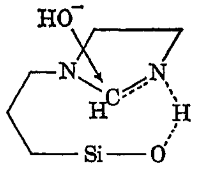
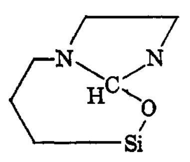
sity.[9] Since the tendency of amino compounds to form complexes with silyl groups with less than three Si–O bonds is negligible,[10] the effects seen here would be expected only in the case when R = $(MeO)_3SiCH_2CH_2CH_2$.

Other possible interactions could involve intramolecular hydrogen bonding with the imino nitrogen and a silanol as in VII or silicon–oxygen bond formation with the 2-carbon atom of the ring (VIII). In the latter case the intermediate B would result after hydrolysis of the silicon–oxygen–carbon bond. These intermediates resemble those advanced to explain the enhanced rates of hydrolysis for certain α-keto phosphate esters[11] and p-nitrophenyl salicylates.[12] However, with such interactions all of the methoxysilanes studied should show effects similar to V unless an unusual acidity for the corresponding silanol of V is postulated to explain its unique behavior.



VII



VIII

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[10] See, for example, C. Frye, G. E. Vogel, and J. A. Hall, *J. Am. Chem. Soc.*, **83**, 996(1961).

[11] F. Ramirez, B. Hansen, and N. B. Desai, *ibid.*, **84**, 4588 (1962).

[12] M. L. Bender, F. J. Kezdy, and B. Zerner, *ibid.*, **85**, 3017 (1963).

Bistetracyclones and Bishexaphenylbenzenes. II

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Six additional representatives of the class of colored compounds, the bistetraphenylcyclopentadienones (**1**), have been prepared linked by $(CH_2)_2$, $(CH_2)_3$, $(CH_2)_4$, $(CH_2)_5$, and $(CH_2)_6$, respectively, and one in which one of the phenyl groups links two cyclopentadienone rings. New intermediates for their syntheses have been described including the required bisdeoxybenzoins and bisbenzils. Analogs of hexaphenylbenzene, melting in the range 337–470°, were prepared from each bistetraphenylcyclopentadienone by reaction with tolan. The absorption spectra of bistetracyclones and bishexaphenylbenzenes have been discussed based on tetracyclone and hexaphenylbenzene as models.

A previous paper[3] discussed the syntheses and absorption spectra of the first four representatives of this new class of colored compounds, the bistetraphenylcyclopentadienones (**1**), in which the two tetraphenylcyclopentadienone moieties are linked directly by CH_2, O, and S, respectively. In the present paper we wish to report on the syntheses and absorption spectra of six additional bistetracyclones (**1**) and their corresponding bishexaphenylbenzenes (**4**).

Syntheses.—As outlined in our previous paper[3] the route chosen to prepare the bistetraphenylcyclopentadienones consisted of the condensation of 2 moles of benzyl ketone with an appropriate bisbenzil. Charts I and II outline the paths selected.

Bibenzyl reacted with 2 moles of phenylacetyl chloride as described in the literature[4] to give the bisdeoxybenzoin (**2e**). 1,3-Diphenylpropane, 1,4-diphenylbutane, 1,5-diphenylpentane, and 1,6-diphenylhexane also reacted with 2 moles of phenylacetyl chloride to give the bisdeoxybenzoins (**2f–i**) without exceptional difficulty. However, the bisphenylacetyl derivative of benzene could not be prepared this way; instead, it was prepared by the addition of a large excess of benzylmagnesium chloride (8 moles/nitrile group) to terephthalonitrile, followed by acid hydrolysis, which gave the bisdeoxybenzoin (**2j**) in 28% yield.

Conversion of compounds **2e–j** to the bisbenzils **3e–j** was effected *via* condensation with p-nitrosodiethylaniline followed by acid hydrolysis in 25–63% yield.

Potassium hydroxide catalyzed condensation of compounds **3e–i** with benzyl ketone proceeded without particular difficulty to give the bistetracyclones, **1e–i**. However, compound **3j** did not condense with benzyl ketone under these conditions, but was converted to the bistetracyclone **1j** using n-butyl alcohol as solvent and Triton B (benzyltrimethylammonium hydroxide) as the base in 46% yield.

For derivative purposes the bistetracyclones were converted to the hexaphenylbenzene analogs by reaction with diphenylacetylene. As with the previously reported bistetracyclones, the melting points of the diphenylacetylene derivatives of this series of bistetracyclones are unusually high. The observed melting points range from **4h**, m.p. 337–340° dec., to **4j**, m.p. 468–470° (lit.[5] m.p. 462–463° uncor.).

To complete the family of bishexaphenylbenzene analogs prepared, the missing member, 2′,3′,5′,6′,-2″,3″,5″,6″-octaphenylquaterphenyl (**4k**) was prepared by treating 2 moles of tetracyclone with 1 mole of diphenyldiacetylene. Chart III outlines the path.

The diphenyldiacetylene required was prepared by the Fieser modification[6] of the Glaser reaction of phenylacetylene as reported in the literature.[7]

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[1] Taken from part of the dissertation submitted to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June 1965.

[2] To whom inquiries should be sent at the University of Massachusetts—Boston, Boston, Mass. 02116.

[3] M. A. Ogliaruso, L. A. Shadoff, and E. I. Becker, *J. Org. Chem.*, **28**, 2725 (1963); see also L. F. Fieser and M. Fieser, "Current Topics in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1964, p. 50.

[4] Ng. Ph. Buu-Hoï, Ng. Hoan, and P. Jacquignon, *J. Chem. Soc.*, 1381 (1951).

[5] W. Reid and K. H. Bönninghausen, *Chem. Ber.*, **93**, 1769 (1960).

[6] L. Fieser, "Organic Experiments," D. C. Heath and Co., Boston, Mass., 1964, p. 80.

[7] G. M. Mkryan and N. A. Papazyan, *Dokl. Akad. Nauk Arm. SSR*, **21**, 107 (1955).

