  Bull. Chem. Soc. Jpn., 57, 3494—3506 (1984) [Vol. 57, No. 12

Syntheses and Physical Properties of Several Polyphenylenes Containing Mixed Linkages[1)]

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(Received May 12, 1984)

Fourteen macrocyclic polyphenylenes, including the following ten new compounds, were synthesized by intra- or intermolecular homo-coupling of di-Grignard compound and by cross-coupling of two kinds of di-Grignard compounds with copper(II) chloride: *m,m,o,p,o*-pentaphenylene; *o,o,p,o,o,p*-, *m,o,p,m,o,p*-, *o,p,o,p,o,p*-, *m,o,p,o,p,o*-, *m,o,m,o,m,o*-, and *m,m,m,o,m,o*-hexaphenylene; *m,o,p,p,o,m,p*-, and *m,m,m,m,p,o,p*-heptaphenylene; and *m,o,o,m,o,o,m,o,o,m,o,o*-dodecaphenylene. ^{1}H NMR spectra of the polyphenylenes, compared with those of open-chain analogues, provide valuable information on the nonplanar spacial relationship of constituting phenylene rings. UV spectra of the compounds containing *p*-phenylene ring(s) suggest that the lack or decrease in intensity of K-band above *ca.* 260 nm or a marked shift of that band provides useful conformational information. Empirical Hückel molecular orbital calculations of longest-wavelength absorption bands of twelve polyphenylenes were also carried out. The calculations furnish additional bases for their conformational aspects deduced from their spectral data and Dreiding stereomodels. IR spectra indicate that lack of intense band(s) near 700 cm^{-1} may generally be regarded as a piece of plausible evidence for the macrocyclic structure containing no *m*-phenylene ring. Stabilities of the polyphenylenes to electron bombardment are also discussed.

In our previous studies[2)] a series of closely related linear and branched polyphenyls was synthesized and the relationship was discussed between the number and arrangement of benzene rings and physical properties including IR, UV, and ^{1}H NMR spectral characteristics. In addition, empirical Hückel molecular orbital (HMO) calculations were performed of longest-wavelength absorption bands of forty-two linear polyphenyls. The results indicated that the common parameters (cos θ and β) used might successfully apply to linear polyphenyls. In connection with these works on polyphenyls, I was much interested in studying syntheses of macrocyclic polyphenylenes in which both terminal rings of polyphenyls are linked to each other so that the rotation of pivot bonds is restricted significantly because of their rigid geometry.

Previously, syntheses and properties of several polyphenylenes have been reported by Rapson *et al.*[3)] and Wittig *et al.*[4)] for the *o*-series and by Staab *et al.*[5)] for the *m*-series from the viewpoint of transannular π-electronic interactions in macrocyclic systems. Recently, some of their heterocyclic analogues have also been prepared by Kauffmann.[6)] In addition, Vögtle *et al.*[7)] have synthesized helical compounds which are clamped by methylenes or other bridges at the ends of a linear polyphenyl chain. Nevertheless, only a few polyphenylenes consisting of mixed phenylene linkages have so far been reported.[8)]

The present study was undertaken to synthesize hitherto unknown polyphenylenes consisting of all of three or two kinds of phenylene linkages, and to investigate their spectral characteristics attributable to their macrocyclic structures. Their IR, UV, ^{1}H NMR, and mass (MS) spectra have been measured. By comparing data with those of open-chain analogues, restricted rotation of pivot bonds caused by the rigid geometry, π-electronic interactions, and other conformational problems have been discussed. Further, HMO calculations of longest-wavelength absorption bands of polyphenylenes have been performed to obtain additional valuable information about their conformational aspects.

Results and Discussion

Syntheses. The earlier reactions used for the preparation of polyphenylenes are based mainly on the following reactions: 1) Homo-coupling of di-Grignard compounds with copper(II) or cobalt(II) chloride,[3a,5)] 2) homo-coupling of dilithium aromatics with transition metal halides,[4,9)] and 3) Ullmann homo-coupling of appropriate diiodo compounds.[8b,10)] In the present work, reaction 1 has been adopted because of the facile preparation of the starting and intermediate materials, as well as of the facile isolation of polyphenylenes from several by-products. Thus eleven polyphenylenes (**1**—**11**) (Chart 1), including nine hitherto unknown compounds, were synthesized by the intra- or intermolecular homo-coupling of di-Grignard compound or by cross-coupling of two kinds of di-Grignard compounds, with copper(II) chloride.

The key intermediate dibromo compounds were prepared as follows: First, the following six intermediate dinitroterphenyls were prepared by the Ullmann cross-coupling of *o*- or *m*-diiodobenzene (**15** or **16**) and 2-chloro- or 3-iodonitrobenzene (**17** or **18**), and of 4-iodo-2′- or 4-iodo-3′-nitrobiphenyl (**19** or **20**) and **17** or **18**: 3,3″-dinitro-*o*-(**21a**), 2,2″-dinitro-*m*-(**22a**), and 3,3″-dinitro-*m*-terphenyl (**23a**), and 2,2″-(**24a**), 2,3″-(**25a**), and 3,3″-dinitro-*p*-terphenyl (**26a**). The dinitro compounds (**21a**—**26a**) thus obtained were reduced to the corresponding diamino compounds (**21b**—**26b**) with activated iron in hot benzene, and then converted into dibromoterphenyls (**21c**—**26c**) by the Sandmeyer

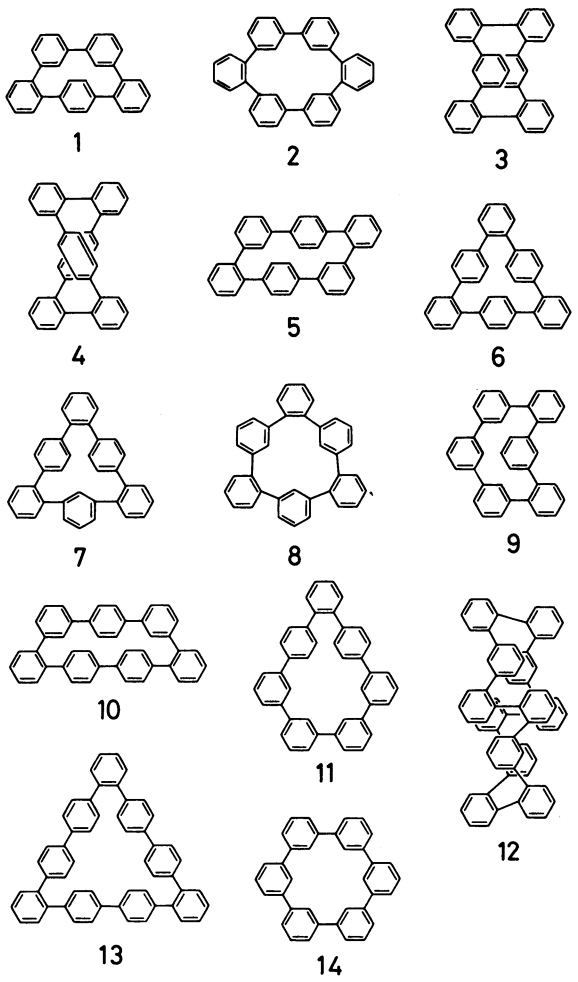
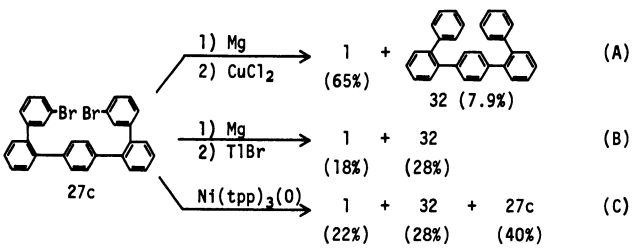


Chart 1.

reaction. Similarly, the dinitroquinquephenyls (2,2″-bis(3-nitrophenyl)-*p*-(**27a**) and 4,4″-bis(3-nitrophenyl)-*o*-terphenyl (**28a**)), obtained by the Ullmann cross-coupling of **18** and 2,2″-diiodo-*p*-(**24d**) or 4,4″-diiodo-*o*-terphenyl, were converted into the dibromo compounds (**27c** and **28c**) *via* the corresponding diamines (**27b** and **28b**). Analogously, 2,2‴-dibromo-*p*-quaterphenyl (**29c**) and 3,3′-dibromobiphenyl (**30c**) were prepared by the Sandmeyer reaction of the corresponding diamines, whereas only 4,4″-dibromo-*o*-terphenyl (**31c**) was obtained by direct bromination of *o*-terphenyl.

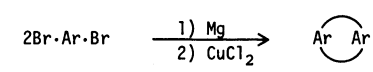
For the synthesis of polyphenylene **1**, three methods have primarily been applied (Scheme 1). Thus, the intramolecular homo-coupling of the di-Grignard compound derived from **27c** with anhydrous copper(II) chloride in a tetrahydrofuran (THF)–benzene (1 : 1, v/v) mixture (method A), gave macrocyclic pentaphenylene



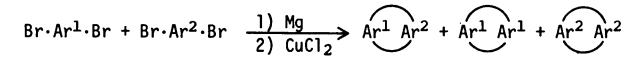
Scheme 1.

