Chem. Pharm. Bull.
28(5)1468—1476(1980)

Syntheses and Physical Properties of Several Symmetrical Sexiphenyls

EIICHI IBUKI, SHIGERU OZASA, YASUHIRO FUJIOKA,[1] and HIROHIKO KITAMURA[1a)]

Kyoto College of Pharmacy[1]

(Received October 15, 1979)

Seven sexiphenyls, including three new isomers, 3,4,3′,4′-tetraphenylbiphenyl (Id), 2,5,2′,5′-tetraphenylbiphenyl (IIId), and 2,2′-di(3-biphenylyl)biphenyl (Vd), were synthesized by Ullmann homo-coupling of iodoterphenyl. The characteristic bands of the infrared spectra (675—920 cm^{-1}) and signals of the nuclear magnetic resonance spectra of the sexiphenyls were assigned tentatively and are discussed briefly. Infrared studies indicated that the range 730—770 cm^{-1}, generally accepted as the position of the C–H out-of-plane bending bands of phenyl rings, should be widened slightly to 730—782 cm^{-1}. The ultraviolet spectra commonly displayed a intense E-band in the narrow region of 192—207 nm. The prominent K-band above *ca.* 260 nm of branched sexiphenyls was taken as indicative of the presence of one or more *p*-linkages, as in the case of linear compounds.

Keywords——polyphenyls; Ullmann reaction; infrared spectra; ultraviolet spectra; NMR spectra; iodoterphenyls

In the previous work,[2] a series of linear sexiphenyls and quinquephenyls was synthesized to study the relationship between the number and arrangement of the benzene rings and the physical properties of polyphenyls. The Ullmann cross-coupling reactions of mono- and diiodobiphenyls as well as of iodobiphenyls and diiodobenzenes were used for the syntheses. However, the isolation and purification procedures were rather troublesome, and the yields of the polyphenyls were low. Moreover, the attempted coupling of 3-iodo- and 2,2′-diiodobiphenyl to prepare Vd was unsuccessful, yielding instead triphenylene and 1- and 2-phenyltriphenylenes.

To overcome these disadvantages and to develop syntheses for branched polyphenyls, the Ullmann homo-coupling of appropriate iodoterphenyls has been utilized for the syntheses of seven branched and linear sexiphenyls. The infrared (IR), ultraviolet (UV), and nuclear magnetic resonance (NMR) spectra of the sexiphenyls were measured, and the relation between the arrangement of the benzene rings and these physical properties is discussed.

For the preparation of iodoterphenyls, the intermediate nitroterphenyls were prepared either by the Gomberg–Bachmann–Hey reaction or by the Ullmann reaction. The former reaction was applied to the preparation of 4′-nitro-*o*- (Ia), 4′-nitro-*m*-(IIa), and 2′-nitro-*p*-terphenyl (IIIa) from corresponding aminonitrobiphenyls. The latter reaction was adopted to prepare 2-nitro-*p*-(IVa), 2-nitro-*m*- (Va), 2-nitro-*o*- (VIa), and 3-nitro-*o*-terphenyl (VIIa) by the coupling of iodobiphenyls and iodonitrobenzenes. The nitroterphenyls (Ia—VIIa)[3] thus obtained were reduced to the corresponding aminoterphenyls (Ib—VIIb)[6] with activated

---

[1] Location: *Misasagi-nakauchicho, Yamashina-ku, Kyoto 607, Japan*; *a*) Present address: *Nippon Abbott Kabushiki Kaisha* (*Osaka*).

[2] *a*) E. Ibuki, S. Ozasa, and K. Murai, *Bull. Chem. Soc. Jpn.*, **48**, 1868 (1975); *b*) S. Ozasa, N. Hatada, Y. Fujioka, and E. Ibuki, *ibid.*, accepted.

[3] Wardner *et al.* obtained IIa (by nitration of *m*-terphenyl) as a viscous oil, whereas it was obtained as crystals of mp 57—58° in the present work (Ref. 4, 5).

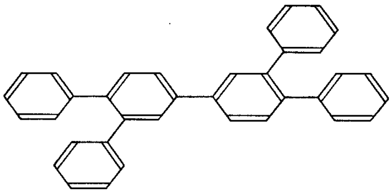
[4] C.A. Wardner and A. Lowy, *J. Am. Chem. Soc.*, **54**, 2510 (1932).

[5] H. France, I.M. Heilbron, and D.H. Hey, *J. Chem. Soc.*, **1939**, 1288.

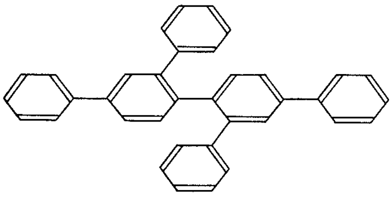
[6] Allen *et al.* gave a lower mp of 67—68° for IIb (Ref. 7, 8).

[7] C.F.H. Allen and D.M. Burness, *J. Org. Chem.*, **14**, 175 (1949).

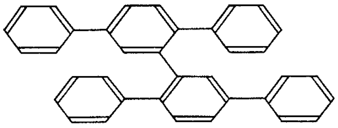
[8] W.A. Cook and K.H. Cook, *J. Am. Chem. Soc.*, **64**, 2485 (1942).



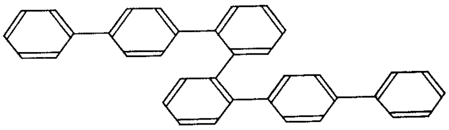
Id



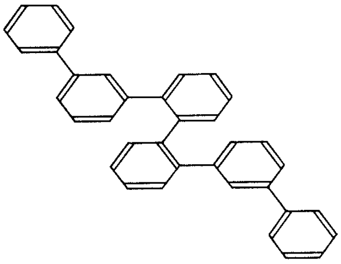
IId



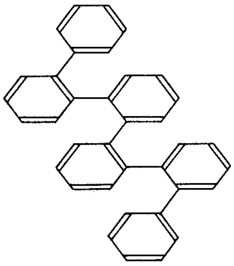
IIId



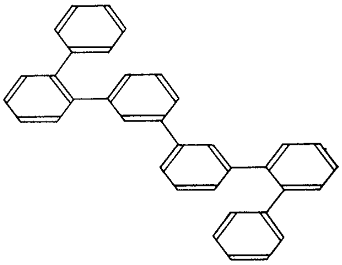
IVd



Vd



VId



VIId

Chart 1

iron in hot benzene,[9] and then converted into the iodoterphenyls (Ic—VIIc)[10] by the usual method. The unusually low yield of 2-iodo-*o*-terphenyl (VIc, 19%) as compared with other iodo compounds (47—70%) is due to the undesired formation of triphenylene.