CHART I

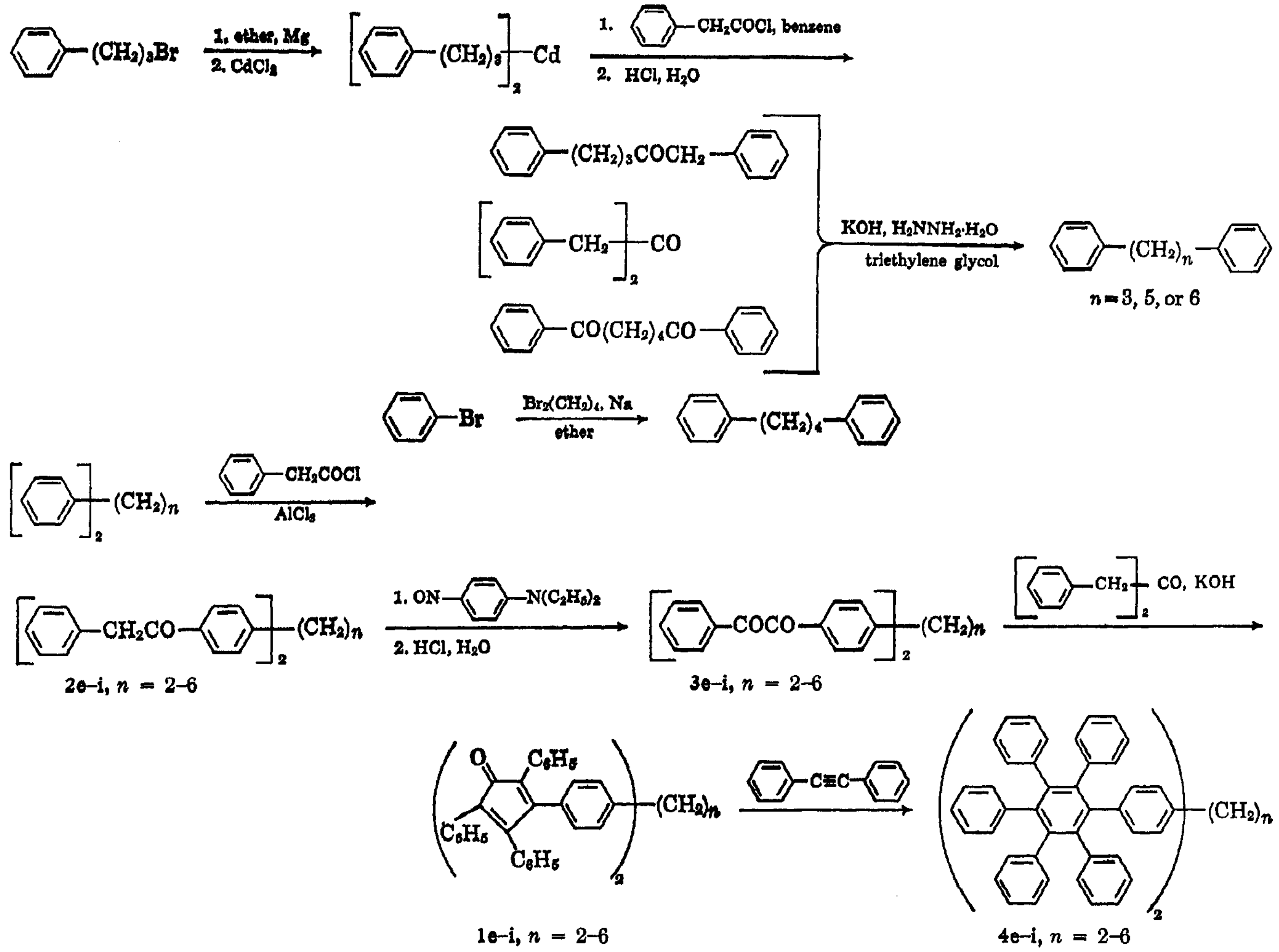
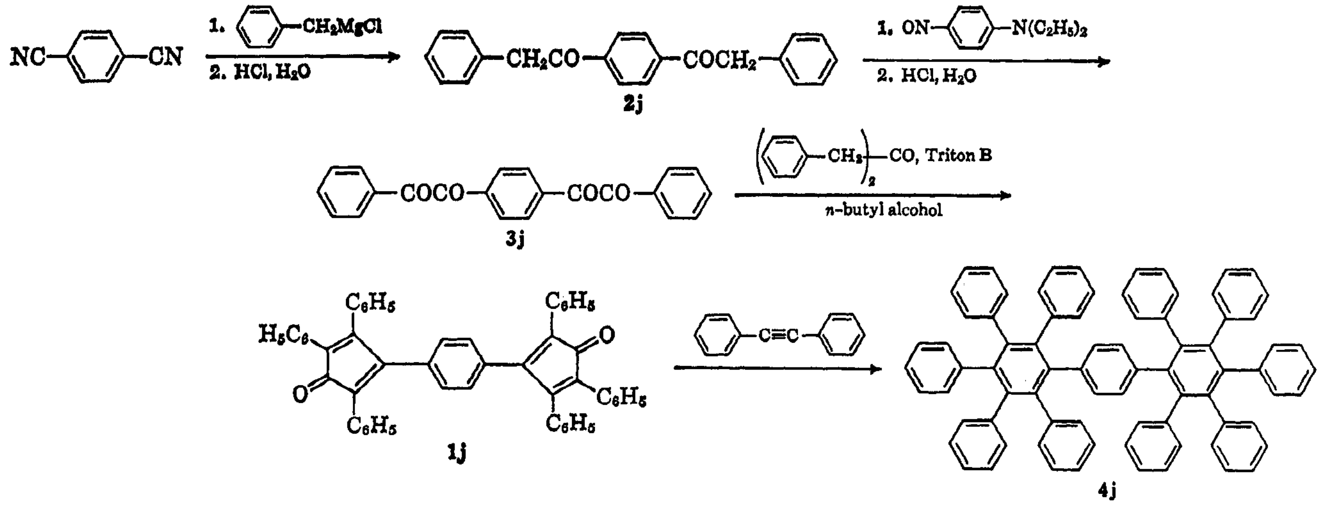


CHART II



Although there are two reports in the literature[5,8] of the reaction of 1 mole of tetracyclone with 1 mole of diphenyldiacetylene to give 2,3,4,5,6-pentaphenyltolan, in neither case was an excess of tetracyclone used or an attempt made to prepare octaphenylquaterphenyl *via* this condensation.

Spectra of Bistetracyclones.—The electronic spectra of the bistetracyclones obtained earlier[3] showed that for compounds **1b–d** the spectra are largely similar to that for tetracyclone.[9] This similarity is also true for the newer members of this series of compounds (Figures 1 and 2 and Table I). The broad absorption band of low intensity near 500 mμ corresponds to that for tetracyclone at 335 mμ (cyclohexane). The band in cyclohexane at 343–375 mμ (this also includes the values reported earlier[3]) corresponds to that of tet-

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[8] W. Dilthey, W. Schommer, W. Höschen, and H. Deiricks, *Ber.*, **68**, 1159 (1935).

[9] See V. F. D'Agostino, M. J. Dunn, A. E. Ehrlich, and E. I. Becker, *J. Org. Chem.*, **23**, 1539 (1956), and papers cited therein.