(**1**) in a fairly good yield (65%) with its open-chain analogue (2,2″-diphenyl-*p*-terphenyl (**32**), 7.9%). The coupling of the same di-Grignard compound with thallium(I) bromide (method B)[11] and that of **27c** with tris(triphenylphosphine)nickel(0)[12] (method C) afforded **1** only in low yields (18 and 22%, respectively), with predominant formation of **32** accompanied.

On the basis of these results, method A was adopted for the preparation of the remaining ten polyphenylenes (**2**—**11**). Thus, each of **2**—**5** was prepared by the intermolecular homo-coupling reaction of the di-Grignard compound derived from each of dibromides (**21c**, **22c**, **24c**, and **25c**) with anhydrous copper(II) chloride according to the reaction



while each of **6**—**11** was obtained by the intermolecular cross-coupling of two kinds of di-Grignard compounds derived from each of dibromides (**21c**—**24c**, **26c**, and **28c**—**31c**) according to the reaction



The yields of desired polyphenylenes and of other macrocyclic compounds, obtained as by-products, are given in Table 1.

The polyphenylenes **1**—**14**, thus prepared, gave satisfactory analytical results and spectral (IR and MS) data consistent with their proposed structures. Of these polyphenylenes, alternative syntheses of four species have been reported earlier by other workers (**2**,[8c] **3**,[8b] **13**,[8a] and **14**[5b]). The melting points and spectral data of these compounds except **2**[13] are practically consistent with those of previous authors.

In contrast to the yield of **1** (65%), those of the intermolecular homo-coupling products **2**—**5** were rather low (14—16%). Furthermore, the yields of the intermolecular cross-coupling products, except that of **6** (16%), were low (2.3—5.1%) as expected, presumably due to the competitive homo-coupling of each of the reactants and to more or less hindered conformations of the polyphenylenes. Indeed, in the preparations of **6**—**9** and **11**, one or two reasonable homo-coupled

Table 1. Syntheses of polyphenylenes

Reactants	Polyphenylene (Yield/%)	Other polyphenylenes (Yield/%)
27c	**1** (65)	—
21c	**2** (16)	—
22c	**3** (14)	**12** (1.3)
24c	**4** (13)	—
25c	**5** (14)	—
24c+**31c**	**6** (16)	**13** (4.5)
22c+**31c**	**7** (4.5)	**3** (6.5), **13** (2.6)
21c+**22c**	**8** (2.3)	**2** (3.3), **3** (4.4)
22c+**23c**	**9** (3.3)	**3** (4.9), **14** (4.1)
26c+**29c**	**10** (5.0)	—
28c+**30c**	**11** (5.1)	**14** (2.9)

polyphenylenes (**2**, **3**, **13**, and **14**) were isolated in yields of 2.6—6.5%. Beside these, macrocyclic dodecaphenylene (**12**), a tetramer of the reactant, was obtained. In spite of the low yields of the polyphenylenes, most of them were isolated rather with ease from a complex mixture of by-products[14] because of their sparing solubilities and distinguishable crystal forms.

Most of the polyphenylenes melt at much higher temperatures than the open-chain analogues,[15] and the rise in their melting points may be ascribed to the rigid geometry caused by their endless macrocyclic structures.

In the preparations of **3** and **8**, formation of two atropisomers were expected. However, only one compound in each, presumably having a centro-symmetrical conformation on the basis of spectral data to be described later, was isolated. Although the polyphenylene **4** would be a racemate, no identification of antipodes by resolution was attempted.

Physical Properties. *IR Spectra*: The IR spectra of the polyphenylenes **1**—**14** were measured by the KBr-disk method. All the polyphenylenes commonly give the following absorptions: A group of prominent bands due to C–H out-of-plane deformation vibrations in the 675—920 cm^{-1} region; intense bands due to C–C out-of-plane deformation vibrations in the fairly narrow region of 685—715 cm^{-1} (except for **4**, **6**, and **13**); medium bands due to C–C in-plane deformation vibrations near 1000 cm^{-1}; and weak bands due to C–H in-plane deformation vibrations in the 975—1350 cm^{-1} region. In addition, groups of medium bands due to C–C stretching vibrations and weak bands due to aromatic C–H stretching vibrations in the 1350—1600 and 3000—3100 cm^{-1} regions, respectively, are observed.

It has already been known that the prominent bands in the 675—920 cm^{-1} region of the linear polyphenyls are correlated closely to the substitution patterns of the benzene rings comprising each of the compounds.[2,16] A precise examination of the characteristic bands of the polyphenylenes in the same region, has proved that the assignments of the bands generalized for the polyphenyls may also apply to the macrocyclic polyphenylenes. Thus, the prominent bands of the polyphenylenes in the 675—920 cm^{-1} region correspond to the kinds of phenylene rings constituting each of the polyphenylenes as shown in Table 2.

Of the spectra of the fourteen polyphenylenes, those of **1**—**3**, **5**, **7**—**12**, and **14**, which contain *m*-phenylene ring(s), show without exception the strong C–C out-of-plane deformation vibration bands due to *m*-phenylene ring in the narrow range of 704—713 cm^{-1}, whereas those of remaining **4**, **6**, and **13**, which have no *m*-phenylene ring, do not show any analogous intense bands. Concerning these bands of polyphenyls, Stewart and Hellmann[16a] have pointed out that the strong bands due to the C–C out-of-plane bending vibrations near 700 cm^{-1} are characteristic of phenyl and *m*-phenylene rings, whereas the bands corresponding to the *o*- and *p*-phenylene rings are forbidden in IR. The above results, therefore, suggest that the lack of intense bands near 700 cm^{-1} with macrocyclic polyphenylenes may generally be regarded as a piece of plausible evidence for the macrocyclic structure containing no *m*-phenylene ring.

^1H NMR Spectra: The ^1H NMR spectra of the polyphenylenes **1**—**13** were measured at 200 and 80 MHz in $CDCl_3$ solution, and the chemical shifts from tetramethylsilane are summarized in Table 3.

The isolated *m*-phenylene proton signals of **1**, **5**, and **10** (δ=6.61—6.63, 6.23—6.26, and 6.50—6.53, respectively) are observed at much higher fields (by *ca.* 1.18, 1.56, and 1.29 ppm) than that of *m*-terphenyl (δ=7.78—7.83, m).[2e] The remarkable high-field shifts may reflect the anisotropic effects caused by the *p*-phenylene ring on which the isolated *m*-phenylene protons are located. On the other hand, the *p*-phenylene proton signals are found at higher field in **1** (0.43 ppm) and at much higher field in **5** (0.70 ppm) than that of *p*-terphenyl (δ=7.68, s),[2a,e] owing to the anisotropic effect of the inclined *m*-phenylene rings in **1** and **5** and an additional effect of the parallel *p*-phenylene rings in **5**. The analogous high-field shifts of the *p*-phenylene proton signals of **10** can also be explained in terms of the anisotropic effect similar to that described above. The foregoing considerations are fully substantiated by inspection of the Dreiding stereomodels.

The two *p*-phenylene rings of **4** are forced to face-to-face arrangement,[17] analogously to the *m*-phenylene rings of **3**.[8b] The *p*-phenylene proton signals (δ=6.68 and 6.90) of **4** are remarkably shifted toward high field (by *ca.* 1.00 and 0.78 ppm) relative to that of *p*-terphenyl (δ=7.68). This corresponds to the behavior of phenylene protons observed in [2.2]paracyclophane,[18] 4,4‴-dimethylene-*o*-quaterphenylophane,[7a] and a cyclic pyrazole analogue of **4**,[17b] and the marked high-field shift of **4** undoubtedly reflects the anisotropic effect of the faced *p*-phenylene rings. Analogous but more significant high-field shifts over 1 ppm are also observed in the *m*-phenylene proton signals of **3**. Furthermore, the spectrum of **3** is superimposable with that of the compound prepared alternatively by Wittig *et al.*[8b] Therefore, the macrocycle **3** obtained in the present work is evidently a "crosslike" conformer[8b] in the two possible atropisomers.

In the spectrum of **6**, consisting of two equivalent singlets (δ=6.97 and 7.41), the low-field one is assigned to the protons of the three *o*-phenylene rings by comparison with the *o*-phenylene proton signal of *o*-terphenyl (δ=7.41, s)[2a,e] and of **13** (δ=7.40—7.50), and therefore the high-field one is assignable to those of the three *p*-phenylene rings without any contradiction. The high-field shifts (by 0.71 and 0.20 ppm) of the singlet (δ=6.97), relative to the signal of the *p*-phenylene protons of *p*-terphenyl (δ=7.68) and that of the phenyl protons of *o*-terphenyl (δ=7.17),[2a,e] may be

TABLE 2. POSITIONS AND TENTATIVE ASSIGNMENTS OF THE CHARACTERISTIC BANDS IN THE IR SPECTRA (675—920 cm^{-1}) OF POLYPHENYLENES[a)]

