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Syntheses and Spectral Properties of Several Unsymmetrical Sexiphenyls[1]

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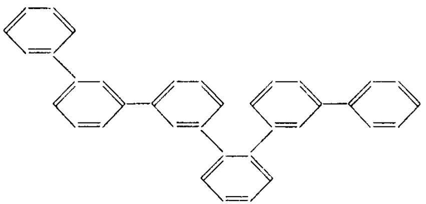
Six sexiphenyls, including four new isomers, 2,3'-di(4-biphenylyl)biphenyl (**2**), 4-(2-biphenylyl)-*o*- (**4**), 4-(2-biphenylyl)-*m*-quaterphenyl (**5**), and 2-phenyl-*p*-quinquephenyl (**6**), were synthesized by the Ullmann cross-coupling of iodobiphenyl and diiodobiphenyl or of two kinds of iodoterphenyls. The characteristic bands of the infrared spectra (680—920 cm^{-1}) and signals of the proton magnetic resonance spectra of the sexiphenyls were assigned tentatively and are discussed briefly. The remarkable high field shifts of the *p*-phenylene proton signals in **4** (1.23 and 0.89 ppm) as compared with that of *p*-terphenyl (δ 7.68) presumably reflect the ring current effects caused by the presence of adjacent *o*-phenylene rings. Ultraviolet spectral studies indicated that the absorption curves of the sexiphenyls were related closely to those of the polyphenyls corresponding to their partial structures.

Keywords——Ullmann reaction; IR; UV; ^{1}H-NMR; sexiphenyls; polyphenyls

In previous studies, a series of closely related symmetrical quinque- to octiphenyls have been synthesized to elucidate the relation between the structures and the physical properties of polyphenyls.[2] Their spectral characteristics, which originate from the number and arrangement of the benzene rings, have been thoroughly discussed.

The present work was undertaken to develop further the structure-property correlation study to polyphenyls of linear unsymmetrical structure.

Thus six sexiphenyls (**1**—**6**) were synthesized and their infrared (IR), ultraviolet (UV), and proton magnetic resonance (^{1}H-NMR) spectra were measured.



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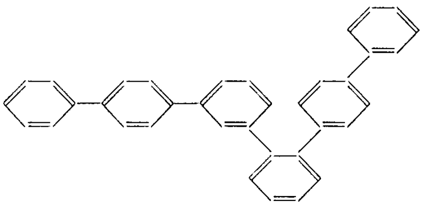

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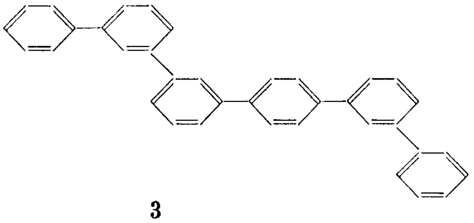

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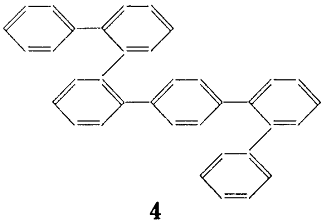

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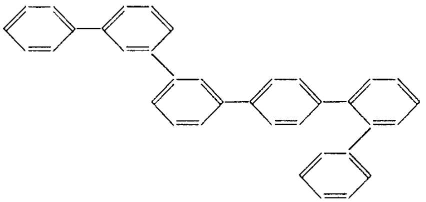

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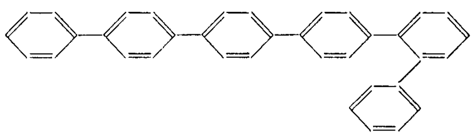

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For the syntheses of the unsymmetrical polyphenyls, the Ullmann cross-coupling reaction of aryl halides and arylene dihalides or of different aryl halides was employed. The aromatic iodides used, iodobiphenyls (2- (**7**), 3- (**8**), and 4-iodobiphenyl (**9**)),[2a] diiodobiphenyls (2,3'-(**10**), 3,4'- (**11**), and 2,4'-diiodobiphenyl (**12**)),[3] and iodoterphenyls (4-iodo-*o*- (**13**),[2b] 3-iodo-*m*-(**14**),[2d] and 4-iodo-*p*-terphenyl (**15**)[2b]) were prepared as reported previously. A mixture of

$$2\,ArX + Ar'X_2 \longrightarrow Ar\cdot Ar'\cdot Ar \qquad (A)$$

$$Ar''X + Ar'''X \longrightarrow Ar''\cdot Ar''' \qquad (B)$$

iodobiphenyl and diiodobiphenyl in the molar ratio of 2 to 1 or of two kinds of iodoterphenyls in equimolar ratio was subjected to the reaction at 255—275 °C with copper powder, and the products were separated by column chromatography on alumina. The sexiphenyls (including four new compounds, **2**, **4**, **5**, and **6**) and by-products thus obtained are given in Table I.