TABLE I

SPECTRAL CHARACTERISTICS OF BISTETRACYCLONES[a]

No.	Solvent[b]	λ_1	$\epsilon_1 \times 10^{-3}$	λ_2[c]	$\epsilon_2 \times 10^{-3}$	λ_3	$\epsilon_3 \times 10^{-3}$	λ_4[d]	$\epsilon_4 \times 10^{-3}$	λ_5[d]	$\epsilon_5 \times 10^{-3}$	λ_6	$\epsilon_6 \times 10^{-3}$
1b	C	261	55.5	282	32.6	347	16.96						
	B							448	1.6	463	2.2	502	2.2
1e	C	261	55.5	282	33.3	347	17.67						
	B							448	1.6	478	2.2	503	2.7
1f	C	261	52.6	281	36.1	343	17.41						
	B							448	1.6	475	2.0	500	2.4
1g	C	261	53.8	...	...	347	16.76						
	B							448	1.5	475	2.0	506	2.3
1h	C	261	54.3	...	...	345	16.30						
	B							447	1.1	478	2.0	506	2.4
1i	C	261	53.6	...	...	345	16.56						
	B							450	0.8	478	2.1	505	2.2
1j	C	258	49.2	277	34.4	367	17.94						
	B							445	1.8	482	2.1	507	2.2

[a] Wave lengths are given in millimicrons. [b] C = cyclohexane, B = benzene. [c] Inflection. [d] Shoulder.

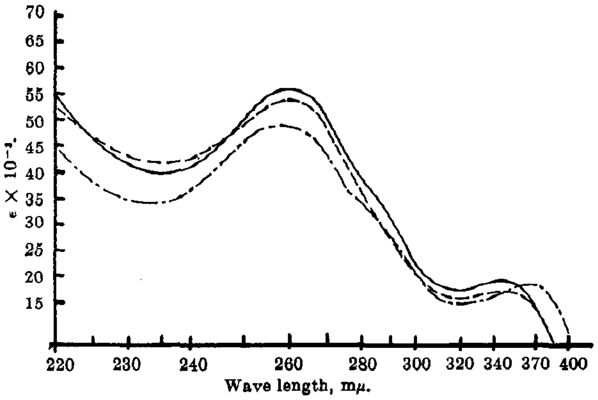


Figure 1.—Absorption spectra of **1e** (———), **1g** (- - - -), and **1j** (— - —).

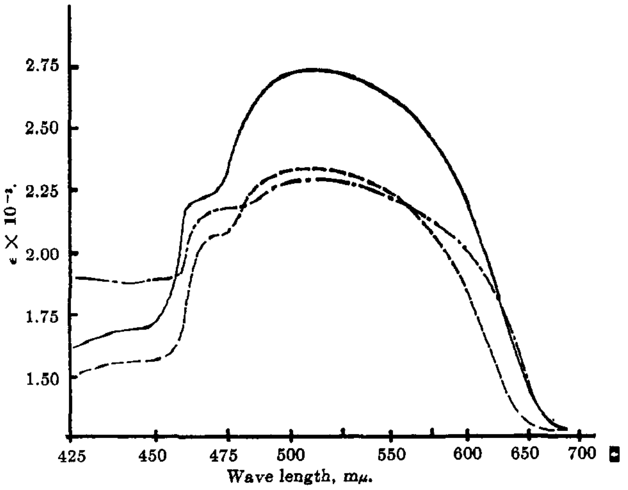
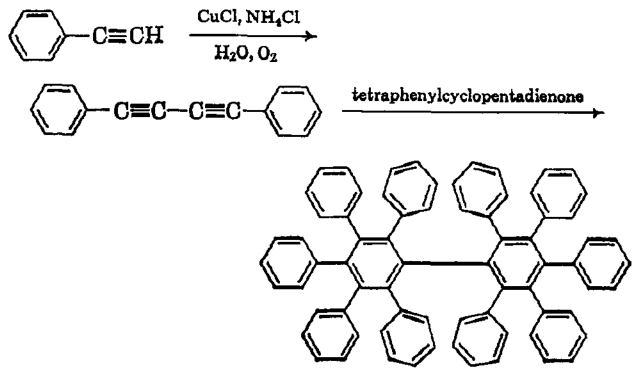


Figure 2.—Absorption spectra of **1e** (———), **1g** (- - - -), and **1j** (— - —).

CHART III



4k

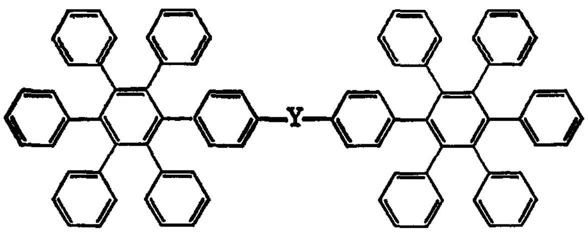
racyclone at 335 mμ (cyclohexane). Concomitantly there is a hypsochromic shift of the band at 512 mμ. These shifts are in accord with what has been observed for electron-releasing groups in the *para* position of the 3-phenyl in tetracyclone.[10]

In the previous paper[3] an implication was made that a shoulder at 297 mμ observed diminishing in the **1a-d** spectra (**1a** > **1d** > **1c** > **1b**) would have a significant structural correlation. In the series of alkylene-α,ω-bistetracyclones this band disappears as the alkylene chain increases in length and is actually absent in the spectra of **1g-i** (Table I). No correlation with structure has been possible.

Spectra of Bishexaphenylbenzenes.—Hexaphenylbenzene exhibits an absorption maximum at 247 mμ (Figure 3 and Table II), which is exactly at the same wave length as for the major absorption band of di-

TABLE II

SPECTRAL CHARACTERISTICS OF HEXAPHENYLBENZENE AND BISHEXAPHENYLBENZENES[a]



No.	Y	λ_1	$\epsilon_1 \times 10^{-3}$	λ_2[b]	$\epsilon_2 \times 10^{-3}$
4b	CH_2	247	102.8	267	50.7
4e	$(CH_2)_2$	247	97.8	266	54.6
4f	$(CH_2)_3$	247	93.0	268	51.3
4g	$(CH_2)_4$	247	98.3	268	53.2
4h	$(CH_2)_5$	248	99.0	267	62.8
4i	$(CH_2)_6$	247	99.3	268	58.5
4c	O	248	95.4	270	59.0
4d	S	248	96.3	268	63.3
Hexaphenylbenzene		247	56.8	266	34.7

[a] Solvent used was 1,2-dichloroethane; wave lengths are given in millimicrons. [b] Shoulder.

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(10) E. L. Shapiro and E. I. Becker, *J. Am. Chem. Soc.*, **75**, 4769 (1953).

phenyl[11]; however, its molar extinction coefficient (Table II) is 56.8 × 10^3 compared with 20.3 × 10^3 for diphenyl. The alkylene-α,ω-bishexaphenylbenzenes (**4b–i**) also exhibit a maximum at 247–248 mμ (Figure 3 and Table II), which is the same as for hexaphenylbenzene and diphenyl, while their molar absorptivities (Table II) remain constant and are almost twice that of hexaphenylbenzene itself, as would be expected. Thus, no shift in wave length is observed in this series of compounds in going from one member to the next. These results indicate that in this series of compounds the optical properties are consistent with the presence of two identical, nonconjugated absorbing units, that is, two hexaphenylbenzene units.