Each of the iodoterphenyls (Ic—VIIc) was used in the Ullmann reaction, and the products were subjected to column chromatography on alumina. All the sexiphenyls except for VId were obtained in good yields (40—67%) and at high levels of purity.[11] Beside these sexiphenyls, small amounts of the corresponding terphenyls were separated as by-products. In the case of VId, however, a lower yield (21%) was obtained owing to the additional formation of triphenylene, apparently by intramolecular elimination of hydrogen iodide (Table I). In the same reaction, Cade and Pilbeam[12] isolated only triphenylene, and failed to obtain VId. They also reported a lower yield of IId (10%) as compared with ours (45%). These remarkable differences in the Ullmann reaction are probably due to insufficient purity of the iodoterphenyls as well as to the rather higher reaction temperature used by them.

The IR spectra of the sexiphenyls were measured by the KBr–disk method. The characteristic bands of sexiphenyls (Id—IIId and Vd) in the 675—920 cm^{-1} region are listed in Table II. These bands are consistent with the kinds of benzene rings constituting each sexiphenyl.

---

9) S.E. Hazlet and C.A. Dornfeld, *J. Am. Chem. Soc.*, **66**, 1781 (1944).

10) Cook and Cook have reported a lower mp of 67° for IIc (Ref. 8).

11) Each of the sexiphenyls (Id—VIId) showed a single peak on inspection by gas-liquid chromatography, which was carried out with a Shimadzu GC-5APTF gas chromatograph using a glass column (ϕ 3 mm × 1 m) of Shimalite impregnated with Silicone OV-17 (3%).

12) J.A. Cade and A. Pilbeam, *J. Chem. Soc.*, **1964**, 114.

Table I. Ullmann Syntheses of Sexiphenyls

Iodide	Sexiphenyl (yield, %)	By-product
Ic	Id (67)	*o*-Terphenyl
IIc	IId (45)	*m*-Terphenyl
IIIc	IIId (64)	*p*-Terphenyl
IVc	IVd (49)	*p*-Terphenyl
Vc	Vd (40)	*m*-Terphenyl
VIc	VId (21)	*o*-Terphenyl Triphenylene
VIIc	VIId (60)	*o*-Terphenyl

Table II. Positions and Tentative Assignments of Characteristic Bands in The IR Spectra (675—920 cm^{-1}) of Sexiphenyls[a)]

Id		IId		IIId		Vd	
698 s	γ_{C-C}	679 w		692 s	γ_{C-C}	702 s	γ_{C-C}
702 s		697 s	γ_{C-C}	697 s		745 s	γ_{C-H} (M, *o*)
740 m	γ_{C-H} (M)	715 w		737 m	γ_{C-H} (M)	751 s	
762 s		738 s	γ_{C-H} (M)	752 s		767 s	
773 s		752 s		758sh, s		778 s	γ_{C-H} (*o*)
815 m	γ_{C-H} (as)	762 s		781 m		802 m	γ_{C-H} (*m*)
826 w		772 s		840sh, m	γ_{C-H} (as)	821 vw	
845 vw		777 m		845 m		849 vw	
884 m	γ_{C-H} (as)	782 m		853 w		875 w	
912 vw	γ_{C-H} (M)	834 m	γ_{C-H} (as)	896 m	γ_{C-H} (as)	881 w	
		844 w		911 w	γ_{C-H} (M)	896 m	γ_{C-H} (*m*)
		850 m				905 w	
		893 m	γ_{C-H} (as)			911 w	γ_{C-H} (M, *m*)
		901 m					
		915 w	γ_{C-H} (M)				

a) v: very, s: strong, m: medium, w: weak, sh: shoulder. 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 as in parentheses refer to mono-, *ortho*-, *meta*-, and asymmetrically substituted rings.

The prominent bands in the 745—767 cm^{-1} region of Vd, which contains two *o*-phenylene rings, should be due not only to the C–H out-of-plane deformation vibrations of the terminal rings, but also to those of *o*-phenylene rings, as discussed in the previous paper.[2a)]

The strong band observed in the spectrum of Vd at 778 cm^{-1} can be assigned to the C–H out-of-plane deformation vibrations of *o*-phenylene rings, as suggested by Stewart and Hellmann,[13)] as well as by Sandroni and Geiss.[14)] The medium band at 802 cm^{-1} in the spectrum of Vd, and the medium or weak bands in the 884—905 cm^{-1} region of Id—IIId and Vd were assigned to the C–H out-of-plane bending vibrations of three adjacent hydrogens in *m*-phenylene rings and to those of single isolated ring hydrogens, respectively.

In the spectra of Id—IIId, medium C–H out-of-plane bending vibration bands of two adjacent ring hydrogens were observed at 815, 834, and 845 cm^{-1}, respectively. In IIId and IVd, which have two isolated *p*-linkages, the bands were found to be shifted towards higher frequency as compared with *p*-terphenyl. In constrast to this, in Id and IId, which contain two continuous *p*-linkages, marked shifts of the bands towards lower and higher frequencies, respectively, as compared with *p*-quaterphenyl were observed. With respect to these bands, several examples having closely related structures are shown as follows: 2-phenyltriphenylene,

---

13) J.E. Stewart and M. Hellmann, *J. Res. Natl. Bur. Stand.*, **60**, 125 (1956).

14) S. Sandroni and F. Geiss, *Z. Anal. Chem.*, **220**, 321 (1966).