Table I. Syntheses of Unsymmetrical Sexipheyls

Reactants	Sexiphenyl (Yield, %)	Other products
8+**10**	**1** (11.2)	**16**
9+**10**	**2** (9.3)	**17**, **18**, **19**, **20**, **21**
8+**11**	**3** (11.9)	**16**, **18**, **21**
7+**12**	**4** (13.7)	**19**
13+**14**	**5** (20.3)	**22**, **23**, **24**, **25**
13+**15**	**6** (23.9)	**22**, **25**, **26**, **27**

The sexiphenyls (**1**—**6**) showed IR spectral data consistent with their structures and gave acceptable results in elemental analyses and molecular weight determinations by mass speetra(MS). The melting points of **1** and **3** coincide (within 1 °C) with the reported values.[4] Further, the melting points of **1**, **3**, and **4** fall within 1—4 °C of those of the corresponding sexiphenyls alternatively prepared by us using the Kharash-type Grignard cross-coupling of biphenylylmagnesium bromides and diiodobiphenyls in the presence of bis(acetylacetonato)-nickel(II).[2f] The yields of all the pure sexiphenyls (**1**—**6**) were 9—24%. In the cross-coup-

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

2		**4**		**5**		**6**	
678 w		678 m		680 m		692 sh m	γ_{C-C}
698 s	γ_{C-C}	698 sh s	γ_{C-C}	694 s	γ_{C-C}	699 s	
731 m		700 s		703 s		703 sh m	
734 sh m		711 w		713 w		733 sh m	
747 sh m	γ_{C-H}(M, *o*)	730 m		736 m		746 s	γ_{C-H}(M, *o*)
754 s		742 s	γ_{C-H}(M, *o*)	753 s	γ_{C-H}(M, *o*)	759 s	
760 s		754 s		757 s		767 sh m	
767 sh m		757 sh s		766 s		778 w	γ_{C-H}(*o*)
800 m	γ_{C-H}(*m*)	769 s	γ_{C-H}(*o*)	778 m	γ_{C-H}(*o*)	818 s	γ_{C-H}(*p*)
843 m	γ_{C-H}(*p*)	774 s		781 m		843 vw	
876 vw	γ_{C-H}(*o*)	779 s		789 s	γ_{C-H}(*m*)	853 vw	
906 w	γ_{C-H}(*m*)	841 s	γ_{C-H}(*p*)	812 w		874 vw	γ_{C-H}(*o*)
915 w	γ_{C-H}(M)	871 w	γ_{C-H}(*o*)	831 m	γ_{C-H}(*p*)	912 w	γ_{C-H}(M)
		878 w		842 m			
		913 w	γ_{C-H}(M)	849 m			
		921 w		883 vw	γ_{C-H}(*o*)		
				893 m	γ_{C-H}(*m*)		
				912 w	γ_{C-H}(M)		
				918 w			

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

ling reactions, the supposed routes of formation of the chief by-products isolated can be classified briefly into the following: i) the hydrogenolytic deiodinations of starting iodides (biphenyl (**18**), *o*- (**22**), *m*- (**23**), and *p*-terphenyl (**27**)); ii) the homo-coupling of starting aryl iodides (*p*-quaterphenyl (**17**), *m*- (**24**) and *p*-sexiphenyl (**26**), and 2,2‴-diphenyl-*p*-quaterphenyl (**25**)); iii) the partial coupling of arylene diiodides followed by the hydrogenolytic deiodination of the intermediate diiodoquaterphenyls (*o*-quaterphenyl (**19**) in the case of **9**+**10**); iv) the partial coupling of aryl iodides and arylene diiodides followed by the hydrogenolytic deiodination of the intermediate iodoquaterphenyls (2- (**20**) and 3-phenyl-*p*-terphenyl (**21**)). In the case of **8**+**11**, the by-product (*m*-quaterphenyl (**16**)) seems to be formed not only by route (ii) but by route (iii). Further, in the cases of **8**+**10** and **7**+**12**, in each of which only one by-product could be isolated, **16** and **19** were presumably formed by routes (ii) through (iv).