2′,3′,5′,6′,2′′′′,3′′′′,5′′′′,6′′′′-Octaphenylsexiphenyl (**4a**), 2′,3′,5′,6′,2′′′,3′′′,5′′′,6′′′-octaphenylquinquephenyl (**4j**), and 2′,3′,5′,6′,2′′,3′′,5′′,6′′-octaphenylquaterphenyl (**4k**), the three other analogs of the bishexaphenylbenzenes studied in this series, show absorption maxima at 247, 252, and 254 mμ (Figure 4 and Table III), respectively. Compound **4a** may be viewed as two hexaphenylbenzene moieties directly connected through the *para* position of one phenyl ring in each moiety. Therefore, the absorption spectrum for this compound would be expected to be the same as that for hexaphenylbenzene, the parent compound, with the exception that the molar absorptivity should be doubled. What is observed (Figure 4 and Table III) is that the absorption appears at the same wave length, but that the molar absorptivity is only about 1.4 times that for hexaphenylbenzene. This ratio is to be expected, based on a simple vector sum calculation. With the increased steric effect present in the highly arylated systems **4j** and **4k**, the absorption maximum (λ_1, Table III) is seen to shift appreciably toward the absorption spectrum of benzene itself, while the molar absorptivities shift downward.

Table III

Spectral Characteristics of Analogs of Bishexaphenylbenzenes[a]

No.	λ_1	$\epsilon_1 \times 10^{-3}$	λ_2[b]	$\epsilon_2 \times 10^{-3}$
4a[c]	247	78.5	279	54.2
4j	252	77.7	278	53.0
4k	254	63.5	272	49.0

[a] Solvent used was 1,2-dichloroethane; wave lengths are given in millimicrons. [b] Shoulder. [c] For structure see ref. 3.

As an explanation for the observed electronic spectra of the linear *p*-polyphenyls, Gillam and Hey[11] proposed that all the phenyl rings from diphenyl to *p*-sexiphenyl be coplanar, that conjugation takes place throughout the entire molecule, and, thus, that a quinoid structure contributes to the observed electronic spectra. More recently, Guy[12] has shown that the angle of twist between the phenyl rings of diphenyl may be as large as 22°. Dale[13] has shown that the diphenyl molecule is nonplanar in solution and that there are no significant differences between solution and solid state electronic spectra, indicating that diphenyl has the same conformation in solution as in the crystal lattice.[14] Thus, it becomes difficult to explain the observed electronic spectra of the linear *p*-polyphenyls on the basis of over-all conjugation. In addition, the molecular orbital calculations of Murrell and Longuet-Higgins[15] show that conjugation between the aromatic rings of the polyphenyls can be ignored when explaining their electronic spectra. The last authors explained the electronic spectra on the basis of π-electron repulsions between adjacent aromatic rings, and further asserted that the angle of twist between phenyl rings did not appear to be important since this angular dependence was not included in their calculations.

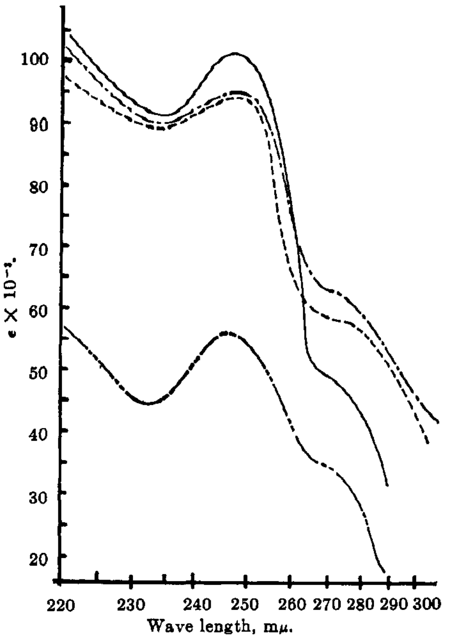

Figure 3.—Absorption spectra of **4b** (———), **4c** (— - —), **4d** (- - - -), and hexaphenylbenzene (— - - —).

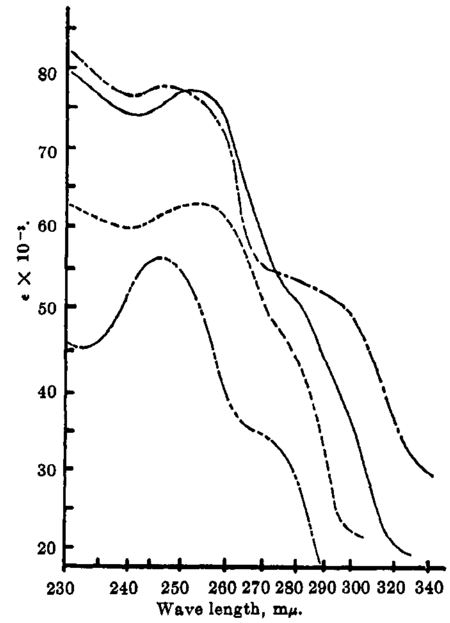

Figure 4.—Absorption spectra of **4a** (— - —), **4j** (———), **4k** (- - - -), and hexaphenylbenzene (— - - —).

In our series of compounds the possibility that any two of the phenyl rings of the hexaphenylbenzene

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(11) A. E. Gillam and D. H. Hey, *J. Chem. Soc.*, 1170 (1939).

(12) J. Guy, *J. chim. phys.*, **46**, 469 (1949).

(13) J. Dale, *Acta Chem. Scand.*, **11**, 640 (1957).

(14) J. Dale, *ibid.*, **11**, 650 (1957).

(15) J. N. Murrell and H. C. Longuet-Higgins, *J. Chem. Soc.*, 2552 (1955).

moieties are coplanar or can contribute as quinoid structures, as was thought possible for diphenyl, is highly unlikely. In *o*-terphenyl the two phenyl rings are twisted about 50° up from the plane of the central ring[16] and electron diffraction studies of hexaphenylbenzene vapor[17] at 340° have shown that the peripheral rings are nearly orthogonal to the central ring and, although the model is not rigid, the outer rings oscillate in a limited angle interval of approximately ±10° from their orthogonal positions. However, Leybold models of our compounds show that steric crowding increases in the sequence: **4b–i** to **4a**, **4j**, and **4k**. The increased crowding is manifested by increased restrictions on the oscillation of the benzene rings and in their becoming more nearly orthogonal to the central ring. Therefore, it seems likely that either the angle between the outer rings and the central ring is important, that the rigidity of the structure is important, or that a combination of the two is required to explain the observed electronic spectra. A detailed explanation for these effects is not yet available.

