835 m, 841 s ($\gamma_{\text{C-H}}$, *p*); 874 w; 895 cm^{-1} m ($\gamma_{\text{C-H}}$, *m*). UV: λ_{max} (ε) 197 (81000), 250 (46200), 275 nm (sh) (29300). Found: C, 93.99; H, 5.92%; mol wt, 382 (M^+). Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80%; mol wt, 382.

*Preparation of 2-Phenyl-*p*-quaterphenyl* (***11***). A mixture of **15** and **16** was treated under conditions similar to those used in the preparation of **5** (Procedure B). The product was then extracted with hot benzene, followed by hot toluene. The benzene extract (3.76 g) was subjected to chromatography on alumina with C–B(9:1) to afford **21** (58 mg). Subsequent elutions with C–B(5:1), then C–B (5:1) and C–B(5:2), and finally with benzene provided

24 (273 mg), **11** and **6** (493 mg, 10.8%), and **27** (199 mg) respectively. Crystallization of the toluene extract (0.17 g) from benzene provided more **27** (110 mg).

11: Colorless needles from benzene; mp 186.9 °C; 788 mg (24.7%). IR: 692 s, 702 s ($\gamma_{\text{C-C}}$); 720 m, 728 m; 748 s, 757 s, 763 sh s, 769 m ($\gamma_{\text{C-H}}$, M, *o*); 780 m ($\gamma_{\text{C-H}}$, *o*); 826 s ($\gamma_{\text{C-H}}$, *p*); 855 w, 876 cm^{-1} w. UV: $\lambda_{\max}$ (ε) 205 (79900), 237 (sh) (19400), 264 (sh) (24900), 295 nm (42100). Found: C, 93.95; H, 5.98%; mol wt, 382 (M$^+$). Calcd for $C_{30}H_{22}$: C. 94.20; H, 5.80%; mol wt, 382.

*Preparation of 3-Phenyl-*p*-quaterphenyl (12).* A mixture of **14** and **17** was heated as has been described in the preparation of **5** (Procedure B). The hot benzene extract (5.81 g) of the product was chromatographed on alumina with cyclohexane to afford **21** (100 mg). Subsequent elutions with C–B(9:1), then C–B(9:1) and C–B(4:1), and finally with benzene provided **26** (453 mg), *p*-terphenyl (**25**) (colorless plates from ethanol; mp 212.4 °C), and **12** respectively. The benzene-insoluble part of the product, upon repeated extraction with concentrated ammonia–water, left a solid which was sublimed at 350—400 °C/0.13 Pa to afford *p*-sexiphenyl (**28**).

12: Colorless leaves from benzene; mp 258.9 °C (lit,[6] mp 259.7—259.9 °C); 1030 mg (27.0%). IR: 698 s ($\gamma_{\text{C-C}}$); 721 w, 736 w; 755 s, 759 sh s, 768 s ($\gamma_{\text{C-H}}$, M); 798 s ($\gamma_{\text{C-H}}$, *m*); 829 s ($\gamma_{\text{C-H}}$, *p*); 855 w; 890 cm^{-1} w ($\gamma_{\text{C-H}}$, *m*). UV: $\lambda_{\max}$ (ε)207 (75300), 253 (sh) (23200), 296 nm (47500). Found: C, 94.38; H, 5.70%; mol wt, 382 (M$^+$). Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80%; mol wt, 382.

28: Colorless leaves; mp 441 °C (lit,[10b] mp 439—445 °C; lit,[24] mp 465 °C); 525 mg (11.5%). Found: C, 94.31; H, 5.53%; mol wt, 458 (M$^+$). Calcd for $C_{36}H_{26}$: C, 94.28; H, 5.72%; mol wt, 458.

The authors would like to express their gratitude to Dr. K. Watanabe for the MO calculations, which were carried out on the FACOM 230-OS2/VS at the Inst. Chem. Res. Kyoto University. The authors are also indebted to Nippon Shinyaku Co., Ltd., for kindly performing the measurements of IR spectra. Thanks are due to Mr. Y. Fujiwara of this college for his help in ^{1}H-NMR spectral measurements.

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