The IR spectra of the sexiphenyls (**1**—**6**) were measured by the KBr-disk method. The characteristic bands of the sexiphenyls in the 680—920 cm^{-1} region are listed in Table II. These bands were confirmed to be consistent with the kinds of benzene rings constituting each unsymmetrical sexiphenyl.

In the spectra of **2**—**5**, 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 831—850 cm^{-1} region. In the case of **6**, in which three consecutive *p*-phenylene rings are present, an analogous intense band was observed at 818 cm^{-1}. These spectral data indicate that the position of strong or medium C–H bands in the 818—850 cm^{-1} range of the sexiphenyls, regardless of the presence of *m*- and/or *o*-phenylene unit(s) in them, is shifted toward lower wave number in accord with the sequence length of *p*-phenylene units. These results are fully compatible with those previously observed on linear polyphenyls having one to four consecutive *p*-phenylene units.[2b,d,e]

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

TABLE III. ^1H-NMR Spectral Data for Sexiphenyls in $CDCl_3$[a]

1	7.30 (5H, s, $o\text{-}C_6H_4\cdot m\text{-}C_6H_4\cdot C_6\underline{H}_5$)
	7.19—7.62 (21H, m, other protons)
2	7.18—7.65 (26H, m, all protons)
3	7.76 (4H, s, $p\text{-}C_6H_4$)
	7.84—7.92 (3H,m, $m\text{-}C_6H$)
	7.33—7.77 (19H, m, $m\text{-}C_6H_3$ and C_6H_5)
4	6.45 and 6.79 (4H, AA′BB′-q, $J=8.6$ Hz, C_2,C_6-H and C_3,C_5-H)
	7.38 (4H, s, $p\text{-}C_6H_4\cdot o\text{-}C_6\underline{H}_4\cdot C_6H_5$)
	6.53—7.45 (18H, m, $o\text{-}C_6H_4\cdot o\text{-}C_6H_4$ and C_6H_5)
5	7.21 (5H, s, $o\text{-}C_6H_4\cdot C_6\underline{H}_5$)
	7.23 and 7.52 (4H, AA′BB′-q, $J=8.5$ Hz, C_3,C_5-H and C_2,C_6-H)
	7.34—7.73 (11H, m, $C_6H_5\cdot m\text{-}C_6H_3\cdot m\text{-}C_6H_3$)
	7.45 (4H, s, $o\text{-}C_6H_4$)
	7.80—7.86 (2H, m, $m\text{-}C_6H$)
6	7.22 (5H, s, $o\text{-}C_6H_4\cdot C_6\underline{H}_5$)
	7.24 and 7.51 (4H, AA′BB′-q, $J=8.4$ Hz, $C_{2'}$, $C_{6'}$-H and $C_{3'}$, $C_{5'}$-H)
	7.32—7.77 (5H, m, $C_6\underline{H}_5\cdot p\text{-}C_6H_4$)
	7.45 (4H, s, $o\text{-}C_6H_4$)
	7.69 (4H, s, $C_6H_5\cdot p\text{-}C_6H_4\cdot p\text{-}C_6\underline{H}_4$)
	7.70 (4H, s, $C_6H_5\cdot p\text{-}C_6\underline{H}_4$)

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

The spectrum of **1** shows a sharp 5H singlet at δ 7.30, which can be assigned to the phenyl protons of $o\text{-}C_6H_4\cdot m\text{-}C_6H_4\cdot C_6\underline{H}_5$ by comparison with the phenyl proton signal of 3,3″-diphenyl-*o*-terphenyl (δ 7.32, 10H).[2f] In the case of **3**, a 4H singlet (δ 7.76) and a 3H multiplet (δ 7.84—7.92) are assignable to the *p*-phenylene ring protons and to the isolated protons of *m*-phenylene rings, respectively, by analogy with the signals of the corresponding protons of 3,3''-diphenyl-*p*-terphenyl (δ 7.75, 4H, s, *p*-C_6H_4; δ 7.84—7.89, 2H, m, *m*-C_6H).[2b)]