1		756 s	$\gamma_{C-H}(o)$	766 sh,s		834 sh,w	$\gamma_{C-H}(p)$
691 w	γ_{C-C}	766 s		797 m	$\gamma_{C-H}(m)$	844 s	
704 m		775 sh,w		805 m		887 sh,m	
709 m		837 s	$\gamma_{C-H}(p)$	875 w		891 m	$\gamma_{C-H}(m)$
741 sh,m	$\gamma_{C-H}(o)$	880 w		900 m	$\gamma_{C-H}(m)$	897 w	
751 s		**5**		907 sh,m		902 w	
756 s		708 s	γ_{C-C}	**9**		**12**	
767 m		713 sh,m		704 s	γ_{C-C}	680 w	
794 w	$\gamma_{C-H}(m)$	719 w		713 s		707 s	γ_{C-C}
801 m		736 m	$\gamma_{C-H}(o)$	721 w		721 w	
809 w		743 s		752 s	$\gamma_{C-H}(o)$	746 sh,s	$\gamma_{C-H}(o)$
839 m	$\gamma_{C-H}(p)$	757 s		757 s		751 s	
848 m		765 s		769 m		764 sh,m	
869 w		796 sh,s	$\gamma_{C-H}(m)$	787 m	$\gamma_{C-H}(m)$	776 m	
900 m	$\gamma_{C-H}(m)$	799 s		803 m		802 m	$\gamma_{C-H}(m)$
916 m		804 s		815 w		821 w	
2		808 sh,w		873 w		879 w	
708 s	γ_{C-C}	836 s	$\gamma_{C-H}(p)$	895 m	$\gamma_{C-H}(m)$	910 m	$\gamma_{C-H}(m)$
725 m		839 sh,s		907 w		**13**	
761 s	$\gamma_{C-H}(o)$	847 m		**10**		733 m	$\gamma_{C-H}(o)$
766 sh,s		873 w		678 m		746 m	
781 sh,m		905 m	$\gamma_{C-H}(m)$	691 m	γ_{C-C}	756 s	
788 s	$\gamma_{C-H}(m)$	912 m		706 m		764 sh,m	
806 w		**6**		733 m	$\gamma_{C-H}(o)$	822 s	$\gamma_{C-H}(p)$
826 w		674 m		753 s		839 w	
875 m		751 s	$\gamma_{C-H}(o)$	758 sh,s		853 w	
883 m	$\gamma_{C-H}(m)$	756 s		792 s	$\gamma_{C-H}(m)$	**14**	
3		770 w		797 sh,s		703 s	γ_{C-C}
705 s	γ_{C-C}	826 sh,m	$\gamma_{C-H}(p)$	822 s	$\gamma_{C-H}(p)$	723 m	
707 s		834 s		826 s		776 s	$\gamma_{C-H}(m)$
714 w		838 s		838 m		813 s	
744 s	$\gamma_{C-H}(o)$	**7**		843 w		892 s	$\gamma_{C-H}(m)$
750 s		705 s	γ_{C-C}	874 w		917 w	
759 s		715 w		902 m	$\gamma_{C-H}(m)$		
763 sh,m		736 m	$\gamma_{C-H}(o)$	**11**			
778 w		756 s		678 w			
805 s	$\gamma_{C-H}(m)$	806 m	$\gamma_{C-H}(m)$	702 s	γ_{C-C}		
872 m		823 w	$\gamma_{C-H}(p)$	707 s			
882 w		836 s		734 w			
885 w		872 w		763 sh,s	$\gamma_{C-H}(o)$		
899 m	$\gamma_{C-H}(m)$	890 w	$\gamma_{C-H}(m)$	769 s			
906 w		901 w		774 sh,m			
4		**8**		784 m	$\gamma_{C-H}(m)$		
679 w		707 sh,s	γ_{C-C}	791 s			
699 w		712 s		792 sh,s			
744 sh,m		751 sh,s	$\gamma_{C-H}(o)$	799 m			
751 s		756 s		807 m			

a) v, very; s, strong; m, medium; w, weak; sh, shoulder. γ_{C-C} and γ_{C-H} refer to the vibrations which are primarily the out-of-plane C-C and out-of-plane C-H bending motions, respectively. *o*, *m*, and *p* in parentheses refer to *ortho*-, *meta*-, and *para*-substituted rings, respectively.

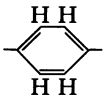
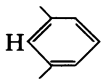
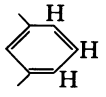
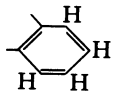
ascribed to the mutual anisotropic effect of *p*-phenylene rings situated oppositely.

Furthermore, in the case of **7**, one of *m*-phenylene analogues of **6**, the isolated proton signal (δ=6.40—6.42) and the *p*-phenylene proton signals (δ=6.68 and 6.73, and 6.95 and 7.15) are observed in the high-field regions as compared with that of *m*-terphenyl (δ=7.78—7.83) and with those of *p*-terphenyl (δ=7.68) and **6** (δ=6.97), respectively. The significant high-field shifts reasonably reflect the conformation in which the *m*-phenylene ring is situated oppositely to two angular *p*-phenylene rings.

Finally, in the spectra of **2**, **8**, **9**, and **11**, a comparison of the characteristic features in phenylene proton signals with those of open-chain analogues[2)] is in full support of the validity of the conformational considerations developed based on the Dreiding stereomodels.

The foregoing results suggest that the prominent

Table 3. ^{1}H NMR spectral data for polyphenylenes (**1**—**13**) in $CDCl_3$[a)]

Compound				
1	7.25 (4H, s)	6.61—6.63 (2H, apparent t, J=1.8 Hz)	7.21—7.77 (14H, m)	
2	———	7.15—7.31 (16H, m)		7.40—7.53 (8H, m, AA'BB'-type)
3	———	5.98—6.00 (2H, apparent t, J=1.7 Hz)	6.42—6.66 (6H, m)	7.19—7.56 (16H, m)
4	6.68 and 6.90 (8H, qd, J=8.1 and 2.0 Hz)	———	———	7.37—7.57 (16H, m)
5	6.98 (8H, s)	6.23—6.26 (2H, m)	7.24—7.66 (14H, m)	
6	6.97 (12H, s)	———	———	7.41 (12H, s)
7	6.68 and 6.73 (4H, qd, J=8.0 and 1.7 Hz) 6.95 and 7.15 (4H, qd, J=7.8 and 1.7 Hz)	6.40—6.42 (1H, m)	7.15—7.52 (15H, m)	
8	———	6.63—6.66 (3H, m)	7.22—7.25 (9H, m)	7.29—7.39 (12H, m, AA'BB'-type)
9	———	6.47—6.49 (1H, m, m-C_6H_4·m-$C_6\underline{H}$·m-C_6H_4)	6.75—6.91 (3H, m, o-C_6H_4·m-$C_6\underline{H}_3$·o-C_6H_4)	
		7.91—7.94 (1H, m, o-C_6H_4·m-$C_6\underline{H}$·o-C_6H_4)	7.30—7.68 (19H, m, o-C_6H_4 and m-$C_6\underline{H}_4$·m-$C_6\underline{H}_3$·m-$C_6\underline{H}_4$)	
10	7.07 (4H, s, p-C_6H_4) 7.05 and 7.40 (8H, q, J=8.6 Hz, p-C_6H_4·p-C_6H_4)	6.50—6.53 (2H, m)	7.36—7.71 (14H, m)	
11	7.23 and 7.53 (8H, q, J=8.5 Hz)	7.90—7.92 (2H, m, m-$C_6\underline{H}$·(m-C_6H_4)$_2$·m-$C_6\underline{H}$) 8.04—8.06 (2H, m, m-C_6H_4·(m-$C_6\underline{H}$)$_2$·m-C_6H_4)	7.47—7.78 (16H, m)	
12	———		5.71—7.54 (48H, m)	
13	7.15 and 7.49 (24H, q, J=8.4 Hz)	———	———	7.40—7.50 (12H, m)

a) δ (ppm) from the internal standard TMS.

high-field shift found for the phenylene proton signals of macrocyclic polyphenylenes, as compared with those of open-chain analogues, may reflect the anisotropic effect of the neighboring phenylene rings, which, originating from the rigid geometry of the macrocyclic structures, may result in a restricted rotation of pivot bonds and an overcrowded conformation. Consequently, the ^{1}H NMR spectra of macrocyclic polyphenylenes, when compared with those of open-chain analogues, may provide useful information for the nonplanar spacial relationship of constituting phenylene rings in solution.

UV Spectra: The UV spectra of the polyphenylenes **1**—**14** were measured in cyclohexane solution. The absorption curves are shown in Figs. 1—6. The absorption maxima above 220 nm for **3**, **13**, and **14** coincide within 3 nm with those of other workers.[5b,8a,b)] All of the polyphenylenes, similarly to the open-chain analogues,[2,19)] display the E-band in the fairly narrow region of 190—210 nm and the K-band in the broad region of 230—320 nm with high intensity.

Previous studies on the UV spectra of the polyphenyls[2)] have indicated that a twist of the pivot bond in the conjugated system influences the interaction of π-electrons across the pivot bond as well as the conjugation of the system, and that the arrangement of the p-phenylene unit(s) in the molecule, even in the presence of o- or m-phenylene units, has a tendency to maintain the coplanarity of the benzene rings. In the case of the polyphenylenes, their overcrowded spacial relationship due to the rigid geometry may cause an enhanced restricted rotation of the pivot bonds, and consequently affects inevitably the spectral feature of K-band.

The spectrum of **1**, containing one *p*-phenylene ring, displays none of bands near 280 nm, which have been found characteristic of the *p*-phenylene unit in the spectrum of the open-chain analogue (**32**: 242 and 280 nm),[2a] but rather intense K-bands (237 and 256 (sh), ε=53700 and 36600), which are related closely to the K-bands of the open-chain compound (ϕommoϕ:[20] 237 and 252 (sh), 74100 and 45400) containing no *p*-phenylene rings.[2b,g] The lack of K-band near 280 nm provides conclusive evidence for the conformation, in which *o*- and *p*-phenylene rings should be highly twisted to one another owing to the steric repulsion of both the isolated hydrogen atoms (*m*-phenylene rings) and the π-electron cloud (*p*-phenylene ring) (Fig. 1). An analogous lack of K-band was also observed in the case of **7** (Fig. 2).