829 (m), 824 (m);[15] *p*-terphenyl, 838 (s); 2′-phenyl-*p*-terphenyl, 842 (m);[16] bis(2-triphenylyl), 818 (m), 813 (m);[15] 2-(4-biphenylyl)triphenylene, 825 (s), 821 (s);[15] *p*-quaterphenyl, 826 (s) cm^{-1}. These data suggest that the presence of a planar triphenylene ring in the structure results in a shift of the bands towards lower frequency, probably owing to enhanced coplanarity of the structure. Therefore the shift towards lower frequency in Id may be caused by the increased coplanarity in the crystalline state. Hence, Id can be regarded as an exceptional case which deviates from the usual correlation between the chain length of *p*-phenylene ring(s) and the positions of the characteristic bands in the 815—845 cm^{-1} region.

A series of strong or medium bands in the 737—782 cm^{-1} region of Id—IIId, all of which contain two 1,2,4-trisubstituted rings, should be assigned to C–H out-of-plane deformation vibrations of five adjacent hydrogens in the terminal rings. Although this region includes absorptions at rather high frequencies 773—782 cm^{-1}, which were not included as absorptions due to C–H out-of-plane deformation vibrations of terminal rings by Bellamy,[17] Sandroni and Geiss,[14] and Doss and Solomon,[16] the following examples[16,18] support the present assignment. Thus, each of the following compounds shows absorptions in the 770—783 cm^{-1} region: 1,2,3,4-tetraphenylbenzene, 763 (s), 770 (s); pentaphenylbenzene, 760 (s), 772 (s); hexaphenylbenzene, 783 (s); 2′-phenyl-*p*-terphenyl, 756 (s), 772 (m), 783 (m); 3′-phenyl-*p*-

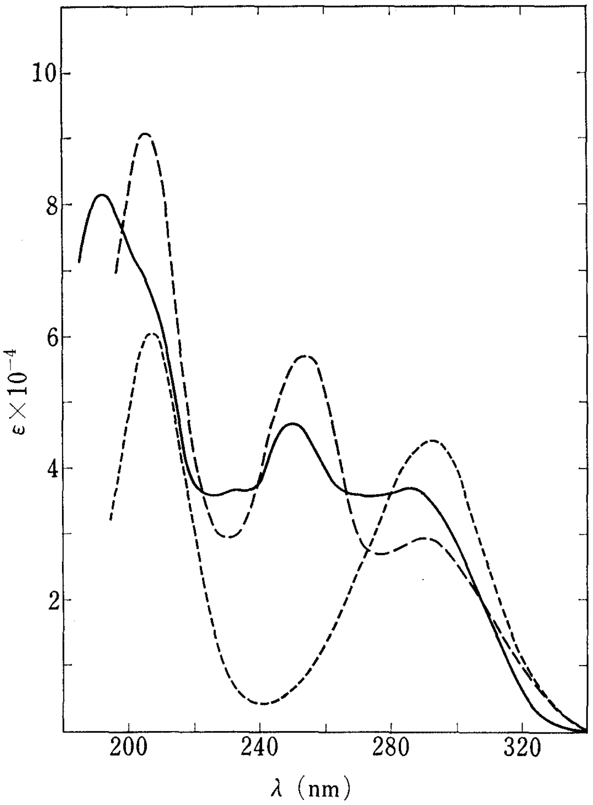


Fig. 1. UV Spectra of Quaterphenyl and Sexiphenyls in Cyclohexane

———: 3,4,3′, 4′-tetraphenylbiphenyl (Id),
– – – –: 2,4,2′,4′-tetraphenylbiphenyl (IId),
…………: *p*-quaterphenyl.

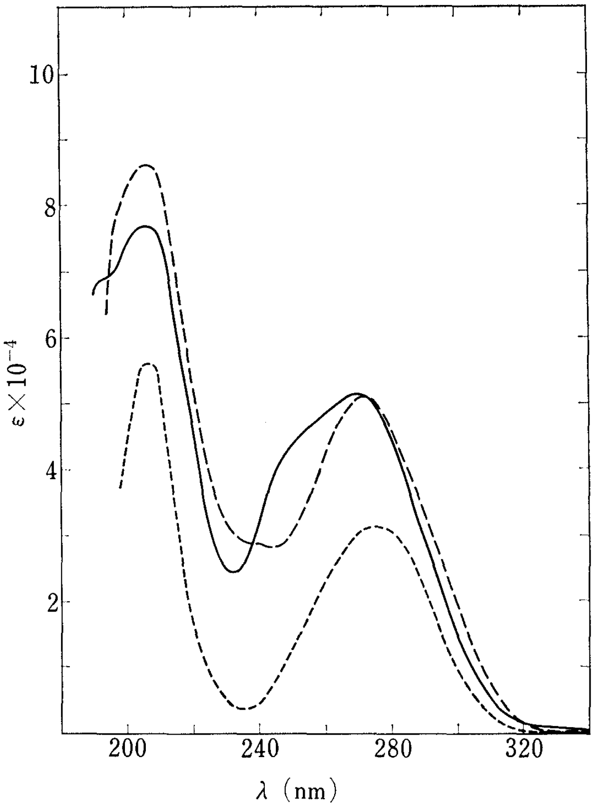


Fig. 2. UV Spectra of Terphenyl and Sexiphenyls in Cyclohexane

———: 2,5,2′, 5′-tetraphenylbiphenyl (IIId),
– – – –: 2,2′-di (4-biphenylyl)biphenyl (IVd),
…………: *p*-terphenyl.

---

15) E. Ibuki, S. Ozasa, and Y. Fujioka, unpublished work.
16) R.C. Doss and P.W. Solomon, *J. Org. Chem.*, **29**, 1567 (1964).
17) L.J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, 1954, p. 64.
18) S. Sandroni and F. Geiss, DMS-spectra catalogue, Butterworths, London and Verlag Chemie, Weinheim.

quaterphenyl, 731 (s), 748 (s), 765 (s), 775 (s); 3,5-diphenyl-*p*-terphenyl, 756 (s), 768 (s), 783 (m); 3-(4-biphenylyl)-5-phenyl-*p*-terphenyl, 765 (s), 770 (s) cm^{-1}. Because the compounds have neither three nor four adjacent ring hydrogens, the absorptions up to 783 cm^{-1} can undoubtedly be assigned to C–H out-of-plane deformation bands of the terminal rings.