The spectrum of **4** displays an apparent AA'BB'-q pattern, δ 6.45 and 6.79, J=8.6 Hz, which may be assigned to the *p*-phenylene protons at the 2-, 6- and 3-, 5-positions, respectively, by comparison with the corresponding *p*-phenylene proton signals of analogous 4,4'''-di(2-biphenylyl)-*o*-quaterphenyl (δ 6.39 and 6.74, J=8.4 Hz, C_2, C_6-H and C_3, C_5-H).[2e)] The remarkable high-field shift of the *p*-phenylene proton signals in **4** (1.23 and 0.89 ppm) as compared with that of *p*-terphenyl (**27**) (δ 7.68, s), presumably reflect the ring current effects caused by the presence of adjacent *o*-phenylene rings. In the spectrum of **5**, an apparent AA'BB'-q pattern (δ 7.23 and 7.52, J=8.5 Hz), a 5H singlet (δ 7.21), and a 4H singlet (δ 7.45) were assignable to the protons of *p*-phenylene (3-, 5-, and 2-, 6-positions), phenyl (*o*-$C_6H_4 \cdot C_6H_5$), and *o*-phenylene group, by analogy with the corresponding signals of 2-phenyl-*p*-terphenyl (**20**) (4H, δ 7.21 and 7.46, J=8.6 Hz; 5H, s, 7.20; 4H, s, 7.44).[3)]

In the case of **6**, the proton signals corresponding to the partial structure *p*-C_6H_4·*o*-C_6H_4·C_6H_5 may easily be assigned analogously, by comparison with the spectrum of 2-phenyl-*p*-terphenyl (**20**). Beside these, two 4H singlets in a very narrow region (δ 7.69—7.70) can probably be assigned to the *p*-phenylene protons of C_6H_5·*p*-C_6H_4·*p*-$C_6\underline{H}_4$ and C_6H_5·*p*-$C_6\underline{H}_4$·*p*-C_6H_4, respectively, based on the concept that the ring current effects caused by the presence of the *o*-phenylene ring may be decreased in accordance with an increase of successive *p*-phenylene units (*cf.* *p*-quaterphenyl (**17**): δ 7.71, 8H, s, *p*-$C_6\underline{H}_4$·*p*-$C_6\underline{H}_4$; 2-phenyl-*p*-quaterphenyl: δ 7.66, 4H, s, C_6H_5·*p*-$C_6\underline{H}_4$).[2b)] The remaining sexiphenyl **2** showed multiplet peaks, which are difficult to assign.

The UV spectra of the six sexiphenyls were measured in cyclohexane solution. The absorption curves are shown in Figs. 1—5. All of the sexiphenyls displayed the E-band in the fairly narrow region of 190—210 nm and the K-band in the broad region of 230—310 nm.

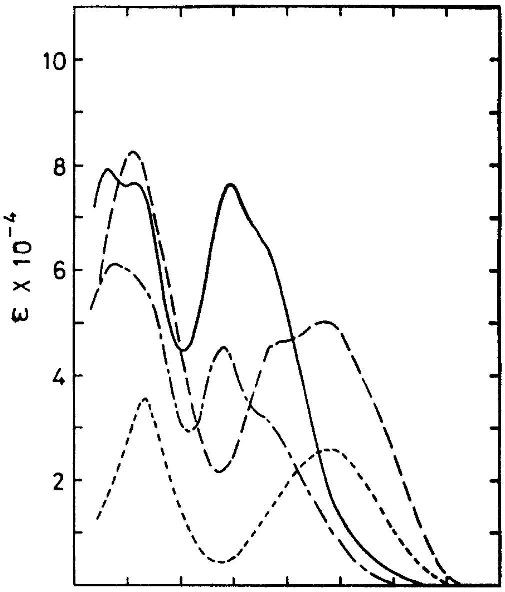

Fig. 1. UV Spectra of Terphenyl, Quaterphenyl, and Sexiphenyls in Cyclohexane

—— : 2-(3-biphenylyl)-*m*-quaterphenyl (**1**),
---- : 2,3'-di(4-biphenylyl)biphenyl (**2**),
—·— : 2-phenyl-*m*-terphenyl,
······ : *p*-terphenyl (**27**).

The spectrum of **1** is closely related to those of 2-phenyl-*m*-terphenyl and *m*-quaterphenyl (**16**), both of which are involved in the molecule of **1**. Thus, the K-band of **1** (239 nm, $\varepsilon = 77100$; 250 (sh) nm, $\varepsilon = 66700$) appeared at wavelengths similar to those of 2-phenyl-*m*-terphenyl (237, 45900)[3)] and **16** (248, 57400).[2d)] In the spectrum of **2**, in which two isolated *p*-phenylene rings are present, the intense K-band (275, 51300) was observed at similar wavelength with an intensity about twice that of *p*-terphenyl (**27**) (276, 25500) (Fig. 1).