Similarly, an analogous spacial situation of *p*-phenylene ring may result in decrease of π-π interaction across the pivot bonds. Indeed, the spectrum of **5** (246 and 264 (sh)) shows a remarkable hypsochromic shift of the characteristic band for *p*-linkage, compared with those of the corresponding open-chain analogues (ϕmpoϕ: 250 and 275 (sh);[2a] ϕmopmϕ: 249 and 276 (sh)[2f]) (Fig. 3). Also, the spectrum of **6**, which has an alternate arrangement of *o*- and *p*-phenylene rings, has a K-band (276 (sh), 13500) similar in loca-

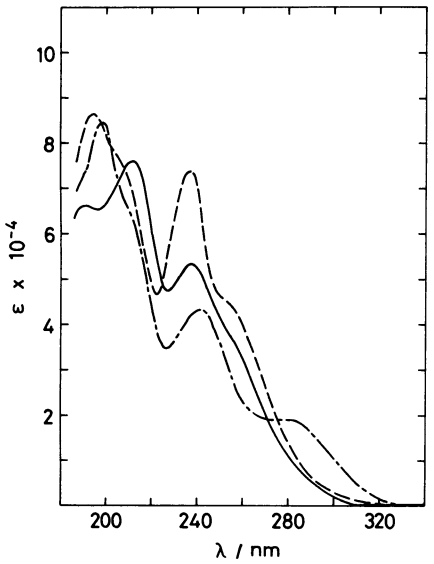


Fig. 1. UV spectra of pentaphenylene and open-chain analogues.
——: *m,m,o,p,o*-Pentaphenylene (**1**), ———: ϕommoϕ, —·—·—: ϕopoϕ (**32**).

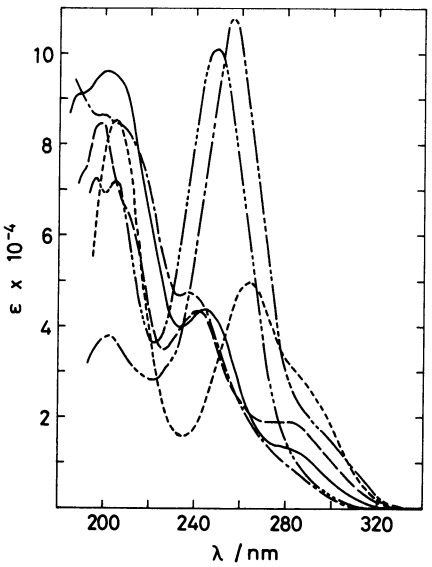


Fig. 2. UV spectra of hexa- and heptaphenylene and open-chain analogues.
——: *o,p,o,p,o,p*-Hexaphenylene (**6**), —·—·—: *m,o,p,o,p,o*-hexaphenylene (**7**), ——·——: *m,m,m,m,p,o,p*-heptaphenylene (**11**), ———: ϕopoϕ (**32**), ------: ϕpopϕ, ——·——: *m*-sexiphenyl.

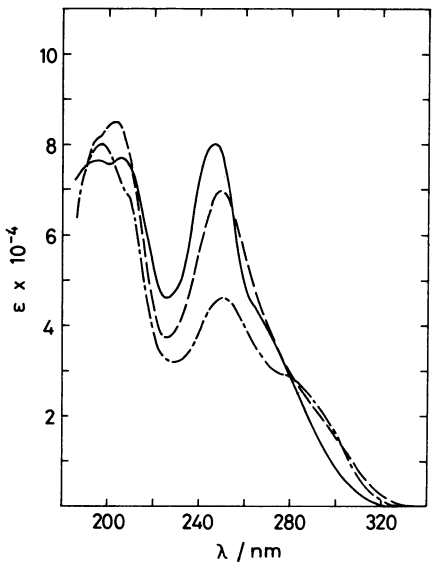


Fig. 3. UV spectra of hexaphenylene and open-chain analogues.
——: *m,o,p,m,o,p*-Hexaphenylene (**5**), ———: ϕmopmϕ, —·—·—: ϕmpoϕ.

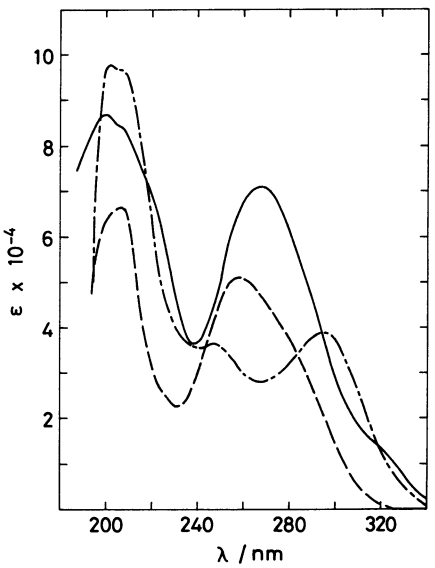


Fig. 4. UV spectra of heptaphenylene and open-chain analogues.
——: *m,o,p,p,o,m,p*-Heptaphenylene (**10**), ———: ϕmpmϕ, —·—·—: ϕoppoϕ.

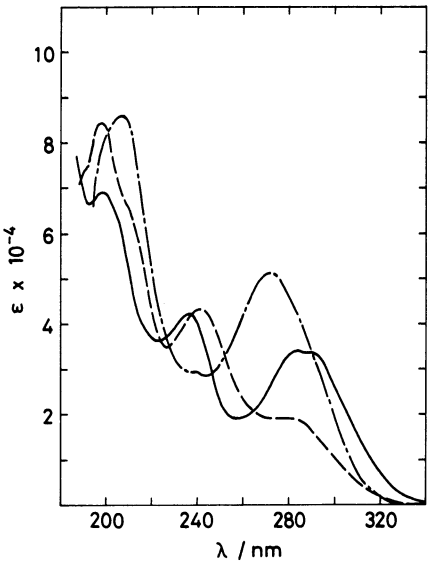


Fig. 5. UV spectra of hexaphenylene and open-chain analogues.
———: *o,o,p,o,o,p*-Hexaphenylene (**4**), — — —: *φopoφ* (**32**), —·—·-: *φpoopφ*.

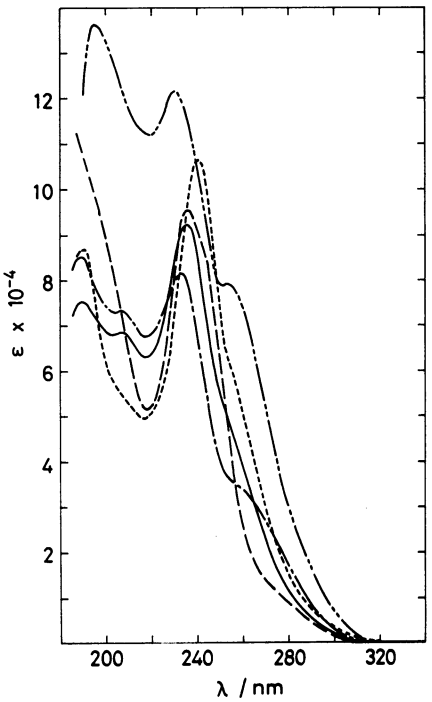


Fig. 6. UV spectra of hexa- and dodecaphenylene.
———: *m,m,o,m,m,o*-Hexaphenylene (**2**), — — —: *m,o,o,m,o,o*-hexaphenylene (**3**), —·—·—: *m,o,m,o,-m,o*-hexaphenylene (**8**),------: *m,m,m,o,m,o*-hexaphenylene (**9**),—··—: *m,o,o,m,o,o,m,o,o,m,o,o*-dodecaphenylene (**12**).

tion to, but much weaker in intensity than, those of the open-chain reference compounds (*cf.* **32**: 280, 18500; *φpopφ*: 284 (sh), 30600).[2a] In the case of **11**, beside an analogous decrease in intensity of K-bands near 280 nm, a significant K-band (256 and 284 (infl), 107700 and 24100) similar to that of *m*-sexiphenyl (249, 101700)[2g] is reasonably observed (Fig. 2). The marked shift or decrease in intensity of the K-band near 280 nm surely reflects the reduced π-π interaction across the pivot bonds of *p*-phenylene ring because of an enhanced twisting of the bonds. In the spectrum of **10**, however, the weak shoulder (312, 16800) found at rather a long wavelength as compared with those of the reference compound (*φoppoφ*: 297, 38900),[2a] seems to be associated with the reduced twisting of *o*-phenylene linkages, caused by the relaxation of steric repulsion of the molecule, in contrast to the cases of **1** and **5** (Fig. 4).

On the other hand, in the spectrum of **4** (236, 286, and 288 (sh); 42300, 34000, and 33600), which has parallel *p*-phenylene rings, longer-wavelength bands are observed at rather red in comparison with those of the open-chain analogues (*cf.* **32**: 242 and 280, 43200 and 18500;[2a] *φpoopφ*: 240 (sh) and 272, 28100 and 51200[2b,g]). The marked shift corresponds to the behavior of [2.2]paracyclophane and other strained compounds[17a] and can be explained on the basis of transannular π-electronic interaction of the two chromophores lying face-to-face (Fig. 5).