Experimental Section

1,4-Diphenylbutane.—To a stirred mixture of 250 ml. of dry ether and 27.6 g. (1.2 g.-atoms) of sodium ribbon at room temperature, a mixture of 53.9 g. (0.25 mole, 30 ml.) of 1,4-dibromobutane and 62.8 g. (0.40 mole, 42 ml.) of bromobenzene was added slowly. The reaction began slowly and continued at a moderate rate without external cooling. After the reaction had subsided, the reaction mixture was stirred at room temperature for 24 hr., the ether was filtered, and the residue was washed with ether. The combined ether extracts were distilled affording 25.5 g. (0.121 mole) of 1,4-diphenylbutane, b.p. 115° (0.5 mm.), m.p. 52–53° (lit.[18] b.p. 315–317°, m.p. 52°).

1,4-Diphenacetylbenzene (**2j**).—To a stirred solution of benzylmagnesium chloride [from 24.32 g. (1.0 g.-atom) of magnesium, 101.3 g. (100 ml., 0.8 mole) of benzyl chloride, and 500 ml. of ether] was added dropwise a solution of 12.8 g. (0.10 mole) of terephthalonitrile in 250 ml. of tetrahydrofuran. After refluxing the mixture for 24 hr., 300 ml. of benzene was added and the tetrahydrofuran and ether were distilled. The benzene solution was slowly poured onto a mixture of 500 g. of ice and 300 ml. of concentrated hydrochloric acid and then the entire mixture was returned to the flask and refluxed for 0.5 hr. After cooling the reaction mixture, the deep brown benzene layer was separated and distilled to dryness at about 4-cm. pressure. The residue was taken up in 300 ml. of hot ethyl acetate and cooled to give 10 g. of crude yellow compound, m.p. 172–174°. Recrystallization from 150 ml. of ethyl acetate afforded 9.0 g. (0.028 mole) of cream-colored material.

p,p'-**Diphenacetylbibenzyl** (**2e**).—This method of preparation was adapted from that of Buu-Hoï, Hoan, and Jaqcuignon.[4] While cooling a stirred solution of 80 g. (0.60 mole) of anhydrous aluminum chloride and 50 g. (0.28 mole) of bibenzyl (m.p. 52.0–52.5°) in 300 ml. of carbon disulfide, in an ice bath, 86 g. (75 ml., 0.56 mole) of phenylacetyl chloride was added during 1 hr. The reaction mixture was then refluxed for about 2 hr. until hydrogen chloride ceased to evolve. After cooling and pouring the contents onto a mixture of 170 g. of ice and 70 g. of hydrochloric acid, the mixture was heated on the steam bath to distil the carbon disulfide (caution!) and the resulting solid was taken up in 1 l. of benzene. Drying the solution over anhydrous sodium sulfate and concentration to 50 ml. afforded a white product which was slurried with pentane and filtered to give 91 g. (0.22 mole) of white material. The physical constants and analyses for intermediates, bistetracyclones, and bishexaphenylbenzenes are listed in Table IV.

p,p'-**Diphenacetyl-1,3-diphenylpropane** (**2f**).—The procedure for this reaction is essentially the one given above starting with 6.7 g. (0.050 mole) of anhydrous aluminum chloride, 3.9 g. (0.020 mole, 4.0 ml.) of 1,3-diphenylpropane[19–21] [b.p. 157° (14 mm.), $n^{25}\text{D}$ 1.5024], 50 ml. of carbon disulfide, and 6.2 g. (0.040 mole) of phenylacetyl chloride. The cooled hydrolyzed mixture was heated on the steam bath to distil the carbon disulfide, and the resulting solid was taken up in 250 ml. of benzene, which upon cooling afforded 5.0 g. of white product, m.p. 116–118°. Recrystallization from 35 ml. of absolute ethanol afforded 4.2 g. (0.010 mole) of white solid.

p,p'-**Diphenacetyl-1,4-diphenylbutane** (**2g**).—The reaction conditions are essentially those given in the above paragraph starting with 40.0 g. (0.30 mole) of anhydrous aluminum chloride, 21.0 g. (0.10 mole) of 1,4-diphenylbutane, 200 ml. of carbon disulfide, and 31.0 g. (0.20 mole, 27 ml.) of phenylacetyl chloride. Crystallization from benzene, filtering the solid, slurrying it with pentane, and filtering afforded 38.8 g. of cream-colored solid, m.p. 179–181°. Recrystallization of the compound from 75 ml. of benzene afforded 33.4 g. (0.071 mole) of white solid.

p,p'-**Diphenacetyl-1,5-diphenylpentane** (**2h**).—The procedure for this reaction is essentially the one given above starting with 6.7 g. (0.050 mole) of anhydrous aluminum chloride, 4.5 g. (0.020 mole) of 1,5-diphenylpentane[22] [b.p. 152–154° (4 mm.), $n^{25}\text{D}$ 1.5445], 50 ml. of carbon disulfide, and 6.2 g. (0.040 mole) of phenylacetyl chloride. The cooled hydrolyzed mixture was heated on a steam bath to distil the carbon disulfide and the remaining solid was taken up in 250 ml. of benzene which was dried and concentrated to a yellow oil on a roto-evaporator. This oil was dissolved in 10 ml. of chloroform, chromatographed on Woelm basic alumina using chloroform as eluent, and the resulting solution was concentrated to essential dryness on a roto-evaporator. Dissolving the resulting solid in 30 ml. of boiling cyclohexane and allowing the solution to cool afforded 5.3 g. of cream-colored solid, m.p. 95–96°. Repeating the chromatography and recrystallization gave 3.7 g. (0.0076 mole) of white solid.

p,p'-**Diphenacetyl-1,6-diphenylhexane** (**2i**).—The reaction conditions are essentially those given in the above paragraph starting with 6.7 g. (0.050 mole) of anhydrous aluminum chloride, 4.7 g. (0.020 mole) of 1,6-diphenylhexane[23] [b.p. 152–153° (2 mm.), $n^{25}\text{D}$ 1.5445], 50 ml. of carbon disulfide, and 6.2 g. (0.040 mole) of phenylacetyl chloride. Dissolving the resulting solid, after distillation of the carbon disulfide, in benzene, evaporation of the benzene, chromatography in chloroform on Woelm basic alumina (chloroform as eluent) followed by concentration of the chloroform to dryness, and crystallization of the resulting solid from 50 ml. of cyclohexane afforded 5.0 g. of cream-colored solid, m.p. 123.5–126.5°. Repeating the chromatography and crystallization afforded 4.0 g. of white product. A final recrystallization from absolute ethanol raised the melting point one degree and afforded 2.5 g. (0.0055 mmole) of white product.