The spectrum of **4** (228 (sh), 45500; 242 (sh), 39300; 275 (sh), 20500) is also closely related to those of reference compounds, *o*-sexiphenyl (231, 52200)[2a)] and 2-phenyl-*p*-terphenyl (**20**) (249, 29100; 278, 25100).[3)] The marked weakening of the K-band at 275 nm, which corresponds to the typical absorption band of *p*-terphenyl (**27**) (276, 25500), presumably reflects reduced π–π interaction across the pivot bonds between both termini of *p*-phenylene ring and *o*-phenylene rings (Fig. 2). In the case of **5**, an intense K-band (249, 67200; 277 (sh), 34000) was observed which is very similar, except for a rather high intensity of the band near 250 nm, to that of 2,3''-diphenyl-

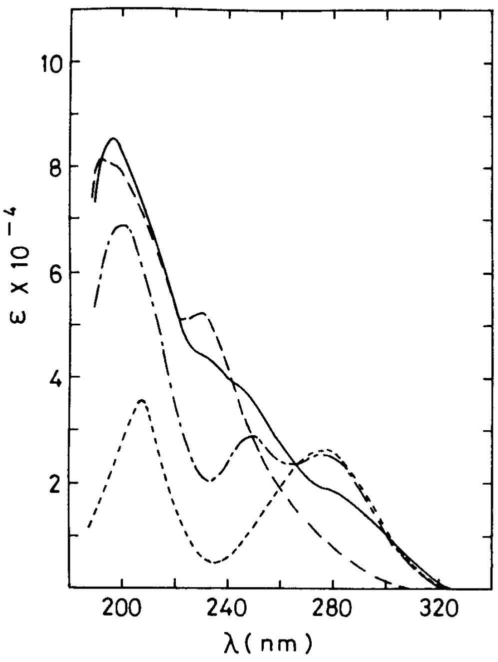

Fig. 2. UV Spectra of Terphenyl, Quaterphenyl, and Sexiphenyls in Cyclohexane

—— : 4-(2-biphenylyl)-*o*-quaterphenyl (**4**),
---- : *o*-sexiphenyl,
—·— : 2-phenyl-*p*-terphenyl (**20**),
······ : *p*-terphenyl (**27**).

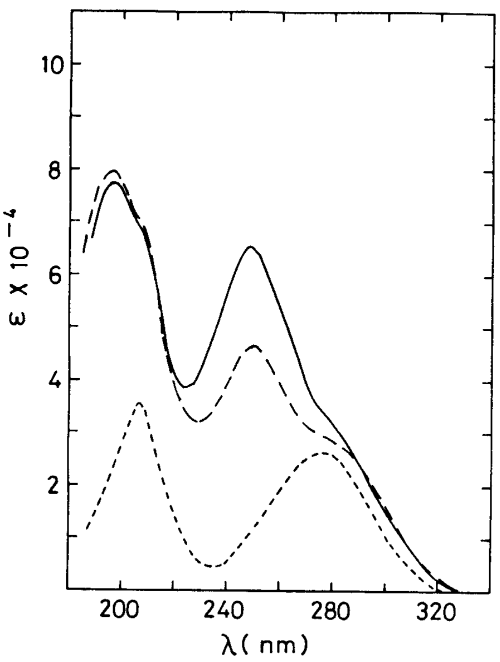

Fig. 3. UV Spectra of Terphenyl, Quinquephenyl, and Sexiphenyl in Cyclohexane

—— : 4-(2-biphenylyl)-*m*-quaterphenyl (**5**),
---- : 2,3″-diphenyl-*p*-terphenyl,
······ : *p*-terphenyl (**27**).

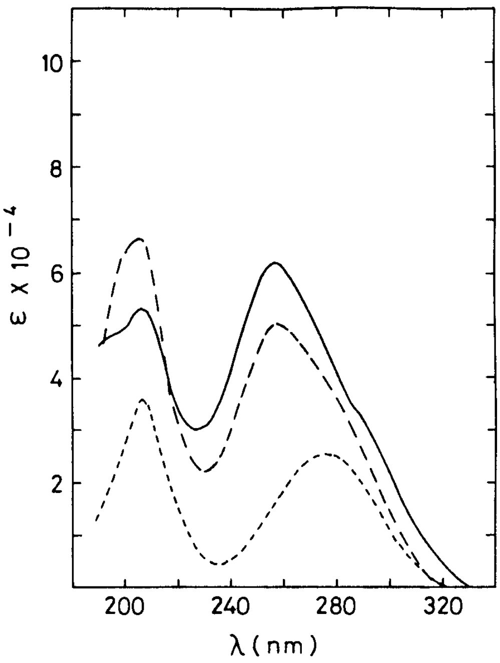

Fig. 4. UV Spectra of Terphenyl, Quinquephenyl, and Sexiphenyl in Cyclohexane

—— : 4-(3-biphenylyl)-*m*-quaterphenyl (**3**),
---- : 3,3″-diphenyl-*p*-terphenyl,
······ : *p*-terphenyl (**27**).