The mass (MS) spectra of the seven sexiphenyls invariably showed a molecular ion corresponding to the molecular weight of 458 as the most abundant ion.

The NMR spectra of the sexiphenyls were measured at 80 MHz in $CDCl_3$ solution. The spectrum of Id shows two 10H singlet peaks at δ 7.21 and 7.22 which can be assigned to the resonances of phenyl protons at the 4-, 4'- and 3-, 3'-positions, respectively, by comparison with the spectrum of 1,2,4-triphenylbenzene[15] (δ 7.20, s, 1-C_6H_5; δ 7.22, s, 2-C_6H_5). The spectrum of IVd shows an apparent AA'BB'-q pattern, δ 6.66 and 7.23, J=8.5 Hz, which may be assigned to the resonances of protons at the 3-, 5- and 2-, 6-positions, respectively, of 4-biphenylyl groups by analogy with the spectrum of the *p*-phenylene protons of 2,4'-diphenylbiphenyl[15] (δ 7.20 and 7.47, AA'BB'-q, J=8.6 Hz, 2'-, 6'-H and 3'-, 5'-H). Thus, the resonances of the *p*-phenylene protons are observed at slightly higher field in 2,4-'diphenylbiphenyl (0.48 and 0.21 ppm) and at much higher field in IVd (1.02 and 0.45 ppm) as compared with *p*-terphenyl (δ 7.68, s). The marked high field shifts in the spectrum of 2,4'-diphenylbiphenyl may reflect the ring current effects of the 2-phenyl ring. Further, the more prominent shifts of the *p*-phenylene proton signals in the spectrum of IVd probably reflect the ring current effects caused by another *p*-phenylene and its adjacent *o*-phenylene rings. The spectrum of VIId shows two singlet peaks of 10H and 8H at δ 7.18 and 7.44, respectively, which are assigned to the resonances of the terminal phenyl protons and those of the *o*-phenylene protons, respectively. The remaining sexiphenyls (IId, IIId, Vd, and VId) showed multiplet peaks which are difficult to assign.

The UV spectra of the sexiphenyls were measured in cyclohexane solution. The absorption curves are shown in Figs. 1—3. The absorption maxima and their intensities for IVd, VId, and VIId agreed very closely with those of the sexiphenyls prepared by the alternative method described in the previous work.[2a] In addition, the absorption maximum above 220 nm of IId coincides within 1 nm with that described by other workers.[12,19]

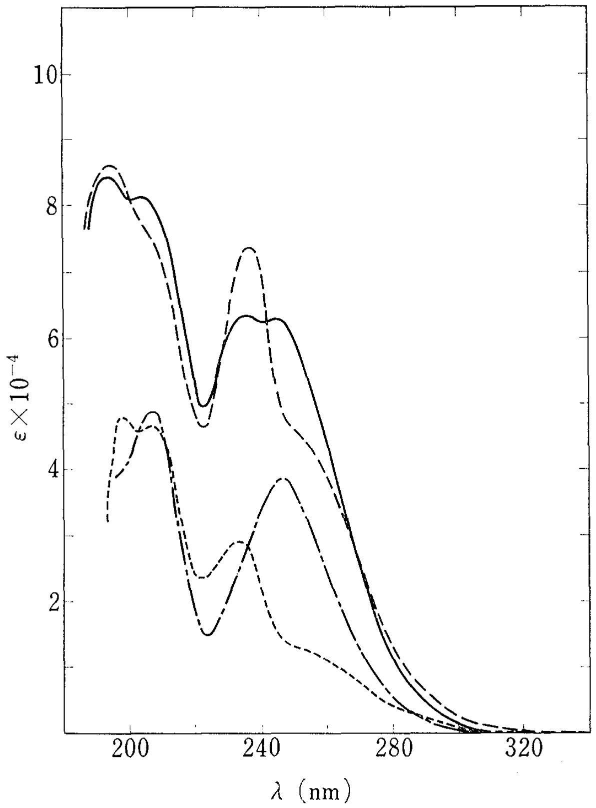


Fig. 3. UV Spectra of Related Terphenyls and Sexiphenyls in Cyclohexane

———: 2,2'-di(3-biphenylyl)biphenyl (Vd),
– – – –: 3,3'-di(2-biphenylyl)biphenyl (VIId),
—·—·—: *m*-terphenyl,
···········: *o*-terphenyl.

Four sexiphenyls (Id—IIId and Vd) showed two groups of prominent bands: one in the fairly narrow region of 192—206 nm (ε=77500—91000) and the other in the broad region

---

19) Woods *et al.* noted absorptions at somewhat shorter wavelength regions (249, 65000; 286.5, 30000 in isooctane) and gave a lower melting point (223—225°) for IId (Ref. 20).

20) G.F. Woods, J.E. Swenarton, and R.B. Isaacson, *J. Org. Chem.*, **26**, 309 (1961).

of 234—291 nm with high intensity. While the band position for the former was found to be rather independent of the structure, that for the latter was substantially affected by the nature and number of linkages between benzene rings. The first one is considered to be the E-band, and the other is regarded as the K-band, as discussed in connection with the spectra of several sexiphenyls in the previous paper.[2a)]

In the spectra of Id—IIId and Vd, all of which have two *m*-linkages of benzene rings, the characteristic band of *m*-polyphenyls near 250 nm was observed in the region of 245—254 nm as an intense band for Id, IId, and Vd, and as a shoulder for IIId. While IId displayed a slight red shift of the K-band (254 nm, $\varepsilon=57400$) as compared with *m*-polyphenyls, Vd showed a slight blue shift (245, 62900). These shifts may be due to the presence of neighboring *p*- and *o*-linkages, respectively.

Id and Vd have two *o*-linkages each, which are isolated in the former but continuous in the latter, and show the K-band at 234 nm (36900) and at 236 nm (63500), respectively. The K-bands of *o*-terphenyl and *o*-quaterphenyl appeared at 233 nm (29100) and at 230 nm (34100), respectively, so the preceding bands of Id and Vd can be ascribed to the *o*-linkages, as observed in the spectra of VId and VIId.