4-Phenylglyoxalylbenzil (**3j**).—Preparation of this compound by selenium dioxide oxidation in acetic anhydride[24] produced an impure product which was difficult to recrystallize due to the presence of trace amounts of selenium metal. This method was abandoned in favor of the following procedure. A solution of 3.2 g. (0.010 mole) of 1,4-diphenacetylbenzene and 5.3 g. (0.030 mole) of *p*-nitrosodiethylaniline (m.p. 85–86°) in 100 ml. of absolute ethanol was refluxed for 5 hr. After distilling the ethanol, 30 ml. of dilute hydrochloric acid (1:1) was added, and the mixture refluxed for 30 min. Another 30-ml. portion of the dilute acid was added and the mixture refluxed again for 30 min. After cooling the solution, the solid was filtered and washed with two 50-ml. portions of cold, absolute ethanol affording 2 g. of impure yellow product, which was taken up in 50 ml. of acetone and chromatographed on Woelm acid alumina using acetone as the eluent. Concentration of the eluent to dryness and crystallizing from 50 ml. of absolute ethanol afforded 1.5 g. (0.0039 mole) of bright yellow needles.

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[16] C. J. B. Clews and K. Lonsdale, *Proc. Roy. Soc.* (London), **A161**, 493 (1937).

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[18] V. N. Ipatiev, N. A. Orlov, and B. N. Dolgov, *Compt. rend. acad. sci. URSS*, **A**, 1 (1928).

[19] D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, **73**, 5701 (1951).

[20] J. van Alphen, *Rec. trav. chim.*, **59**, 580 (1940).

[21] A. K. Barbaus, G. B. Barlow, and J. C. Tatlow, *J. Appl. Chem.* (London), **2**, 127 (1952).

[22] N. L. Allinger and D. J. Cram, *J. Am. Chem. Soc.*, **76**, 2362 (1954).

[23] J. Abell and D. J. Cram, *ibid.*, **76**, 4406 (1954).

[24] J. Schmitt, P. Comoy, J. Boitard, and M. Suguet, *Bull. soc. chim. France*, **636** (1956).

TABLE IV

PHYSICAL CONSTANTS AND ANALYSES FOR INTERMEDIATES, BISTETRACYCLONES, AND BISHEXAPHENYLBENZENES

				Carbon, %		Hydrogen, %	
No.	M.p., °C.	Yield, %	Formula	Calcd.	Found	Calcd.	Found
2e	178.0–179.0[a]	78	$C_{30}H_{26}O_2$				
2f	118.0–119.0	51	$C_{31}H_{28}O_2$	86.08	85.86	6.52	6.34
2g	181.5–182.5	71	$C_{32}H_{30}O_2$	86.06	86.29	6.77	6.97
2h	97.6– 98.0	38	$C_{33}H_{32}O_2$	86.03	86.25	7.00	7.23
2i	127.5–128.5	28	$C_{34}H_{34}O_2$	86.04	86.17	7.22	7.36
2j	179.0–180.0	28	$C_{22}H_{18}O_2$	84.05	84.27	5.77	5.84
3e	183.0–184.5	25	$C_{30}H_{22}O_4$	80.70	80.63	4.97	5.12
3f	145.6–146.4	63	$C_{31}H_{24}O_4$	80.85	80.63	5.25	4.97
3g	150.5–151.5	57	$C_{32}H_{26}O_4$	80.99	80.90	5.52	5.75
3h	108.0–108.8	62	$C_{33}H_{28}O_4$	81.12	81.17	5.78	5.77
3i	110.5–111.5	48	$C_{34}H_{30}O_4$	81.25	81.34	6.02	6.32
3j	125.0–126.0[b]	39	$C_{22}H_{14}O_4$	77.18	77.26	4.12	4.20
1e	253.0–254.0	63	$C_{60}H_{42}O_2$	90.65	90.79	5.33	5.40
1f	255.0–256.0	62	$C_{61}H_{44}O_2$	90.56	90.82	5.48	5.64
1g	234.0–235.0	52	$C_{62}H_{46}O_2$	90.48	90.61	5.63	5.93
1h	120.8–123.0	78	$C_{63}H_{48}O_2$	90.40	90.34	5.78	6.06
1i	109.0–110.0	52	$C_{64}H_{50}O_2$	90.32	90.30	5.92	5.91
1j	302.0–304.0	46	$C_{52}H_{34}O_2$	90.41	90.19	4.96	5.18
4e	422.0–424.0 dec.[c]	58	$C_{86}H_{62}$	94.29	93.64	5.71	6.13
4f	404.0–406.0 dec.[c]	60	$C_{87}H_{64}$	94.19	94.20	5.81	6.08
4g	398.0–400.0 dec.[c]	47	$C_{88}H_{66}$	94.08	93.99	5.92	6.17
4h	337.0–340.0 dec.[c]	12	$C_{89}H_{68}$	93.98	93.89	6.02	5.96
4i	356.0–358.0 dec.[c]	10	$C_{90}H_{70}$	93.87	93.90	6.13	5.98
4j	468.0–470.0[c,d]	57	$C_{78}H_{54}$	94.51	94.39	5.49	5.60
4k	322.0–324.0[c]	61	$C_{72}H_{50}$	94.49	94.25	5.51	5.76[e]

[a] Lit.[4] m.p. 179° uncor. [b] Lit.[24] m.p. 125–126° uncor. [c] Melting point was taken on an electrically heated aluminum block. [d] Lit.[5] m.p. 462–463° uncor. [e] Mol. wt.: calcd., 915; found, 870.

p,p'-**Diphenylglyoxalylbibenzyl (3e).**—Starting with 4.2 g. (0.010 mole) of *p,p'*-diphenacetylbibenzyl, 5.3 g. (0.030 mole) of *p*-nitrosodiethylaniline, and 100 ml. of absolute ethanol, the conditions for this reaction are given above to the point of purification by chromatography. The product was taken up in a mixture of 50 ml. of acetone and 20 ml. of benzene and chromatographed on Woelm acid alumina using acetone as the eluent. Concentration of the eluent to essential dryness and slurrying the residue with 50 ml. of pentane afforded 3.4 g. of a yellow solid, m.p. 174–178°. Recrystallization of this material from 60 ml. of benzene (charcoal) gave 2.1 g. of light yellow product, m.p. 180.5–184.5°. Two more recrystallizations, first from ethanol and then from benzene, gave 1.1 g. (0.025 mole) of a cream-colored solid.

p,p'-**Diphenylglyoxalyl-1,3-diphenylpropane (3f).**—Starting with 4.3 g. (0.010 mole) of *p,p'*-diphenacetyl-1,3-diphenylpropane, 5.3 g. (0.030 mole) of *p*-nitrosodiethylaniline, and 100 ml. of absolute ethanol, the conditions for this reaction are given above to the point of purification by chromatography. Acetone was used as the solvent and eluent in the chromatography. Concentration of the acetone to 15 ml. and cooling afforded 3.5 g. of yellow product, m.p. 145–148°. Recrystallization of the latter from 30 ml. of acetone afforded 2.9 g. (0.063 mole) of yellow crystals.