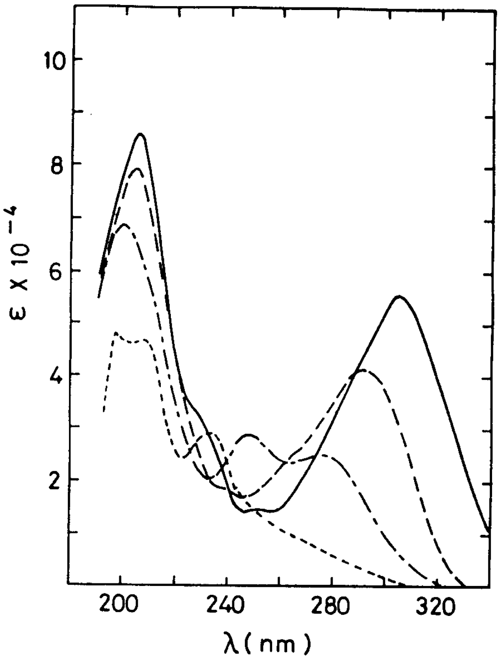

Fig. 5. UV Spectra of Terphenyl to Sexiphenyl in Cyclohexane

—— : 2-phenyl-*p*-quinquephenyl (**6**),
---- : 2-phenyl-*p*-quaterphenyl,
—·— : 2-phenyl-*p*-terphenyl (**20**),
······ : *o*-terphenyl (**22**).

p-terphenyl (250, 46200; 275 (sh), 29300),[2b] in which one less *m*-phenylene ring than in **5** is present. In addition, analogously to the case of **4**, the presence of the *p*-phenylene linkage was observed as a weak shoulder near 275 nm (Fig. 3). A similar situation was apparent in the spectra of **3** (257, 62500) and 3,3″-diphenyl-*p*-terphenyl (258, 50800; 280 (sh), 38200).[2b] In the present case, however, the presence of the *p*-phenylene linkage was only observed as a discernible shoulder (near 286, 35000) (Fig. 4).

The spectrum of **6**, in which one terminal of three consecutive *p*-phenylene rings is linked to an *o*-phenylene ring, displayed an intense K-band (306, 56900) with a slight shoulder (226 (sh), 35600). As previously discussed for a series of polyphenyls containing *p*-linkage(s),[2b] the wavelength of the intense K-band is fully compatible with that of polyphenyls containing three consecutive *p*-phenylene rings (*cf.* *p*-quinquephenyl:[5] 310, 62500; 2,2″″-diphenyl-*p*-quinquephenyl:[2b] 307, 51000). Further, the slight shoulder is very similar in wavelength to the weak K-band of *o*-terphenyl (**22**) (233, 29100), suggesting the presence of the *o*-phenylene linkage (Fig. 5).

The foregoing UV spectral results indicated that the absorption curves of the unsymmetrical sexiphenyls were closely related to those of the smaller polyphenyls corresponding to their partial structures. In addition, the spectral data suggest that the K-band above *ca.* 260 nm of the sexiphenyls, regardless of the presence of *o*- and/or *m*-phenylene ring(s), may be an indication of isolated or consecutive *p*-phenylene rings.[2b,e]

Experimental

The melting points were determined with a Mettler FP-51 apparatus, except for those above 300°C, which were determined with a Shimadzu DSC-30M differential scanning calorimeter. The UV spectra were measured on Shimadzu MPS-50L and UV-240 spectrophotometers, the IR spectra on a Leitz III-G spectrophotometer, and the ^{1}H-NMR spectra on a Varian CFT-20 spectrometer at 80 MHz using tetramethylsilane as an internal standard. The MS were recorded on a Hitachi RMU-6E mass spectrometer.