The spectra of **2**, **3**, **8**, **9**, and **12**, all of which consist of *o*- and *m*-phenylene rings without any *p*-phenylene rings, show similar characteristic K-bands (near 235 and near 250 (sh)) related closely to those of the reference open-chain analogues (*cf.* *φommoφ*: 237 and 252 (sh); *φmoomφ*: 236 and 245;[2b] *φomooφ*: 232 and 250 (sh);[2f] *φmomφ*: 237 and 249 (sh); *φomoφ*: 234 and 250 (sh);[2a] *φmmomφ*: 239 and 250 (sh)).[2f] From these observations it may be deducible that the restricted rotation of pivot bonds caused by the macroring formation of such open-chain analogues will give no appreciable influence on the spectral feature of K-band (Fig. 6).

The foregoing results on the spectra of polyphenylenes containing *p*-phenylene ring(s) suggest the following aspect: The lack or decrease in intensity of K-band above *ca.* 260 nm, or a marked shift of the band, reflects the enhanced restricted rotation of the pivot bonds of *p*-phenylene ring(s), and consequently provides useful conformational information. The proposed conformations of the polyphenylenes based on the UV spectral data have been confirmed to agree qualitatively with those obtained from the ^{1}H NMR spectral data.

HMO Calculations: Previously HMO calculations of longest-wavelength absorption bands of forty-two linear polyphenyls up to octiphenyls were performed by assuming dihedral angles of pivot bonds to be as follows: 50° for the phenyl—*o*- and *o*-—*o*-phenylene linkages, 35° for the *o*-—*p*- and *m*-—*o*-phenylene linkages, and 20° for the other linkages.[2a,c,d] Resonance integrals (π-π) were used with the values of cos θ of these dihedral angles. The results indicated that the parameters (cos θ and β) used successfully applied to many such linear polyphenyls.

In the present study, two sets of HMO calculations (A and B) of longest-wavelength absorption bands of

TABLE 4. CALCULATED AND OBSERVED LONGEST- WAVELENGTH ABSORPTION BANDS OF POLYPHENYLENES (**1—11** AND **14**)

Compound	Calcd trans. energy β[a)]		Absorption band			Presumed dihedral angle of the pivot bond for B[b)]
			Calcd		Obsd	
	A	B	A λ_{max}/nm	B λ_{max}/nm	λ_{max}/nm	
1	−1.1654	−1.3026	287	257	256 sh	m(60)m(40)o(50)p(50)o(40)m
2	−1.2538	−1.3416	267	250	248 sh	m(55)m(40)o(40)m(55)m(40)o(40)m
3	−1.2592	−1.3874	266	241	242 sh	m(50)o(55)o(50)m(50)o(55)o(50)m
4	−1.1260	−1.1856	298	283	288 sh	o(45)o(45)p(45)o(45)o(45)p(45)o
5	−1.1386	−1.2544	294	267	264 sh	m(40)o(45)p(45)m(40)o(45)p(45)m
6	−1.1918	−1.2268	281	273	276 sh	o(40)p(40)o(75)p(75)o(40)p(40)o
7	−1.1309	−1.4061	296	238	237	m(70)o(70)p(40)o(70)p(40)o(70)m
8	−1.2682	−1.3072	264	256	254 sh	m(40)o(40)m(40)o(40)m(40)o(40)m
9	−1.2532	−1.3234	267	253	252 sh	m(35)m(35)m(35)o(50)m(50)o(35)m
10	−1.0894	−1.0778	308	311	312 sh	m(30)o(30)p(30)p(30)m(30)o(20)p(20)m
11	−1.1322	−1.1728	296	286	284 infl	m(30)m(30)m(30)m(35)p(35)o(35)p(35)m
14	−1.2698	−1.3416	264	250	247	m(35)m(35)m(35)m(35)m(35)m(35)m

a) For β, −3.70 eV was used as a mean value calculated from the absorption bands of biphenyl and the first four *p*-polyphenyls (Refs. 2a, 2c, and 2d). b) m, o, and p refer to *m*-, *o*-, and *p*-phenylene rings. The figures in parentheses refer to the dihedral angle of the pivot bond. Both terminal phenylene rings are duplicated.

the polyphenylenes were carried out by assuming the dihedral angles of the pivot bonds as those 1) previously used for the linear polyphenyls (for A) and 2) obtained by an apparent inspection of the Dreiding stereomodels (for B). The results obtained are summarized in Table 4.

The calculated and observed longest wavelengths of the polyphenylenes show a poor agreement for the values by calculation A, except in the cases of **6** and **10**, but a fairly good agreement within 5 nm for those by calculation B. Evidently the above poor agreement is due to unsuitable parameters (cos θ) derived from the impractically small dihedral angles of the pivot bonds instead of relatively large ones caused by the rigid geometry of macrocyclic structure. The above favorable agreement presumably justifies the estimates of their dihedral angles, and supports the proposed conformations of the polyphenylenes based on the UV and ^{1}H NMR spectral data.

The foregoing results indicate that prediction of the longest-wavelength absorption bands of the polyphenylenes by HMO calculations is possible with a fairly good precision by use of the dihedral angles of the pivot bonds as estimated by inspection of the Dreiding stereomodels. The calculations gave also additional bases for their conformational aspects deduced from their spectral data and stereomodels.

MS Spectra: Only a few studies have been reported on MS spectra of polyphenylenes and related polyphenyls consisting of three or more benzene rings.[2e,5e,21)] The MS spectra of the polyphenylenes **1—13** containing mixed linkages and of **14** were measured at 70 eV. The spectral data are briefed in Tables 5 and 6.

All of the spectra commonly display the molecular ion (M^+) as the most abundant ion. As fragment ions, $(M-Hy)^+$ and $(M-CxHy)^+$ are found in appreciable amounts. The spectra show also considerable amounts of doubly charged ions M^{2+}, $(M-Hy)^{2+}$, and $(M-CxHy)^{2+}$ together with small amounts of corresponding triply charged ions.

An inspection of each spectrum discloses the following facts: Firstly, the second most abundant ion is M^{2+} or $(M-1)^+$. Secondly, the amount of singly to triply charged molecular ions (including isotope ions) of **1—13**, each of which contains one or more *o*-phenylene rings, seems to be low in comparison with that of **14**, which consists of only *m*-phenylene rings. Furthermore, the values $(M^{2+}+M^{3+})/M^+$ of **1—13** increase approximately with increasing number of phenylene rings. The highest value of **14** obviously correlates to the absence of *o*-phenylene ring, which markedly reduces the stability of molecular ions as a result of lowered resonance stabilization. Thirdly, the value of $(M-Hy)^+ + (M-Hy)^{2+}$ is rather high in the spectra of **1** and **11** and slightly high in those of **5—7**.

Previous electron-impact studies have shown that stabilities of *o*-polyphenylenes are less than those of *m*-polyphenylenes,[5e)] and that those of polyphenyls decrease in the order of *p*->*m*->*o*-series.[2e,21)] These results lead to a conclusion that the stabilities to electron bombardment of polyphenylenes containing *o*-phenylene rings, regardless of the presence of *m*- or *p*-phenylene ring(s), are substantially less than those of *m*-polyphenylenes.

Experimental

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. UV spectra were measured on a Shimadzu UV-360 spectrophotometer, IR spectra on a Leitz III-G spectrophotometer, and ^{1}H NMR spectra on Varian XL-200 (200 MHz) and CFT-20 (80 MHz) spectrometers with tetramethylsilane as an internal standard. MS spectra were recorded on a Hitachi RMU-6MG mass spectrometer. HMO

TABLE 5. MOLECULAR IONS OF POLYPHENYLENES (**1**—**14**)

Compound	M^+		M^{2+}		M^{3+}		Sum	$M^{2+}+M^{3+}$
	Irel[a]	$\%\Sigma$[b]	*Irel*	$\%\Sigma$	*Irel*	$\%\Sigma$	$\%\Sigma$	M^+
1	100.0	25.2	5.1	1.3	0.1	0.03	26.5	0.05
2	100.0	41.6	5.9	2.4	0.1	0.04	44.0	0.06
3	100.0	36.9	7.4	2.7	0.1	0.04	39.6	0.07
4	100.0	32.7	6.2	2.0	0.1	0.03	34.7	0.06
5	100.0	33.5	6.5	2.2	0.1	0.03	35.7	0.07
6	100.0	29.7	3.2	1.0	0.1	0.03	30.7	0.03
7	100.0	31.5	6.0	1.9	0.1	0.03	33.4	0.06
8	100.0	36.2	4.9	1.8	0.1	0.04	38.0	0.05
9	100.0	41.9	5.0	2.1	0.1	0.04	44.0	0.05
14	100.0	47.8	29.0	13.9	1.2	0.57	62.3	0.30
10	100.0	39.4	15.5	6.1	0.2	0.08	45.6	0.16
11	100.0	33.2	16.7	5.5	0.7	0.23	38.9	0.17
13	100.0	38.0	24.0	9.1	1.3	0.49	47.6	0.25
12	100.0	24.3	21.4	5.2	3.9	0.95	30.5	0.25

a) *Irel*: Relative intensity. b) $\%\Sigma$: Percentage of total ionization.