p,p'-**Diphenylglyoxalyl-1,4-diphenylbutane (3g).**—Starting with 4.5 g. (0.010 mole) of *p,p'*-diphenacetyl-1,4-diphenylbutane, 5.3 g. (0.030 mole) of *p*-nitrosodiethylaniline, and 150 ml. of absolute ethanol, the conditions for this reaction are given above. There was obtained 3.0 g. of yellow product, m.p. 149.5–151.0°, from the first purification, and recrystallization from 30 ml. of acetone afforded 2.7 g. (0.057 mole) of yellow crystals.

p,p'-**Diphenylglyoxalyl-1,5-diphenylpentane (3h).**—Starting with 4.6 g. (0.010 mole) of *p,p'*-diphenacetyl-1,5-diphenylpentane, 5.3 g. (0.030 mole) of *p*-nitrosodiethylaniline, and 100 ml. of absolute ethanol, the conditions for this reaction are given above to the point of hydrolysis of the reaction mixture with dilute hydrochloric acid (1:1). Extraction of the reaction mixture with benzene, drying, and evaporation of the benzene to essential dryness on a roto-evaporator gave a yellow-green oil which was taken up in acetone and chromatographed on Woelm acid alumina using acetone as eluent. Concentration of the acetone solution left a yellow semisolid which was crystallized from absolute ethanol affording 3.6 g. of a yellow solid, m.p. 105.8–107.0°. Two recrystallizations of the compound, first from absolute ethanol and then from acetone, afforded 3.0 g. (0.062 mole) of a yellow solid.

p,p'-**Diphenylglyoxalyl-1,6-diphenylhexane (3i).**—Starting with 4.7 g. (0.010 mole) of *p,p'*-diphenacetyl-1,6-diphenylhexane, 5.3 g. (0.030 mole) of *p*-nitrosodiethylaniline, and 100 ml. of absolute ethanol, the conditions for this reaction are given above to the point of crystallization from absolute ethanol which afforded 3.01 g. of a yellow solid, m.p. 109–111°. Recrystallization of the above compound from 12 ml. of absolute ethanol gave 2.4 g. (0.0048 mole) of a light yellow solid.

3,3'-(1,4-Phenylene)bis(2,4,5-triphenylcyclopentadienone) (1j).—To a solution of 0.55 g. (2.5 mmoles) of benzyl ketone and 0.30 g. (1.0 mmole) of **3h** in 20 ml. of *n*-butyl alcohol heated to incipient boiling was added 0.21 g. (0.5 mmole) of 40% solution of Triton B (benzyltrimethylammonium hydroxide) in methanol, and the solution was refluxed for 1 hr. At this time another equal portion of 40% solution of Triton B in methanol was added through the condenser and the solution was refluxed an additional 2 hr. After cooling thoroughly in ice, the mixture was filtered and the solid was washed with cold ethanol, leaving 0.40 g. of purple-black product, m.p. 298–302°. Recrystallization from benzene–ethanol (1:3) gave 0.32 g. (4.63 mmoles) of purple-black crystals.

4,4'-Ethylenedi-*p*-phenylenebis(2,4,5-triphenylcyclopentadienone) (1e).—To a solution of 5.3 g. (2.5 mmoles) of benzyl ketone and 2.3 g. (0.5 mmole) of **3e** in 50 ml. of absolute ethanol heated to incipient boiling was added 0.28 g. (0.5 mmole) of potassium hydroxide in 10 ml. of absolute ethanol, and the mixture was refluxed for 30 min. After cooling in ice the mixture was filtered and the solid was washed with 15 ml. of cold ethanol, leaving 3.30 g. of purple powder, m.p. 260–263°. Recrystallization from benzene–ethanol (1:3) gave 2.54 g. (3.16 mmoles) of red-purple crystals.

4,4'-Propylenedi-*p*-phenylenebis(2,4,5-triphenylcyclopentadienone) (1f).—Starting with 2.3 g. (5 mmoles) of **3f**, 5.3 g. (25 mmoles) of benzyl ketone, 50 ml. of absolute ethanol, and 0.28 g. (5 mmoles) of potassium hydroxide in 10 ml. of absolute ethanol, the reaction conditions are essentially those given above. After 1 hr. of reflux, the mixture was cooled and filtered, and the precipitate was washed with 15 ml. of cold ethanol, affording 4.0 g. of purple crystals, m.p. 248–255°. Recrystallization twice from benzene–ethanol (1:3) gave 2.5 g. (3.1 mmoles) of purple crystals.

4,4'-Butylenedi-*p*-phenylenebis(2,4,5-triphenylcyclopentadienone) (1g).—Starting with 2.4 g. (5 mmoles) of **3g**, 5.3 g. (25 mmoles) of benzyl ketone, 50 ml. of absolute ethanol, and 0.28 g. (5 mmoles) of potassium hydroxide in 10 ml. of absolute ethanol, the reaction conditions are essentially those given above. Cooling, filtering and washing the precipitate with 15 ml. of cold ethanol afforded 3.05 g. of red-purple crystals, m.p. 219–220°. Two recrystallizations from benzene–ethanol (1:3) gave 2.14 g. (2.60 mmoles) of purple crystals.

4,4′-Pentylenedi-*p*-phenylenebis(2,4,5-triphenylcyclopentadienone) (1h).—Starting with 2.4 g. (5 mmoles) of **3h**, 5.3 g. (25 mmoles) of benzyl ketone, 50 ml. of absolute ethanol, and 0.28 g. (5 mmoles) of potassium hydroxide in 10 ml. of absolute ethanol, the reaction conditions are essentially those given above. After 1 hr. of reflux, the mixture was cooled and filtered, and the precipitate was washed with 15 ml. of cold ethanol, affording 4.1 g. of reddish solid, m.p. 118–120°. The solid was dissolved in 15 ml. of benzene and chromatographed on Alcoa alumina (F-20) using benzene as eluent. Evaporation of the benzene and recrystallization of the resulting solid from heptane gave 3.27 g. (3.91 mmoles) of reddish, microcrystalline solid.

4,4′-Hexylenedi-*p*-phenylenebis(2,4,5-triphenylcyclopentadienone) (1i).—Starting with 2.5 g. (5 mmoles) of **3i**, 5.3 g. (25 mmoles) of benzyl ketone, 50 ml. of absolute ethanol, and 0.28 g. (5 mmoles) of potassium hydroxide in 10 ml. of absolute ethanol, the reaction conditions are essentially those given above. After 1 hr. of reflux, the mixture was cooled and filtered, and the precipitate was washed with 15 ml. of cold ethanol, affording 4.7 g. of reddish solid, m.p. 90–92°. The solid was dissolved in 15 ml. of benzene and chromatographed on Alcoa alumina (F-20) using benzene as eluent. Evaporation of the benzene to essential dryness on a roto-evaporator and recrystallizing the resulting solid from ethanol–benzene (3:1) gave 2.8 g. of a reddish solid, m.p. 108–110°. Recrystallization from benzene–ethanol (1:3) gave 2.24 g. (2.62 mmoles) of reddish microcrystalline solid.