2- (**7**), 3- (**8**), and 4-Iodobiphenyl (**9**),[2a] 2,3′- (**10**), 3,4′- (**11**), and 2,4′-diiodobiphenyl (**12**),[3] 4-iodo-*o*- (**13**),[2b] 3-iodo-*m*- (**14**),[2d] and 4-iodo-*p*-terphenyl (**15**)[2b] were prepared as reported previously.

Preparation of 2-(3-Biphenylyl)-*m*-quaterphenyl (1)——A mixture of 3-iodobiphenyl (**8**) (8.40 g, 30 mmol) and 2,3′-diiodobiphenyl (**10**) (6.10 g, 15 mmol) in a reaction tube (ϕ 2.5 × 20 cm) was heated in an oil bath at 265—270°C, and copper powder (30.5 g, 480 mg-atom) was added under stirring in portions over a two-hour period, after which the mixture was heated at 275°C for an additional hour. After cooling, the reaction product was extracted with hot benzene, then the solvent was distilled off. The residue (6.20 g) was subjected to chromatography on alumina with a cyclohexane–benzene (5: 1, v/v) mixture (C-B (5: 1)) as the eluent, to provide *m*-quaterphenyl (**16**) (colorless plates from ethanol; mp 87.1°C (lit.[6] mp 85.5—86°C); yield, 1454 mg) and **1**. The properties of the latter are as follows.

1: Colorless cubes from ethanol–benzene (1: 1); mp 60.3°C (lit.[4] mp 58—60°C); yield, 769 mg (11.2%). IR (KBr) cm^{-1}: 698 s (γ_{C-C}); 751 s (γ_{C-H}, M, *o*); 795 m, 803 sh m (γ_{C-H}, *m*); 843 w; 876 sh w (γ_{C-H}, *o*); 896 m (γ_{C-H}, *m*). UV $\lambda_{max}^{cyclohexane}$ nm (ε): 192 (81000), 203 (77200), 239 (77100), 250 sh (66700). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.41; H, 5.57. MS *m/e*: 458 (M^+).

Preparation of 2,3′-Di(4-biphenylyl)biphenyl (2)——A mixture of 4-iodobiphenyl (**9**) (8.40 g) and **10** (6.10 g) was treated with copper powder (23.0 g) under conditions similar to those used in the preparation of **1**. The product was extracted with hot benzene followed by hot toluene, then the solvents were distilled off. The benzene extract (6.30 g) was treated with 150 ml of C-B (5: 1) to separate the product into soluble and insoluble parts. Recrystallization of the latter (0.65 g) together with the toluene extract (0.45 g) from benzene afforded *p*-quaterphenyl (**17**) (colorless plates; mp 319°C (lit.[7] mp 317.7—318.7°C); yield, 830 mg). The former (5.16 g) was dissolved in C-B (5: 1) and then subjected to chromatography on alumina with the same solvent as the eluent, to give biphenyl (**18**) (colorless leaves from ethanol; mp 68.9°C; 36 mg), *o*-quaterphenyl (**19**) (colorless cubes from ethanol; mp 118.0°C (lit.[8] mp 118°C); 22 mg), 2-phenyl-*p*-terphenyl (**20**) (colorless prisms from ethanol; mp 119.2°C (lit.[9] mp 119—119.5°C); 204 mg), 3-phenyl-*p*-terphenyl (**21**) (colorless needles from ethanol; mp 166.7°C (lit.[10] mp 166—167°C); 285 mg), and **2**.

2: Colorless leaves from benzene; mp 204.5°C; 642 mg (9.3%). UV $\lambda_{max}^{cyclohexane}$ nm (ε): 203 (84200), 258 sh (47700), 275 (51300). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 93.99; H, 5.96; MS *m/e*: 458 (M^+).

Preparation of 4-(3-Biphenylyl)-*m*-quaterphenyl (3)——A mixture of **8** (8.40 g) and 3,4′-diiodobiphenyl (**11**) (6.10 g) was heated with copper powder (30.9 g), as has been described for the preparation of **1**. The hot benzene extract (6.26 g) was digested with 80 ml of C-B (5: 1) to remove insoluble material. The soluble part (5.65 g) was subjected to chromatography on alumina with the same solvent to give **18** (65 mg) and **16** (1432 mg). Subsequent elution with C-B (5: 2) provided **21** (236 mg) and **3**.