TABLE 6. PRINCIPAL FRAGMENT IONS OF POLYPHENYLENES (**1**—**14**)

Compound	$(M-1)^+$		$(M-Hy)^+$[a]	$(M-Hy)^{2+}$[a]	$(M-CxHy)^+$[b]	$(M-Cx'Hy)^+$[c]
	Irel	$\%\Sigma$	$\%\Sigma$	$\%\Sigma$	$\%\Sigma$	$\%\Sigma$
1	25.4	4.6	18.2	11.3	16.6	1.5
2	4.2	1.2	4.4	5.3	12.3	3.8
3	5.8	1.4	4.6	4.8	13.6	5.3
4	4.5	1.0	3.9	5.6	11.9	4.9
5	7.8	1.8	6.7	6.4	14.0	3.0
6	11.3	2.2	9.0	5.7	17.4	4.1
7	12.6	2.7	7.8	5.5	17.3	5.1
8	5.4	1.3	4.8	4.8	12.9	5.7
9	2.8	0.9	4.4	5.5	11.3	4.7
14	2.4	0.8	3.6	5.2	5.5	2.7
10	8.9	2.2	4.6	5.4	8.5	2.7
11	28.5	6.0	11.2	6.1	9.2	4.4
13	8.6	1.8	3.8	5.0	5.7	0.7
12	9.4	1.0	1.7	1.9	4.5	0.9

a)—c) The generic ions $(M-Hy)^+$, *etc.* refer to the sums of fragment ions corresponding to the loss of one to ten H atoms, to the loss of one to six carbon units, and to the loss of seven to twelve carbon units, respectively, from the molecular ions.

calculations were carried out on a Hewlett-Packard HP-85 personal computer with a 16K RAM attached.[22]

Commercially available *o*- (**15**) and *m*-diiodobenzene (**16**) and *o*-chloro- (**17**) and *m*-iodonitrobenzene (**18**) were purified before use. 4-Iodo-2′- (**19**) and 4-iodo-3′-nitrobiphenyl (**20**), 2,2‴-diamino-*p*-quaterphenyl,[2d] and 3,3′-diaminobiphenyl[2f] were prepared by the methods previously reported.

2,2″-Diiodo-*p*-terphenyl (**24d**) was prepared from the corresponding diamine (**24b**, described below) by a method similar to that of Cade and Pilbeam.[23] Colorless needles from ethanol: Mp 158.9°C; yield 50%. Found: C, 44.84; H, 2.42%. Calcd for $C_{18}H_{12}I_2$: C, 44.84; H, 2.51%.

4,4″-Dibromo-*o*-terphenyl (**31c**) was prepared by direct bromination[8a] of commercially available *o*-terphenyl. Colorless plates from ethanol: Mp 170.5°C (lit,[8a] 170°C); yield 61%. (Found: C, 55.55; H, 2.93%).

*Preparation of Dinitropolyphenyls (**21a**—**28a**).* *Procedure A*: A solution of two kinds of iodides in dimethylformamide (DMF) was brought to reflux. Copper powder was added in three portions at intervals of 2h with stirring, and the mixture was refluxed for an additional 16h. The hot reaction mixture was filtered, and the solid material was washed several times with hot DMF and benzene. The filtrates were combined and then cooled, and the resulting solid was removed by filtration.[24] After removal of the solvents *in vacuo*, the residue (after distillation *in vacuo* for the preparation of **23a**)[24] was subjected to a chromatography on alumina using a cyclohexane–benzene (3:7, v/v) mixture (C-B(3:7)) and benzene, or benzene as the eluents.[24]

*3,3″-Dinitro-o-terphenyl (**21a**)*: A solution of **15** (26.4g) and **18** (159g) in DMF (600ml) was treated with copper powder (254g). The eluate with a C-B (3:7) mixture gave **21a** as pale yellow prisms from ethanol: Mp 142.0°C; yield 10.3g (40%). Found: C, 67.73; H, 3.65; N, 8.93%. Calcd for $C_{18}H_{12}N_2O_4$: C, 67.50; H, 3.78; N, 8.75%.

*3,3″-Dinitro-m-terphenyl (**23a**)*: A solution of **16** (66.0g) and **18** (399g) in DMF (1300ml) was treated with copper powder (572g). A double crystallization of the eluate from benzene provided **23a** as pale yellow needles: Mp 142.1°C; 23.6g (37%). Found: C, 67.77; H, 4.08; N, 8.88%.

Procedure B: A mixture of two kinds of halides in a reaction tube (ϕ 4.5×20cm) was heated in an oil bath at 205—220°C (225—235°C for the preparation of **26a**—**28a**), copper powder was added in portions with stirring over a 2-h period, and then the mixture was heated at 215—230°C (230—240°C for the preparation of **26a**—**28a**) for an additional hour. After

cooling, the reaction product was extracted with hot benzene and then the solvent was distilled off. The remaining was distilled *in vacuo* to separate a distillate (bp 100—210 °C/667 Pa, 161—220 °C/667 Pa, 80—205 °C/933 Pa, and 150—240 °C/400 Pa in the preparation of **22a**, **24a**, **25a**, and **26a**—**28a**, respectively)[26] from a tarry or soild residue. The residue was recrystallized or chromatographed on alumina with benzene (C-B(1:1) in the preparation of **26a**).

2,2″-Dinitro-m-*terphenyl (22a)*: A mixture of **16** (8.25 g) and **17** (39.4 g) was treated with copper powder (95.3 g). Repeated crystallizations of the residue from benzene and then from ethanol afforded **22a** as pale yellow needles: Mp 163.4 °C; 2.5 g (31%). Found: C, 67.41; H, 3.93; N, 8.64%. Calcd for $C_{18}H_{12}N_2O_4$: C, 67.50; H, 3.78; N, 8.75%.

2,2″-Dinitro-p-*terphenyl (24a)*: A mixture of **19** (16.3 g) and **17** (39.4 g) was heated with copper powder (95.3 g). The eluate gave **24a** as pale yellow cubes from benzene: Mp 235.5 °C (lit,[27] 228—230.5 °C); 10.0 g (62%). (Found: C, 67.69; H, 4.02; N, 8.70%).

2,3″-Dinitro-p-*terphenyl (25a)*: A mixture of **20** (16.3 g) and **17** (39.4 g) was treated with copper powder (95.3 g). The eluate provided **25a** as pale yellow needles from benzene: Mp 145.4 °C; 4.9 g (31%). Found: C, 67.47; H, 3.75; N, 8.88%.

3,3″-Dinitro-p-*terphenyl (26a)*: A mixture of **20** (16.3 g) and **18** (49.8 g) was heated with copper powder (79.4 g). Several crystallizations of the eluate from benzene afforded **26a** as yellow needles: Mp 211.3 °C; 4.4 g (27%). Found: C, 67.78; H, 3.88; N, 8.90%.

2,2″-Bis(3-nitrophenyl)-p-*terphenyl (27a)*: A mixture of **24d** (9.64 g) and **18** (49.8 g) was treated with copper powder (76.3 g). Recrystallization of the eluate from benzene gave **27a** as pale yellow prisms: Mp 240.1 °C; 3.8 g (40%). Found: C, 76.52; H, 4.15; N, 5.97%. Calcd for $C_{30}H_{20}N_2O_4$: C, 76.26; H, 4.27; N, 5.93%.

4,4″-Bis(3-nitrophenyl)-o-*terphenyl (28a)*: A mixture of 4,4″-diiodo-*o*-terphenyl[2e] (12.1 g) and **18** (49.8 g) was treated with copper powder (79.4 g). Recrystallization of the eluate from benzene afforded **28a** as yellow needles: Mp 228.0 °C; 2.7 g (23%). Found: C, 76.42; H, 4.12; N, 5.68%.

Preparation of Diaminopolyphenyls (21b—28b). A solution of each of the dinitro compounds (**21a**—**26a**: 16.0 g, **27a** and **28a**: 14.2 g) in hot benzene (800—1200 ml) was treated with activated iron by a method similar to that of Hazlet and Dornfeld.[28] After filtration, hydrobromic acid (about 47%) was added in portions to the filtrate with stirring, and then the precipitate formed was collected, washed with benzene and small amount of water, and dried; yield 96—98%. A portion of the salt was treated in the usual manner with aqueous alkali into the free base, which crystallized from ethanol or benzene.

3,3″-Diamino-o-*terphenyl (21b)*: Brown oil. **21b**·2HBr: White powder. Found: C, 51.33; H, 4.22; N, 6.73%. Calcd for $C_{18}H_{18}Br_2N_2$: C, 51.21; H, 4.30; N, 6.64%.

2,2″-Diamino-m-*terphenyl (22b)*: Colorless prisms; mp 120.9 °C. Found: C, 83.12; H, 6.22; N, 10.54%. Calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.76%.

3,3″-Diamino-m-*terphenyl (23b)*: Colorless oil. Found: C, 83.23; H, 5.96; N, 10.70%.

2,2″-Diamino-p-*terphenyl (24b)*: Colorless needles; mp 212.0 °C (lit,[27] 204.5—205.5 °C). (Found: C, 82.99; H, 6.10; N, 10.86%).

2,3″-Diamino-p-*terphenyl (25b)*: Colorless needles; mp 180.0 °C. Found: C, 82.76; H, 6.08; N, 10.82%.

3,3″-Diamino-p-*terphenyl (26b)*: Colorless needles; mp 196.6 °C. Found: C, 83.24; H, 6.40; N, 10.66%.

