257. *Absorption Spectra and Structure of Compounds containing Chains of Benzene Nuclei.*

By A. E. Gillam and D. H. Hey.

The general failure of chemical tests to disclose the existence of conjugation between the two aryl nuclei in diphenyl and its derivatives suggested that the internuclear link was an invariable single bond uniting two independent *cyclo*hexatrienoid systems. Evidence from dipole measurements, however, indicated that this independence was by no means complete, a view which was supported by the results of the *X*-ray analysis of diphenyl and related compounds. The latter results indicate that the internuclear bond is hybrid in type and assumes some measure of double-bond character. The existence of such internuclear conjugation is now confirmed by an examination of the absorption spectra of diphenyl, *p*-terphenyl, *p*-quaterphenyl,

p-quinquiphenyl and *p*-sexiphenyl, which reveals a progressive displacement of the main absorption band towards longer wave-lengths together with an increase in intensity as the chain of benzene nuclei is lengthened at the *para*-positions. On the other hand in the *meta*-series the absorption spectra of *m*-terphenyl and of hydrocarbons containing from nine to sixteen benzene nuclei united at the *meta*-positions exhibit one band at approximately 2530 A (in chloroform) for the whole series, with a progressive increase in intensity as the chain is lengthened. These results indicate that, although in the *para*-series there is a measure of conjugation throughout the molecule as a whole, yet in the *meta*-series, where the structure does not permit simple conjugation to extend beyond two benzene units, the conjugation responsible for the absorption is that inherent in two benzene nuclei as in diphenyl itself. Evidence is put forward which indicates that the chromophoric unit in both series of hydrocarbons is half a diphenyl molecule as distinct from a benzene molecule.

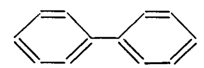
CONSIDERABLE speculation has arisen on the nature of the carbon–carbon link uniting two aryl nuclei (*e.g.*, the 1 : 1′-link in diphenyl and its derivatives), from the point of view, not only of the possibility of restricted rotation with resulting molecular dissymmetry, but also of the possible transmission of electrical effects and electronic displacements from one nucleus to another.

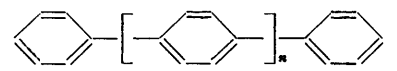
Le Fèvre and Turner (J., 1928, 247), on the basis of the absence of 3′-substitution in the nitration of 2- and 4-nitrodiphenyl and the non-activation of halogen atoms in one nucleus by the presence of nitro-groups in the second nucleus, suggested that the two nuclei in diphenyl should be regarded as two independent mobile *cyclo*hexatrienoid systems united at the 1 : 1′-positions by an invariable single bond, which is not a link in a true conjugated system. Evidence in support of these views had been provided by Burton and Kenner (J., 1922, **121**, 489) and by Robinson and Zaki (J., 1927, 2485), and confirmation of the mutual independence of the two nuclei was later provided by Gull and Turner (J., 1929, 491) by a quantitative study of the further nitration of various nitro-derivatives of diphenyl. Later work by Le Fèvre and Le Fèvre (J., 1936, 1130), however, indicated that the independence of the two nuclei in diphenyl was not so complete as was first suggested. It was evident that inductive influences might be transmitted from one nucleus to the other, but extensive tautomeric displacements were so reduced at the internuclear link that they could exert no effects which could be detected by substitution reactions in the second nucleus. On the other hand, measurements of the dipole moments of a number of 1 : 4-disubstituted benzene derivatives and the corresponding 4 : 4′-disubstituted diphenyl derivatives revealed the existence of a mesomeric effect, *i.e.*, a permanent electronic rearrangement occurring by the mechanism of the tautomeric effect, which seemed to indicate that the two benzene nuclei in diphenyl and its derivatives do not exist as isolated conjugated systems but are partly interdependent. Again, Gilbert, Turkevich, and Wallis (*J. Org. Chem.*, 1939, **3**, 611) were unable to detect any indication of the existence of double-bond character in the carbon–carbon link uniting the benzene and naphthalene nuclei in *d*-3 : 5-dinitro-6-α-naphthylbenzoic acid by a study of the effect on the racemisation of this compound of reagents which are known to bring about *cis-trans*-isomerisation in ethylene derivatives.

Further evidence of the nature of the 1 : 1′-link in diphenyl and similar compounds arises out of the relationship between bond length, as revealed, *e.g.*, by *X*-ray analysis, and bond character. *X*-Ray examination of diphenyl, *p*-terphenyl, and *p*-quaterphenyl (Dhar, *Indian J. Physics*, 1932, **7**, 43; Pickett, *Nature*, 1933, **131**, 513; *Proc. Roy. Soc.*, 1933, **142**, *A*, 333; *J. Amer. Chem. Soc.*, 1936, **58**, 2299) shows that the molecules consist of flat regular hexagons of carbon atoms lying in one plane, with a distance of 1·42 A between the centres of adjacent carbon atoms in any one ring and a distance of 1·48 A for the carbon–carbon bonds which unite the nuclei. The normal length for a single aliphatic carbon–carbon bond is 1·54 A, and the diminution of bond length thus revealed for the bond (or bonds) uniting the nuclei is indicative of hybrid character and shows that the true structure of these hydrocarbons is one in which resonance occurs between a number of alternative representations. Among these, in addition to the Kekulé or benzenoid forms (I) and (II), quinonoid forms such as (III) and (IV) will be found in which the internuclear bond assumes double-bond character.