3: Colorless leaves from ethanol; mp 197.0°C (lit.4) mp 192—195°C, lit.11) mp 186—188°C); 818 mg (11.9%). IR (KBr) cm^{-1}: 683 m; 699 s ($\gamma_{\text{C-C}}$); 713 w, 738 m; 756 sh s, 758 s ($\gamma_{\text{C-H}}$, M); 787 s, 798 sh w, 807 w ($\gamma_{\text{C-H}}$, *m*); 842 m, 848 m ($\gamma_{\text{C-H}}$, *p*); 885 w, 901 vw, 907 vw ($\gamma_{\text{C-H}}$, *m*); 917 vw ($\gamma_{\text{C-H}}$, M). UV $\lambda_{\text{max}}^{\text{cyclohexane}}$ nm (ε): 195 sh (48000), 207 (53700), 257 (62500), 286 sh (35000). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.57; H, 5.90. MS *m/e*: 458 (M^+).

Preparation of 4-(2-Biphenylyl)-*o*-quaterphenyl (**4**)——A mixture of 2-iodobiphenyl (**7**) (8.40 g) and 2,4′-diiodobiphenyl (**12**) (6.10 g) was treated with copper powder (30.5 g) at 255—265°C for 1.5 h and then at 265°C for 0.5 h. The hot benzene extract (6.60 g) was chromatographed on alumina with cyclohexane to provide **21** (2450 mg). Subsequent elution with C-B (5: 1) gave **4**.

4: Colorless prisms from ethanol; mp 154.9°C; 944 mg (13.7%). UV $\lambda_{\text{max}}^{\text{cyclohexane}}$ nm (ε): 197 (86800), 205 sh (81900), 228 sh (45500), 242 sh (39300), 275 sh (20500). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.21; H, 5.81. MS *m/e*: 458 (M^+).

Preparation of 4-(2-Biphenylyl)-*m*-quaterphenyl (**5**)——A mixture of 4-iodo-*o*-terphenyl (**13**) (3.56 g, 10 mmol) and 3-iodo-*m*-terphenyl (**14**) (3.56 g, 10 mmol) was heated with copper powder (13.0 g, 205 mg-atom) at 265°C for 2 h. The hot benzene extract (5.26 g) of the product was chromatographed on alumina with cyclohexane to give *o*-terphenyl (**22**) (colorless needles from ethanol; mp 56.7°C; 264 mg) and *m*-terphenyl (**23**) (colorless needles from ethanol; mp 85.5°C; 285 mg). Fractional crystallization of subsequent eluates with C-B (19: 1), C-B (9: 1), and C-B (5: 1) afforded *m*-sexiphenyl (**24**) (colorless needles from ethanol; mp 147.6°C (lit.13) mp 146—147°C); 426 mg) and **5**. Final elution with C-B (5: 1) provided 2,2‴-diphenyl-*p*-quaterphenyl (**25**) (colorless plates from benzene; mp 237.6°C (lit.12) mp 237.9—238.1°C); 521 mg).

5: Colorless plates from ethanol; mp 170.0°C; 931 mg (20.3%). UV $\lambda_{\text{max}}^{\text{cyclohexane}}$ nm (ε): 196 (78700), 204 sh (73400), 249 (67200), 277 sh (34000). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.00; H, 5.67. MS *m/e*: 458 (M^+).

Preparation of 2-Phenyl-*p*-quinquephenyl (**6**)——A mixture of **13** (3.56 g) and 4-iodo-*p*-terphenyl (**15**) (3.56 g) was treated with copper powder (12.7 g) at 270—275°C for 2 h. The product was extracted with hot benzene followed by hot *o*-dichlorobenzene, then the solvents were distilled off. The residue (4.52 g) was treated with hot benzene to separate the product into soluble and insoluble parts. The latter was sublimed at 350—400°C/0.13 Pa to give *p*-sexiphenyl (**26**) (colorless leaves; mp 455°C (lit.13) mp 465°C); 490 mg). The former was dissolved in C-B (9: 1) and then subjected to chromatography on alumina with the same solvent as the eluent, to afford **22** (162 mg) and *p*-terphenyl (**27**) (colorless plates from ethanol; mp 212.4°C; 340 mg). Subsequent elutions with C-B (5: 1) and C-B (3: 1), and with benzene provided **25** (874 mg) and **6**, respectively.

6: Colorless leaves from benzene; mp 276.3°C; 1095 mg (23.9%). UV $\lambda_{\text{max}}^{\text{cyclohexane}}$ nm (ε): 207 (87800), 226 sh (35600), 306 (56900). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.16; H, 5.95. MS *m/e*: 458 (M^+).

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References and Notes

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