2′,3′,5′,6′,2‴,3‴,5‴,6‴-Octaphenylquinquephenyl (4j).—One gram (5.6 mmoles) of diphenylacetylene and 1.04 g. (1.5 mmoles) of **1h** were placed in a thick-walled tube and sealed under nitrogen. The tube was heated for 1 hr. in a Wood's metal bath at 280°, cooled, and opened. The mixture was slurried with acetone and filtered to give 1.3 g. of crude reddish white product. After one recrystallization from nitrobenzene and one from benzene, 0.85 g. (0.86 mmole) of white crystals were collected.

1,2-Bis(2′,3′,5′,6′-tetraphenyl-*p*-terphenyl)ethane (4e).—Starting with 1.24 g. (1.5 mmoles) of **1e** and 1.0 g. (5.6 mmoles) of diphenylacetylene the reaction conditions are essentially those given above, except that the mixture was heated for 30 min. The crude material, collected as before, weighed 1.25 g. After recrystallization from tetralin, 0.95 g. (0.87 mmole) of white crystals were obtained.

1,3-Bis(2′,3′,5′,6′-tetraphenyl-*p*-terphenyl)propane (4f).—Starting with 1.20 g. (1.5 mmoles) of **1f** and 1.0 g. (5.6 mmoles) of diphenylacetylene the reaction conditions are essentially those given above, except that the mixture was heated for 1 hr. in a Wood's metal bath at 250°. The crude material, collected as before, weighed 1.22 g. Recrystallization from tetralin–acetone (1:2) with cooling in Dry Ice–methylene chloride afforded 0.98 g. (0.88 mmole) of white crystals.

1,4-Bis(2′,3′,5′,6′-tetraphenyl-*p*-terphenyl)butane (4g).—Starting with 1.24 g. (1.5 mmoles) of **1g** and 1.0 g. (5.6 mmoles) of diphenylacetylene the reaction conditions are essentially those given above, except that the mixture was heated for 30 min. in a Wood's metal bath at 270°, and 1.0 g. (0.89 mmole, 59%) of crude reddish white product, m.p. 395–397° dec., was isolated. Recrystallization from tetralin afforded 0.8 g. (0.71 mmole) of white crystals.

1,5-Bis(2′,3′,5′,6′-tetraphenyl-*p*-terphenyl)pentane (4h).—Starting with 1.25 g. (1.5 mmoles) of **1h** and 1.0 g. (5.6 mmoles) of diphenylacetylene the reaction conditions are essentially those given above, except that the mixture was heated for 1 hr. in a Wood's metal bath at 270°. The crude material, collected as before, weighed 0.38 g. Recrystallization from 4 ml. of a benzene–acetone (1:2) mixture afforded 0.21 g. (0.184 mmole) of white solid.

1,6-Bis(2′,3′,5′,6′-tetraphenyl-*p*-terphenyl)hexane (4i).—Starting with 1.28 g. (1.5 mmoles) of **1i** and 1.0 g. (5.6 mmoles) of diphenylacetylene the reaction conditions are essentially those given above. The crude material, isolated and collected as before, weighed 0.21 g. Recrystallization from 4 ml. of a benzene–acetone (1:2) mixture afforded 0.18 g. (0.156 mmole) of white solid.

Diphenyldiacetylene.—This method of preparation was adapted from that of Mkryan and Papazyan[7] and incorporates the Fieser[6] modification. The reaction vessel used was a 500-ml., thick-walled, filter flask which had a balloon secured to the side arm by means of wire. Added to the flask were a stirring bar, 25 g. (0.257 mole) of anhydrous cuprous chloride, 50 g. (0.934 mole) of ammonium chloride, 12.5 g. (0.122 mole) of phenylacetylene, and 250 ml. of water, and the flask was capped with a large self-sealing serum stopper. A delivery syringe needle was placed through the cap into the solution and a second needle was placed through the cap and only allowed to protrude 0.5 in. below the cap. Oxygen was then bubbled through the solution in a brisk stream for about 5 min., the smaller needle was then removed, and the oxygen stream was allowed to continue flowing until a sizeable balloon was produced. The larger needle was then removed and the reaction mixture was heated at 50° for 1 hr. with stirring, during which time a large amount of yellow solid appeared. The reaction mixture was then removed from the flask and placed in a 1-l. erlenmeyer flask with 500 ml. of benzene and heated with stirring until the yellow solid completely disappeared (18 hr.). Separation of the benzene layer, extraction of the aqueous layer with 100 ml. of benzene, combining the benzene solutions, washing with 200 ml. of 6 *N* hydrochloric acid, drying, and evaporation gave 20.6 g. (0.102 mole) of white crystals, m.p. 87.0–88.0° (lit.[7] m.p. 87°).

2′,3′,5′,6′,2″,3″,5″,6″-Octaphenylquaterphenyl (4k).—A mixture of 1.01 g. (5 mmoles) of diphenyldiacetylene and 5.8 g. (15 mmoles) of tetraphenylcyclopentadienone[25] in a 25 × 20 cm. Carius tube was heated for 2 hr. in a Wood's metal bath at 315°. The tube was then opened, and the resulting reddish solid mass was slurried with 30 ml. of cold acetone and filtered. The solid was dissolved in benzene and chromatographed on Woelm neutral alumina using benzene as eluent. Evaporation of the benzene almost to dryness on a roto-evaporator, adding methanol, filtering, and drying afforded 2.8 g. (3.02 mmoles) of highly fluorescent, white crystals.

Hexaphenylbenzene was prepared by the method of Fieser[26] in 94% yield, m.p. 464–465° (lit.[26] m.p. 465°).

Determination of Absorption Spectra.—The spectra of the bistetracyclones were taken in benzene and cyclohexane and no solubility problems were encountered. On the other hand, the bishexaphenylbenzenes afforded a problem in solubility until finally two solvents were found which could be used, methylene chloride and 1,2-dichloroethane. Since in some cases the sample had to be refluxed to effect solution, the higher boiling 1,2-dichloroethane was used. The sample (1–1.5 mg.) was weighed out on a microbalance and dissolved in 100 ml. of 1,2-dichloroethane. In the case of **1a**, **1c**, **1d**, and **1j**, the compounds required refluxing to effect solution. The absorption spectra were taken on a Perkin-Elmer 350 recording spectrophotometer using a set of matched 1-cm. quartz cells.

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(25) O. Grummitt and J. R. Johnson, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 806.

(26) L. Fieser, "Organic Experiments," D. C. Heath and Co., Boston, Mass., 1964, p. 307.