2,2″-Bis(3-aminophenyl)-p-*terphenyl (27b)*: Colorless prisms; mp 229.1 °C. Found: C, 87.27; H, 5.64; N, 6.61%. Calcd for $C_{30}H_{24}N_2$: C, 87.35; H, 5.86; N, 6.79%.

4,4″-Bis(3-aminophenyl)-o-*terphenyl (28b)*: Colorless plates; mp 210.4 °C. Found: C, 87.64; H, 5.89; N, 6.70%.

Preparation of Dibromopolyphenyls (21c—30c). A suspension of bishydrobromide of each of the diamino compounds (50 mmol) in 47% hydrobromic acid (100 ml) and water (150 ml) was bis-diazotized with sodium nitrite (7.3 g, 106 mmol) in water (20 ml) at 0—5 °C with stirring for 2 h. The cold suspension of bis(diazonium) salt formed was added in portions to a solution of freshly prepared copper(I) bromide (15.8 g, 110 mmol) in 47% hydrobromic acid (70 ml) with stirring, and the mixture was heated slowly up to *ca.* 80 °C and then cooled. The benzene extract was washed successively with water, sodium thiosulfate solution, sodium hydroxide solution, and water. After removal of the solvent, the residue was chromatographed on alumina with cyclohexane and/or C-B (9:1, 4:1, and 1:1) mixtures as the eluent to give dibromo compounds.

3,3″-Dibromo-o-*terphenyl (21c)*: Colorless needles from ethanol; mp 90.9 °C; yield 42%. Found: C, 55.87; H, 3.01%. Calcd for $C_{18}H_{12}Br_2$: C, 55.71; H, 3.12%.

2,2″-Dibromo-m-*terphenyl (22c)*: Colorless cubes from benzene; mp 76.3 °C; 64%. Found: C, 55.88; H, 3.28%.

3,3″-Dibromo-m-*terphenyl (23c)*: Colorless oil (lit,[5c] colorless viscous oil); 47%. (Found: C, 55.95; H, 3.04%).

2,2″-Dibromo-p-*terphenyl (24c)*: Colorless needles from ethanol; mp 137.4 °C; 58%. Found: C, 55.92; H, 3.14%.

2,3″-Dibromo-p-*terphenyl (25c)*: Colorless plates from ethanol; mp 114.9 °C; 63%. Found: C, 55.98; H, 2.94%.

3,3″-Dibromo-p-*terphenyl (26c)*: Colorless plates from benzene; mp 149.8 °C; 45%. Found: C, 55.83; H, 2.99%.

2,2″-Bis(3-bromophenyl)-p-*terphenyl (27c)*: Colorless prisms from benzene-cyclohexane; mp 190.1 °C; 64%. Found: C, 66.94; H, 3.67%. Calcd for $C_{30}H_{20}Br_2$: C, 66.69; H, 3.73%.

4,4″-Bis(3-bromophenyl)-o-*terphenyl (28c)*: Colorless needles from ethanol-benzene; mp 142.3 °C; 53%. Found: C, 66.89; H, 3.76%.

2,2‴-Dibromo-p-*quaterphenyl (29c)*: Colorless needles from benzene-ethanol; mp 174.8 °C; 30%. Found: C, 61.86; H, 3.32%. Calcd for $C_{24}H_{16}Br_2$: C, 62.10; H, 3.47%.

3,3′-Dibromobiphenyl (30c): Colorless needles from ethanol; mp 54.6 °C (lit,[5c] 53 °C); 55%. (Found: C, 46.31; H, 2.59%).

Preparation of m,m,o,p,o-*Pentaphenylene (1). Procedure A*: A solution of di-Grignard compound was prepared from **27c** (2.70 g, 5.9 mmol), magnesium turnings (0.25 g, 10 mmol), and a THF-benzene (1:1, v/v) mixture (T-B(1:1)) (40 ml) under nitrogen in the usual manner. To the Grignard reagent thus prepared, after dilution with T-B (1:1) (60 ml), anhydrous copper(II) chloride (1.74 g, 13 mmol) was added. The mixture was refluxed with stirring for 4 h and then hydrolyzed with ammonium chloride (2 g) and concentrated hydrochloric acid (4 ml) in water (40 ml). The product was extracted with benzene. The organic layer was separated, washed with water, and then dried. After removal of the solvent, the residue was chromatographed on alumina with C-B (9:1) to give 2,2″-diphenyl-*p*-terphenyl (**32**) as colorless needles from ethanol: Mp 185.7 °C (lit,[2a] 185.8 °C); yield 151 mg (7.9%). Subsequent elutions with C-B (9:1), C-B

(4:1), and C-B (3:1) provided **1**.

1: Colorless cubes from hexane; mp 188.6°C; yield 1233 mg (65%); UV λ_{max} (ε) 190 (66300), 211 (76900), 237 (53700), and 256 nm (sh) (36600). Found: C, 94.97; H, 5.29%; M^+, 380. Calcd for $C_{30}H_{20}$: C, 94.70; H, 5.30%; M^+, 380.

Procedure B: A mixture of the di-Grignard reagent, prepared from **27c** (540 mg, 1.0 mmol) and magnesium turnings (50 mg, 2 mmol) in T-B (1:1) (20 ml), and thallium(I) bromide (569 mg, 2.0 mmol) was stirred and refluxed under nitrogen for 5 h, and then hydrolyzed with dilute hydrochloric acid.[11] The benzene extract of the product was worked up as described for procedure A to afford **32** (105 mg, 28%) and **1** (68 mg, 18%).

Procedure C: A solution of tris(triphenylphosphine)nickel(0) [Ni(tpp)$_3$] was prepared from bis(triphenylphosphine)nickel(II) dichloride[29] (635 mg, 1.0 mmol), triphenylphosphine (524 mg, 2.0 mmol), and zinc powder (66 mg, 1.0 mmol) in dry, O_2-free DMF (5 ml) under nitrogen at 50°C for 1 h, by a method similar to that of Kende *et al.*[12] To the red-brown slurry of Ni(tpp)$_3$ thus prepared, **27c** (540 mg, 1.0 mmol) in dry, O_2-free DMF (2 ml) was added and the reaction mixture was stirred under nitrogen at 50°C for 24 h. It was then cooled, poured into 2% hydrochloric acid (20 ml), extracted into benzene, and washed well with water, and the solvent was distilled off. The products were analyzed by quantitative GLPC, using *p*-terphenyl as an internal standard calibrated against the pure samples, to give **32** (28%), **1** (22%), and starting material **27c** (40%).

Preparation of m,m,o,m,m,o-*Hexaphenylene (2)*. To the solution of di-Grignard compound prepared from **21c** (3.88 g, 10 mmol) and magnesium turnings (0.49 g, 20 mmol) in THF (20 ml), after dilution with THF (80 ml), anhydrous copper(II) chloride (3.40 g, 25 mmol) was added. The mixture was worked up as described for **1**. The benzene extract was chromatographed on alumina, with cyclohexane and then with C-B (9:1) as the eluents, to provide **2** and a bromosexiphenyl: Colorless needles from benzene–ethanol; mp 150.0°C; 39 mg. Found: C, 80.52; H, 4.61%; M^+, 537. Calcd for $C_{36}H_{25}Br$: C, 80.45; H, 4.69%; M^+, 537.

2: Colorless prisms from benzene–ethanol; mp 292.0°C; 363 mg (16%); UV λ_{max} (ε) 188 (75500), 207 (68600), 236 (92800), and 248 nm (sh) (58700). Found: C, 94.86; H, 5.45%; M^+, 456. Calcd for $C_{36}H_{24}$: C, 94.70; H, 5.30%; M^+, 456.

Preparation of m,o,o,m,o,o-*Hexaphenylene (3)*. The Grignard reagent prepared from **22c** (9.70 g), magnesium turnings (1.22 g), and THF (50 ml), after dilution with THF (200 ml) followed by addition of anhydrous copper(II) chloride (8.60 g), was treated as described for the preparation of **1**. The benzene extract was dissolved in benzene and then allowed to stand overnight to separate out colorless, transparent plates and an amorphous precipitate. The plates and liquid part containing the amorphous precipitate were separated by decantation. Recrystallization of the former from benzene gave **3** (425 mg). The latter together with filtrates, after removal of the solvent, was chromatographed on alumina with C-B (4:1) to afford an additional **3** (650 mg) and *m,o,o,m,o,o,m,o,o,m,o,o*-dodecaphenylene (**12**).

3: Colorless plates from benzene; mp 403°C (lit,[8b] 382°C); 799 mg (14%); UV λ_{max} (ε) 235 (95700) and 242 nm (sh) (87300) (lit,[8b] λ_{max} (log ε) 235 (4.98)). (Found: C, 94.62; H, 5.28%; M^+, 456).

12: Colorless needles from benzene; mp 444°C; 73 mg (1.3%); UV λ_{max} (ε) 195 (136400), 230 (121600), and 252 nm (sh) (79200). Found: C, 94.78; H, 5.25%; M^+, 912. Calcd for $C_{72}H_{48}$: C, 94.70; H, 5.30%; M^+, 912.

Preparation of o,o,p,o,o,p-*Hexaphenylene (4)*. The Grignard reagent prepared from **24c** (9.70 g) and magnesium turnings (1.22 g) in T-B (1:1) (80 ml),[30] after dilution with T-B (1:1) (120 ml) followed by addition of anhydrous copper(II) chloride (8.60 g), was worked up as described for **1**. The benzene extract was dissolved in benzene, and then allowed to stand overnight. The precipitate formed was collected and recrystallized from benzene to afford **4** (540 mg). The filtrates, after removal of the solvent, were subjected to a chromatography on alumina with C-B (4:1) to give *p*-terphenyl (**33**) (105 mg). Subsequent elutions with C-B (4:1) and C-B (2:1) provided an additional **4** (230 mg).