Pauling and Sherman (*J. Chem. Physics*, **1933**, **1**, 633) postulated a contribution of a quinonoid type (III) to the ordinary structural formula for diphenyl in a discussion of the resonance energy of the hydrocarbon. Lennard-Jones and Turkevich (*Proc. Roy. Soc.*, **1936**, **158**, *A*, 297) on theoretical grounds have also suggested some approach to double-bond character in the internuclear carbon–carbon link in diphenyl, and it is now generally realised that this form of conjugation between the nuclei may be responsible for the maintenance of molecular structures, such as that of diphenyl, in a planar form (cf. Le Fèvre and Le Fèvre, *loc. cit.*). In connexion with the general inability of substitution reactions to reveal any evidence of the existence of this conjugation, it is significant that an *X*-ray analysis of stilbene (Robertson and Woodward, *Proc. Roy. Soc.*, **1937**, **162**, *A*, 568) shows that the structure of this hydrocarbon is planar, and that there is a resonance between the two forms (V) and (VI), which implies a measure of conjugation throughout the molecule as a whole.

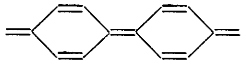
(I.)

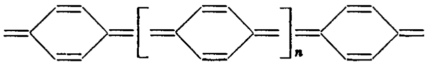




(II.)

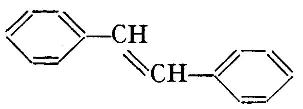
(III.)

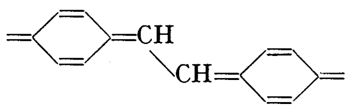




(IV.)

(V.)





(VI.)

In spite of this, however, chemical tests, *e.g.*, substitution reactions, have failed to reveal any evidence of conjugation (Robinson and Zaki, *loc. cit.*). Closely related to this aspect of the subject is kationoid substitution in compounds such as cinnamic acid and ω-nitrostyrene, which gives rise to the more facile *op*-substitution and not *m*-substitution, as might be anticipated if the existence of conjugation throughout the system as a whole manifested itself. This topic has been discussed by Burkhardt, Horrex, and Jenkins (J., **1936**, 1654), who have shown that conjugation between nucleus and side chain, or between nucleus and nucleus, does in fact reveal itself in certain carefully selected qualitative and quantitative observations.

Further insight into the existence and extent of conjugation in organic compounds should be obtainable from a study of absorption spectra. For instance, in stilbene, where *X*-ray evidence reveals a measure of conjugation which chemical tests fail to detect, the absorption spectra yield strong support to the contention that conjugation is present: the absorption maxima for benzene, α-phenylbutadiene, and stilbene are at 2550, 2820, and 2950 A, respectively, and there is a marked increase in the intensity of absorption in passing from benzene to stilbene. These facts are in agreement with one of the accepted generalisations of absorption spectra, *viz.*, that an increase in the number of conjugated double bonds in a system normally results in a displacement of the absorption maxima to longer wave-lengths together with an increase in intensity of absorption (cf. Hausser, Kuhn, *et al.*, *Z. physikal. Chem.*, **1935**, **29**, *B*, 363 *et seq.*).

A study of the absorption spectra of hydrocarbons consisting of more than one benzene nucleus should yield valuable evidence on the nature of the extra-nuclear bonds. Thus the absorption maxima of benzene, diphenylmethane, triphenylmethane, tetraphenylmethane, and diphenylethane are in nearly the same place in all cases, and the intensity of absorption is very approximately that due to a summation of the intensities contributed by the separate benzene nuclei (see Table I). In passing to diphenyl, on the other hand, there is a change of location accompanied by an increase in intensity of some 90 times that exhibited by benzene, which strongly indicates the existence of some measure of conjugation, and Förster (*Z. physikal. Chem.*, **1938**, **41**, *B*, 287) has discussed this spectrum from the point of view of conjugation and of resonance. An alternative hypothesis to account for the greatly increased intensity of diphenyl over that of benzene and the above-mentioned derivatives is not that the 2550 A band of benzene is increased in intensity but that the very short wave band of benzene near 1970 A ($\log \varepsilon = 3{\cdot}9$) is displaced along the spectrum to 2500 A in diphenyl (log ε = 4·25). Either mechanism may be correct, but both agree in indicating that there is a considerable measure of conjugation between the two benzene nuclei in diphenyl, and therefore that the internuclear bond has some of the properties of a double bond.

TABLE I.