The spectra of Id and IId, each of which contains a *p*-quaterphenyl unit, each showed an intense band with $\lambda_{\max}$ at 286 nm (37100) and at 291 nm (29500), respectively. Their intensities are weaker than that of *p*-quaterphenyl (44400), though their locations are similar to that of *p*-quaterphenyl (294). On the other hand, the spectrum of IIId and that of IVd, in which two isolated *p*-terphenyl units are present, displayed intense K-bands with nearly the same values of $\lambda_{\max}$ and $\varepsilon_{\max}$, 271 nm (51800) and 272 nm (51200), respectively, similar in location to, but about twice the intensity of, that of *p*-terphenyl (277, 31600).

It seems likely that a *p*-quaterphenyl or *p*-terphenyl unit in the four sexiphenyls, even in the branched structures, and in the presence of *o*- or *m*-linkages, has a tendency to maintain coplanarity of the rings; a distinct bathochromic shift of the K-band results because of the elongation of the conjugated system.

These results suggest that a prominent K-band above *ca.* 260 nm in the spectra of branched or linear sexiphenyls may be a positive indication of the presence of one or more *p*-linkages.

Experimental

All melting points and boiling points are uncorrected. UV spectra were measured on a Shimadzu QV-50 spectrophotometer and a Hitachi EPS-2 spectrophotometer, IR spectra on a Leitz III-G spectrophotometer, and NMR spectra on a Varian CFT-20 spectrometer at 80 MHz using tetramethylsilane as an internal standard. MS spectra were recorded on a Hitachi RMU-6E mass spectrometer.

4′-Nitro-*o*-terphenyl (Ia)——2-Amino-5-nitrobiphenyl, mp 125—126° (lit,[21)] mp 125°), was prepared by acetylation of 2-aminobiphenyl[22)] followed by nitration[21)] and hydrolysis of the product. Yield, 34% (based on 2-aminobiphenyl).

2-Amino-5-nitrobiphenyl (10.0 g) in hydrochloric acid (22 ml) and water (40 ml) was diazotized with sodium nitrite (3.7 g) in water (7 ml) at 5—10° with stirring. Benzene (100 ml) and sodium acetate (22 g) in water (37 ml) were added to the cold suspension of diazonium salt formed, then the mixture was stirred vigorously at ambient temperature for 8 hr followed by 30—35° for 40 hr. The benzene layer was separated, washed with water and then dried. After removal of the benzene, the residue was distilled *in vacuo* to give an oil (2.6 g); bp 135—180°/4 mmHg. The oil was subjected to chromatography on alumina, with a cyclohexane-benzene (3: 2 v/v) mixture (C-B (3: 2)) as the eluent. The eluate, after removal of the solvent and recrystallization from ethanol, afforded Ia as yellowish plates: mp 117—118° (lit,[23)] mp 118—119°); yield, 1.8 g (14%). *Anal.* Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.26; H, 4.71; N, 4.98.

4′-Amino-*o*-terphenyl (Ib)——A solution of Ia (1.4 g) in hot benzene (100 ml) was treated with activated iron by a method similar to that of Hazlet and Dornfeld.[9)] After filtration, hydrogen chloride was passed into the filtrate, then the precipitate was collected, washed with benzene, and dried; yield, 1.4 g (95%). A

[21)] F. Bell, *J. Chem. Soc.*, **1928**, 2770.

[22)] H.A. Scarborough and W.A. Waters, *J. Chem. Soc.*, **1927**, 89.

[23)] F.H. Case, *J. Org. Chem.*, **21**, 477 (1956).

portion of the salt was treated in the usual manner with aqueous alkali. The free base was crystallized from ethanol to give Ib, mp 94—95°. *Anal.* Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.28; H, 6.39; N, 5.79.

4′-Iodo-*o*-terphenyl (Ic)——A suspension of Ib·HCl (3.9 g) in hydrochloric acid (4 ml) and water (10 ml) was diazotized with sodium nitrite (1.4 g) in water (10 ml) at 0—5° with stirring for 2.5 hr. The cold suspension of diazonium salt formed was added to a solution of potassium iodide (3.5 g) in water (4 ml) with stirring, and the mixture was heated slowly up to *ca.* 80° then cooled. The chloroform extract was washed with water, sodium thiosulfate solution, and then water. After removal of the solvent, the residue was distilled *in vacuo* to give an oil (3.0 g); bp 200—202°/3 mmHg. Recrystallization from ethanol gave Ic as yellowish prisms; mp 118—119°; yield, 2.4 g (49%). *Anal.* Calcd for $C_{18}H_{13}I$: C, 60.69; H, 3.68. Found: C, 60.87; H, 3.76.

3,4,3′,4′-Tetraphenylbiphenyl (Id)——Copper powder (2.8 g, 44 mg-atom) was added in portions to Ic (1.96 g, 5.5 mmol) in a reaction tube (ϕ 2.5 × 21 cm) with stirring at 260° over a 1.5-hr period, then the mixture was heated at 265° for 0.5 hr. After cooling, the product was extracted with hot benzene, and the solvent was distilled off. The residue (1.30 g) was subjected to chromatography on alumina with a C-B (5: 1) mixture to give two fractions. Fraction (Fr.) 1 provided *o*-terphenyl as colorless needles; mp 55—56° (mixed mp 55—56°); 80 mg.

Fr. 2 afforded Id as colorless needles (from benzene); mp 230—231°; yield, 850 mg (67%). NMR ($CDCl_3$) δ: 7.21 (10H, s, 4- and 4′-C_6H_5), 7.22 (10H, s, 3- and 3′-C_6H_5), 7.47—7.78 (6H, m, C_6H_3). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 192 (81700), 234 (36900), 250 (47300), 286 (37100). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 93.98; H, 5.92. MS *m/e*: 458 (M^+).