4: Colorless cubes from benzene; mp 446°C; 770 mg (14%); UV λ_{max} (ε) 198 (69300), 203 (sh) (66000), 236 (42300), 284 (34000), and 288 nm (sh) (33600). Found: C, 94.98; H, 5.13%; M^+, 456. Calcd for $C_{36}H_{24}$: C, 94.70; H, 5.30%; M^+, 456.

Preparation of m,o,p,m,o,p-*Hexaphenylene (5)*. The Grignard reagent prepared from **25c** (7.76 g) and magnesium turnings (0.98 g) in T-B (2:1) (90 ml), after dilution with T-B (2:1) (110 ml), was treated with anhydrous copper(II) chloride (6.80 g) as described for **1**. The benzene extract was chromatographed on alumina with C-B (4:1). The repeated fractional crystallizations of the eluate from hexane–benzene afforded **33** (125 mg) and **5**.

5: Colorless needles from hexane–benzene; mp 292.2°C; 630 mg (14%); UV λ_{max} (ε) 195 (76800), 206 (77800), 246 (80300), and 264 nm (sh) (43600). Found: C, 94.63; H, 5.04%; M^+, 456. Calcd for $C_{36}H_{24}$: C, 94.70; H, 5.30%; M^+, 456.

Preparation of o,p,o,p,o,p-*Hexaphenylene (6)*. To a mixture of two kinds of di-Grignard reagents prepared from **24c** (3.88 g, 10 mmol) and **31c** (19.41 g, 50 mmol), magnesium turnings (2.92 g, 120 mmol), and T-B (2:1) (150 ml), after dilution with T-B (1:2) (150 ml), anhydrous copper(II) chloride (20.4 g, 150 mmol) was added. The mixture was refluxed with stirring for 5 h, and hydrolyzed with a mixture of ammonium chloride (24 g), concentrated hydrochloric acid (48 ml), and water (480 ml), and then the precipitate formed was filtered. The benzene extract of the filtrate was washed with water and then dried. The precipitate was extracted with hot benzene. The combined benzene extract, after removal of the solvent, was treated with 800 ml of hot C-B (4:1) to be separated into soluble and insoluble parts. The benzene solution of the latter was allowed to stand for 2 d to separate out colorless, transparent cubes and an amorphous precipitate. The cubes were separated by decantation followed by several crystallizations from benzene to give *o,p,p,o,p,p,o,p,p*-nonaphenylene (**13**) (350 mg). The former was subjected to a chromatography on alumina with C-B (4:1) and C-B (2:1) to provide **6** and an additional **13** (163 mg).

6: Colorless needles from hexane; mp 312°C; 734 mg (16%); UV λ_{max} (ε) 188 (sh) (91500), 200 (96500), 245 (43700), and 276 nm (sh) (13500). Found: C, 94.95; H, 5.11%; M^+, 456. Calcd for $C_{36}H_{24}$: C, 94.70; H, 5.30%; M^+, 456.

13: Colorless cubes from benzene; mp 488°C (lit,[8a] 492°C); 513 mg (4.5%); UV λ_{max} (ε) 203 (133500), 279 (89100), and 320 nm (sh) (21900) (lit,[8a] 282.5 nm (82300) in $CHCl_3$). (Found: C, 94.69; H, 5.23%; M^+, 684).

Preparation of m,o,p,o,p,o-*Hexaphenylene (7)*. To a solution of two kinds of di-Grignard compounds prepared from **22c** (3.88 g) and **31c** (19.41 g), magnesium turnings (2.92 g), and T-B (1:1) (150 ml), after dilution with T-B (1:1) (150 ml), anhydrous copper(II) chloride (20.4 g) was added,

and then the mixture was worked up as described for **6**. The benzene extract, after removal of the solvent, was treated with hot C-B (4:1) (1000ml) to be separated into soluble and insoluble parts. Several crystallizations of the latter from benzene afforded **13** (180mg). The former was chromatographed on alumina with C-B (4:1) and C-B (1:1) to give two fractions. The repeated fractional crystallizations of the first from C-B (1:1) afforded **3** (148mg, 6.5%) and **7**. The second, upon recrystallization from benzene, provided an additional **13** (116mg; total yield 2.6%).

7: Colorless cubes from benzene; mp 308°C; 205mg (4.5%); UV λ_{max} (ε) 198 (86600), 205 (sh) (84900), and 237nm (46600). Found: C, 94.67; H, 5.28%; M$^+$, 456. Calcd for $C_{36}H_{24}$: C, 94.70; H, 5.30%; M$^+$, 456.

Preparation of m,o,m,o,m,o-*Hexaphenylene (8).* A mixture of two kinds of di-Grignard reagents prepared from **21c** (3.88g) and **22c** (3.88g), magnesium turnings (980mg), and T-B (2:1) (75ml), after dilution with T-B (2:1) (75ml), was terated with anhydrous copper(II) chloride (6.88g) as described for **6**. The benzene extract was chromatographed on alumina with C-B (9:1) and C-B (5:1) to give **3** (100mg, 4.4%), **2** (75mg, 3.3%), and **8**.

8: Colorless needles from hexane; mp 270.8°C; 105mg (2.3%); UV λ_{max} (ε) 189 (85600), 207 (73200), 233 (81800), and 254nm (sh) (36000). Found: C, 94.80; H, 5.35%; M$^+$, 456. Calcd for $C_{36}H_{24}$: C, 94.70; H, 5.30%; M$^+$, 456.

Preparation of m,m,m,o,m,o-*Hexaphenylene (9).* A mixture of two kinds of di-Grignard reagents prepared from **22c** (5.82g), **23c** (3.88g), and magnesium turnings (1.22g) in T-B (1:1) (60ml), after dilution with T-B (1:1) (80ml) followed by addition of anhydrous copper(II) chloride (8.60g), was worked up as described for **6**. After hydrolysis of the reaction mixture, the precipitate formed was filtered off. Recrystallization of the precipitate from xylene gave *m*-hexaphenylene (**14**). The benzene extract of the filtrate, after removal of the solvent, was chromatographed on alumina with C-B (4:1) and C-B (1:1). The repeated fractional crystallizations of the eluate from benzene-hexane provided **9** and **3** (168mg, 4.9%).

9: Colorless prisms from hexane; mp 315°C; 150mg (3.3%); UV λ_{max} (ε) 190 (87500), 240 (107300), and 252nm (sh) (65700). Found: C, 94.82; H, 5.40%; M$^+$, 456. Calcd for $C_{36}H_{24}$: C, 94.70; H, 5.30%; M$^+$, 456.

14: Colorless needles from xylene; mp 505°C (lit,[5b] 507—508°C); 94mg (4.1%); UV λ_{max} (ε) 191 (99800), 198 (sh) (88100), and 247nm (118900) (lit,[5b] 251 (119000) in THF). (Found: C, 94.42; H, 5.59%; M$^+$, 456).

Preparation of m,o,p,p,o,m,p-*Heptaphenylene (10).* A mixture of two kinds of di-Grignard reagents prepared from **26c** (3.88g), **29c** (4.64g), and magnesium turnings (980mg) in T-B (1:1) (150ml), after dilution with T-B (1:1) (150ml), was treated with anhydrous copper(II) chloride (6.88g) as described for the preparation of **6**. The soluble part of the benzene extract in C-B (4:1) (500ml) was chromatographed on alumina with C-B(4:1) and C-B (1:1) to afford **10**.

10: Colorless needles from benzene; mp 341°C; 266mg (5.0%); UV λ_{max} (ε) 198 (87200), 205 (sh) (84600), 267 (71400), and 312nm (sh) (16800). Found: C, 94.59; H, 5.47%; M$^+$, 532. Calcd for $C_{42}H_{28}$: C, 94.70; H, 5.30%; M$^+$, 532.

Preparation of m,m,m,m,p,o,p-*Heptaphenylene (11).* To a solution of two kinds of di-Grignard compounds prepared from **28c** (5.4g), **30c** (15.6g), and magnesium turnings (2.93g) in T-B (2:1) (200ml), after dilution with T-B (2:1) (200ml), anhydrous copper(II) chloride (20.6g) was added, and then the mixture was worked up as described for **6**. The reaction mixture was treated with benzene to be separated into soluble and insoluble parts. Recrystallization of the latter from xylene gave **14** (185mg). The former was subjected to a chromatography on alumina progressively with C-B (4:1) and with C-B (1:1) to provide an additional **14** (38mg, total yield 2.9%) and **11**, respectively.

11: Colorless needles from benzene; mp 378°C; 273mg (5.1%); UV λ_{max} (ε) 202 (38700), 256 (107700), and 284nm (infl) (24100). Found: C, 94.68; H, 5.41%; M$^+$, 532. Calcd for $C_{42}H_{28}$: C, 94.70; H, 5.30%; M$^+$, 532.

The author wishes to thank Professor Aritsune Kaji of Kyoto University for his valuable discussions and suggestions. Thanks are due to Nippon Shinyaku Co., Ltd. and Mr. Yasuhiro Fujiwara of this university for the measurements of ^{1}H NMR spectra.

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