4′-Nitro-*m*-terphenyl (IIa)——3-Amino-4-nitrobiphenyl, mp 115—116° (lit,[24] mp 116°), was prepared by acetylation of 3-aminobiphenyl followed by nitration[24] and hydrolysis of the product. Yield, 35% (based on 3-aminobiphenyl).

3-Amino-4-nitrobiphenyl (10.0 g) was treated as described for the preparation of Ia. The product was distilled *in vacuo*, and the distillate (bp 173—210°/3 mmHg) was chromatographed on an alumina column (170 g) with a C-B (5: 1) mixture. After removal of the solvent, the residue was crystallized from ethanol to give IIa as pale yellow needles; mp 57—58° (lit,[4,5] an oil); 8.4 g (64%). *Anal.* Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.65; H, 4.71; N, 5.19.

4′-Amino-*m*-terphenyl (IIb)——A solution of IIa (5.1 g) in benzene was reduced in the manner described for Ib to give IIb·HCl; 4.2 g (82%). A portion of the salt was converted into the free base, which provided IIb as colorless needles from ethanol; mp 76.5—77.5° (lit,[7] mp 67—68°; lit,[8] mp 74°). *Anal.* Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.20; H, 6.23; N, 5.58.

4′-Iodo-*m*-terphenyl (IIc)——A suspension of IIb·HCl (3.7 g) in hydrochloric acid was worked up in the usual manner. The crude product was purified by chromatography on alumina with a C-B (5: 2) mixture. After removal of the eluent, crystallization from ethanol afforded IIc as colorless prisms; mp 73—74° (lit,[8] mp 67°); 2.4 g (51%). *Anal.* Calcd for $C_{18}H_{13}I$: C, 60.69; H, 3.68. Found: C, 60.99; H, 3.87.

2,4,2′,4′-Tetraphenylbiphenyl (IId)——The iodoterphenyl IIc (1.96 g, 5.5 mmol) was heated with copper powder (3.5 g, 55 mg-atom) at 270—275° for 1.5 hr then at 275—280° for 1 hr. The hot benzene extract of the product was separated into two fractions by chromatography on alumina. Fr. 1, eluted with a C-B (5: 1) mixture, gave *m*-terphenyl as colorless needles (from ethanol); mp 86—87° (mixed mp 86—87°); 498 mg.

Fr. 2, eluted with C-B (5: 1) and C-B (5: 2) mixtures, afforded IId as colorless needles (from benzene); mp 232—233° (lit,[20] mp 223—225°; lit,[12] mp 234.5°); 565 mg (45%). NMR ($CDCl_3$) δ: 6.65—7.73 (26H, m, all protons). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 205 (91000), 254 (57400), 291 (29500). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.45; H, 5.60. MS *m/e*: 458 (M^+).

2′-Nitro-*p*-terphenyl (IIIa)——4-Amino-3-nitrobiphenyl, mp 167—167.5° (lit,[25] mp 167—169°), was prepared by acetylation of 4-aminobiphenyl followed by nitration and hydrolysis of the product.[25] Yield, 66% (based on 4-aminobiphenyl).

4-Amino-3-nitrobiphenyl (16.5 g) was dissolved in concentrated sulfuric acid (15 ml) and water (76 ml), and treated as described for Ia. After separation of the benzene layer, hydrogen chloride was passed into it to separate unchanged amine. A small amount of insoluble salt was filtered off. In this case rapid and repeated treatment was necessary, because the salt readily released hydrogen chloride to give the free amine. After removal of the benzene, the residue (9.3 g) was chromatographed on alumina (140 g) using a C-B (5: 2) mixture. The eluate, after removal of the solvent and crystallization from ethanol, gave IIIa as colorless plates; mp 129—130.5° (lit,[26] mp 131°); 5.5 g (26%). *Anal.* Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.41; H, 4.99; N, 4.88.

2′-Amino-*p*-terphenyl (IIIb)——A solution of IIIa (5.5 g) in benzene was reduced in the manner described above. Several crystallizations from ethanol gave IIIb as colorless needles; mp 178—180° (lit,[26] mp 177°); 4.7 g (95%). *Anal.* Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.41; H, 6.33; N, 5.58.

---

24) W. Blakey and H.A. Scarborough, *J. Chem. Soc.*, **1927**, 3000.

25) N. Campbell, W. Anderson, and J. Gilmore, *J. Chem. Soc.*, **1940**, 446.

2′-Iodo-*p*-terphenyl (IIIc)——A suspension of IIIb (6.6 g) in hydrochloric acid was worked up as described for Ic. The crude product (9.2 g) was chromatographed on alumina (100 g) with C-B (5: 2) and C-B (1: 1) mixtures. After removal of the solvent, crystallization from ethanol gave IIIc as colorless plates; mp 100—101° (lit,[26] mp 99—100°); 6.8 g (70%). *Anal.* Calcd for $C_{18}H_{13}I$: C, 60.69; H, 3.68. Found: C, 60.47; H, 3.61.

2,5,2′,5′-Tetraphenylbiphenyl (IIId)——The iodoterphenyl IIIc (3.20 g, 9.0 mmol) was heated with copper powder at 270—275°. The hot benzene extract of the product (1.95 g) was separated into two fractions by chromatography on alumina. Fr. 1, eluted with a C-B (9: 1) mixture, gave *p*-terphenyl; mp 209—211° (mixed mp 209—211°); 142 mg.

Fr. 2, eluted with a C-B (5: 1) mixture, afforded IIId as colorless needles (from ethanol); mp 194—195°; 1319 mg (64%). NMR ($CDCl_3$) δ: 6.65—7.71 (26H, m, all protons). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 206 (77500), 250 (sh 43800), 271 (51800). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.25; H, 5.98. MS *m/e*: 458 (M^+).

2-Nitro-*p*-terphenyl (IVa)——Copper powder (20 g, 0.32 g-atom) was added in portions to a mixture of 4-iodobiphenyl[2a)] (5.6 g, 0.02 mol) and *o*-iodonitrobenzene[2b)] (4.9 g, 0.02 mol) in a reaction tube (ϕ 3.5×21 cm) with stirring at 230—235° over a 3-hr period, then the mixture was heated at 240° for 1 hr. The hot benzene extract of the product (3.6 g) was treated twice with hot cyclohexane (50 ml) to separate it into soluble and insoluble fractions. The latter gave crude *p*-quaterphenyl (0.5 g). The former (3.1 g) was chromatographed on an alumina column (120 g) with a mixture of C-B (3: 2) to give two fractions then with benzene to give one further fraction.

Fr. 1 gave IVa as pale yellow needles (from ethanol); mp 128—129° (lit,[27] mp 127—128°; lit,[26] mp 129°); 0.65 g (12%). *Anal.* Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.63; H, 4.57; N, 4.94.

In addition, fr. 2 afforded 2,2′-dinitrobiphenyl as yellowish-brown needles; mp 124—125° (mixed mp 124—125°); 0.48 g. Fr. 3 gave *p*-quaterphenyl; mp 310—315° (mixed mp 311—315°); 0.40 g.

2-Amino-*p*-terphenyl (IVb)——A solution of IVa (5.5 g) in benzene was reduced in the manner described for Ib to give IVb·HCl; 5.0 g (90%). Free base IVb: colorless needles from ethanol; mp 162—163° (lit,[26] mp 162—163°). *Anal.* Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.26; H, 6.01; N, 5.99.

2-Iodo-*p*-terphenyl (IVc)——The amine IVb (4.0 g) was converted into IVc as described above. The crude product was distilled *in vacuo* to give a pale yellow solid (bp 217—218°/5 mmHg), which provide IVc as yellowish needles from ethanol; mp 100.5—101° (lit,[28] mp 100°; lit,[26] mp 101°); 3.5 g (62%). *Anal.* Calcd for $C_{18}H_{13}I$: C, 60.69; H, 3.68. Found: C, 60.94; H, 3.78.

2,2′-Di(4-biphenylyl)biphenyl (IVd)——The iodoterphenyl IVc (3.03 g, 8.5 mmol) was treated with copper powder at 255—260°, and the product was extracted with hot benzene. The extract (1.95 g) was subjected to chromatography on alumina with a C-B (9: 1) mixture to give two fractions. Fr. 1 gave *p*-terphenyl; 50 mg.

Fr. 2 afforded IVd as colorless rhombs (from cyclohexane); mp 191—192.5° (lit,[12] mp 189—190°; lit,[2a)] mp 192—194°); 960 mg (49%). IR (KBr) cm^{-1}: 917, 885, 873, 842, 834, 778, 754, 744, 726, 698, 678. NMR ($CDCl_3$) δ: 6.66 and 7.23 (8H, AA′BB′-q, J=8.5 Hz, 3-, 5-H and 2-, 6-H (4-C_6H_4·C_6H_5)), 7.11—7.64 (18H, m, *o*-C_6H_4 and C_6H_5). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 207 (94800), 240 (29700), 272 (52200). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.50; H, 5.78. MS *m/e*: 458 (M^+).

2-Nitro-*m*-terphenyl (Va)——A mixture of 3-iodobiphenyl[2a)] (5.6 g) and *o*-iodonitrobenzene (4.9 g) was treated with copper powder at 230—235°, and the hot benzene extract (3.1 g) was chromatographed on alumina with a C-B (5: 2) mixture to give four fractions.

Fr. 3 afforded Va as pale yellow plates (from cyclohexane); mp 95—96°; 0.64 g (12%). *Anal.* Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.48; H, 4.74; N, 5.03.

Biphenyl (mp 70°, 0.01 g), *m*-quaterphenyl (mp 86—87°, 0.89 g), and 2,2′-dinitrobiphenyl (0.10 g) were obtained as by-products from fr. 1, 2, and 4, respectively.

2-Amino-*m*-terphenyl (Vb)——The nitroterphenyl Va (5.5 g) was reduced with activated iron in hot benzene. Recrystallization from cyclohexane afforded Vb as colorless needles; mp 81—82°; 4.2 g (86%). *Anal.* Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.45; H, 6.23; N, 5.75.

2-Iodo-*m*-terphenyl (Vc)——The amine Vb (3.8 g) was converted into Vc as described above. The crude product was distilled *in vacuo* to afford Vc as a pale yellow oil; bp 204—206°/5 mmHg; 2.6 g (47%). The oil was chromatographed on alumina with cyclohexane to give a colorless oil. *Anal.* Calcd for $C_{18}H_{13}I$: C, 60.69; H, 3.68. Found: C, 60.98; H, 3.94.

2,2′-Di(3-biphenylyl)biphenyl (Vd)——The iodoterphenyl Vc (2.30 g, 6.5 mmol) was treated with copper powder at 255—260°. The hot benzene extract of the product (1.60 g) was chromatographed on alumina to afford two fractions. Fr. 1, eluted with cyclohexane, gave *m*-terphenyl; 252 mg.

---

26) T. Nozaki and Y. Harada, *Bull. Chem. Soc. Jpn.*, **35**, 1783 (1962).
27) H. France, I.M. Heilbron, and D.H. Hey, *J. Chem. Soc.*, **1938**, 1364.
28) J.A. Cade and A. Pilbeam, *Chem. Ind.* (London), **1959**, 1578.

Fr. 2, eluted with C-B (19: 1) and C-B (5: 1) mixtures, afforded Vd as colorless plates (from ethanol); mp 153—154°; 600 mg (40%). NMR ($CDCl_3$) δ: 6.48—7.59 (26H, m, all protons). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 194 (84800), 205 (81300), 236 (63500), 245 (62900). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.00; H, 5.77. MS *m/e*: 458 (M^+).

2-Nitro-*o*-terphenyl (VIa)——A mixture of 2-iodobiphenyl[2a] (5.6 g) and *o*-iodonitrobenzene (4.9 g) was treated with copper powder as described for IVa. The hot benzene extract (5.1 g) was chromatographed on alumina with a mixture of C-B (5: 1) to give three fractions and with a mixture of C-B (1: 3) to give one fraction.

Fr. 3 gave VIa as pale yellow needles (from ethanol); mp 91—92° (lit,[29] mp 93—94°); 1.08 g (20%). *Anal.* Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.77; H, 4.76; N, 5.09.

Biphenyl (0.14 g), *o*-quaterphenyl (mp 115—116°, 1.05 g), and 2,2′-dinitrobiphenyl (0.75 g) were obtained as by-products from fr. 1, 2, and 4, respectively.

2-Amino-*o*-terphenyl (VIb)——The nitroterphenyl VIa (8.3 g) was reduced as described above to give VIb·HCl; 8.2 g (97%). Free base VIb: colorless needles from ethanol; mp 75—76° (lit,[29] mp 75—76°). *Anal.* Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.13; H, 6.25; N, 5.63.

2-Iodo-*o*-terphenyl (VIc)——The salt VIb·HCl (4.9 g) dissolved in concentrated sulfuric acid (5 ml) and water (90 ml) was diazotized at 0—5° with sodium nitrite (2.4 g) in water (6 ml). The suspension of the diazonium salt was treated with a large excess of potassium iodide (40 g) in water (40 ml) at 0—5°. The crude product was treated with 120 ml of a C-B (5: 1) mixture to give soluble and insoluble fractions. After filtration, the precipitate provided triphenylene as colorless needles (mp 193—194°; 1.40 g). The filtrate was subjected to chromatography on alumina (200 g) with a C-B (5: 1) mixture to give two fractions. Fr. 1 gave VIc as colorless prisms (from ethanol); mp 55—56° (lit,[30] mp 55—57°); 1.20 g (19%). *Anal.* Calcd for $C_{18}H_{13}I$: C, 60.69; H, 3.68. Found: C, 60.98; H, 3.77. Fr. 2 afforded additional triphenylene (0.96 g).

***o*-Sexiphenyl (VId)**——The iodoterphenyl VIc (0.80 g, 2.2 mmol) was treated with copper powder (3 g) at 275—280° for 2 hr. The hot benzene extract (0.46 g) was chromatographed on alumina (30 g). Fr. 1, eluted with cyclohexane, gave *o*-terphenyl as colorless needles; 42 mg.

Fr. 2, eluted with the same eluent, afforded VId as colorless cubes (from ethanol); mp 215.5—216.5° (lit,[12,31] mp 216—217°; lit,[2a] mp 217—217.5°); 62 mg (21%). IR (KBr) cm^{-1}: 914, 876, 872, 867, 776, 753, 744, 734, 711, 698. NMR ($CDCl_3$) δ: 5.62—7.31 (26H, m, all protons). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 192 (82100), 231 (52200). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.37; H, 5.95. MS *m/e*: 458 (M^+). Fr. 3, eluted with a C-B (9: 1) mixture, gave triphenylene; mp 192.5—193°; 76 mg.

3-Nitro-*o*-terphenyl (VIIa)——A mixture of 2-iodobiphenyl (5.6 g) and *m*-iodonitrobenzene[2b] (4.9 g) was treated with copper powder as described for IVa. The hot benzene extract (5.1 g) was chromatographed on alumina (250 g) with a C-B (9: 1) mixture to give three fractions and with benzene to give one fraction.

Fr. 3 gave VIIa as pale yellow rhombs (from ethanol); mp 86—87.5° (lit,[32] mp 88—89.5°); 0.97 g (18%). *Anal.* Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.37; H, 4.89; N, 5.31.

Biphenyl (0.01 g), *o*-quaterphenyl (0.42 g), and 3,3′-dinitrobiphenyl (mp 199—201°; mixed mp 200—201°; 0.02 g) were isolated as by-products from fr. 1, 2, and 4, respectively.

3-Amino-*o*-terphenyl (VIIb)——The nitroterphenyl VIIa (4.2 g) was reduced as described above to give VIIb·HCl; 4.2 g (98%). Free base VIIb; a colorless oil. Acetate: mp 154—155.5°.

3-Iodo-*o*-terphenyl (VIIc)——The salt VIIb·HCl (4.0 g) was transformed in the usual manner into VIIc. The crude product was purified by chromatography on alumina (200 g). A C-B (5: 1) mixture gave a colorless oil, which, upon recrystallization from ethanol provided colorless plates; mp 66.5—67.5°; 2.7 g (53%). *Anal.* Calcd for $C_{18}H_{13}I$: C, 60.69; H, 3.68. Found: C, 60.89; H, 3.74.

3,3′-Di(2-biphenylyl)biphenyl (VIId)——The iodoterphenyl VIIc (1.60 g) was treated with copper powder (2 g) as described for the preparation of Id. The benzene extract was chromatographed on alumina (60 g) with cyclohexane and with a C-B (5: 1) mixture to give one fraction in each case. Fr. 1 gave *o*-terphenyl; 47 mg.

Fr. 2 afforded VIId as colorless needles (from ethanol); mp 151—152° (lit,[2a] mp 151.5—152°); 552 mg (60%). IR (KBr) cm^{-1}: 918, 907, 901, 848, 805, 796, 776, 759, 744, 719, 709, 702. NMR ($CDCl_3$) δ: 7.18 (10H, s, C_6H_5), 7.08—7.26 (8H, m, *m*-C_6H_4), 7.44 (8H, s, *o*-C_6H_4). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 194 (86500), 237 (72100), 252 (sh 44200). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.04; H, 5.69. MS *m/e*: 458 (M^+).

Acknowledgement The authors are grateful to the staff of the Center of Elemental Analysis, Faculty of Pharmacy, Kyoto University, for the elemental analyses. Thanks are due to Prof. Y. Masada, Dr. K. Hashimoto, and Mr. Y. Fujiwara of this college for their help in MS and NMR spectrometric measurements. The authors are also indebted to Nippon Shinyaku Co., Ltd., for the measurements of IR spectra.

---

29) D.F. DeTar and C.-C. Chu, *J. Am. Chem. Soc.*, **82**, 4969 (1960).
30) G. Wittig and D. Hellwinkel, *Chem. Ber.*, **97**, 769 (1964).
31) G. Wittig and G. Lehmann, *Chem. Ber.*, **90**, 875 (1957).
32) R.G. Splites and G. Grins, *J. Chem. Eng. Data*, **11**, 442 (1966).