Absorption spectra of some aromatic compounds in ethyl alcohol.

	λ, max, A.	ε.	ε/ (no. of benzene nuclei).		λ, max., A.	ε.	ε/ (no. of benzene nuclei).
Benzene *	2550	213	213	Diphenylethane †	2620	380	190
Diphenylmethane	2620 *	490	245	Diphenyl	2500	18,000	—
	2620 †	380	190		2510 †	17,000	—
Triphenylmethane *	2620	870	290		2480 §	19,500	—
Tetraphenylmethane	2620	2020	505	Stilbene ‡	2950	23,400	—

* Orndorff and collaborators (*J. Amer. Chem. Soc.*, 1927, **49**, 1541; 1928, **50**, 835).

† Mme. Ramart-Lucas (*Bull. Soc. chim.*, 1932, **51**, 289).

‡ Ley, " Handbuch der Physik," vol. XXI, 121 (Berlin).

§ Data for solution in methyl alcohol (Pestemer and Wiligut, *Monatsh.*, 1935, **66**, 119).

Many representative hydrocarbons consisting of chains of benzene nuclei are now available for study: in the *p*-series, terphenyl, quaterphenyl, quinquiphenyl (Gerngross and Dunkel, *Ber.*, 1924, **57**, 739; Busch and Weber, *J. pr. Chem.*, 1936, **146**, 1; Müller and Töpel, *Ber.*, 1939, **72**, 290), sexiphenyl (Pummerer *et al.*, *Ber.*, 1924, **57**, 84; 1931, **64**, 2477; Busch and Weber, *loc. cit.*), and septiphenyl (Busch and Weber, *loc. cit.*); in the *m*-series, terphenyl and hydrocarbons containing 9—16 benzene nuclei (Busch and Weber, *loc. cit.*). In the *p*-polyphenyl * series, if the internuclear bonds take some part in the conjugation of the molecule as a whole then a progressive displacement of the absorption bands would be anticipated as additional benzene nuclei are added to the diphenyl molecule at the *p*-positions. On the other hand, in the *m*-series, because of the valency requirements of the carbon atoms, simple conjugation in the conventional sense cannot extend beyond that inherent in the diphenyl structure, and any hydrocarbon containing *n* benzene nuclei united together at the *m*-positions should act as an absorbing entity made up of *n*/2 diphenyl units independently conjugated. In this case no displacement in the position of the absorption bands would be expected as the chain is lengthened, although a progressive increase in the intensity of the absorption would be expected.

In the present investigation measurements of the absorption spectra of ter-, quater-, quinqui-, and sexi-phenyl have been made in the *p*-series. The expected displacement of the absorption band was revealed, as also was an increase in the intensity of absorption (cf. Table II and Figs. 1 and 2) but the extent of the displacement decreases significantly with the progressive lengthening of the chain.

TABLE II.

Absorption spectra of p*-polyphenyl compounds.*

			In hexane.		In chloroform.	
Compound.	Formula.	*M.*	λ, max., A.	ε, max.	λ, max., A.	ε, max.
(Diphenyl	$C_{12}H_{10}$	154	2460	20,300	2515	18,300)
Terphenyl	$C_{18}H_{14}$	230	2760	35,000	2800	25,000
Quaterphenyl	$C_{24}H_{18}$	306	2920	55,000	3000	39,000
Quinquiphenyl	$C_{30}H_{22}$	382	—	—	3100	62,500
Sexiphenyl	$C_{36}H_{26}$	458	3080	—	3175	>56,000

In the *m*-series of compounds containing 3, 9, 10, 11, 12, 13, 14, 15, or 16 benzene nuclei, only one absorption band was exhibited by the chloroform solution of each compound, the maximum being in each case at 2530 ± 20 A, which is almost identical with that found in diphenyl itself. On the other hand, a regular increase in the intensity of absorption was

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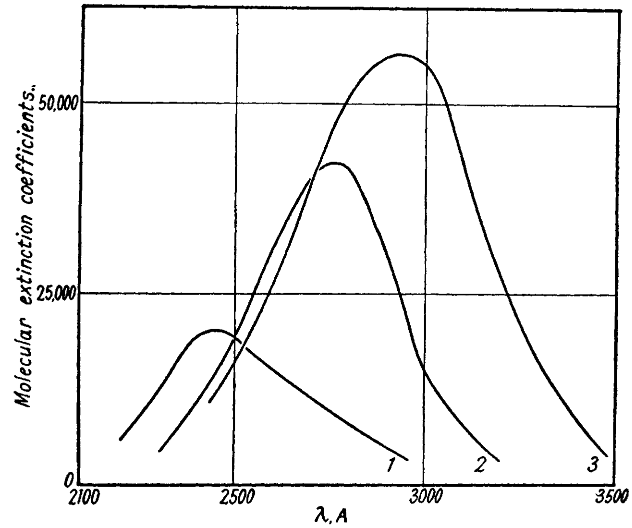
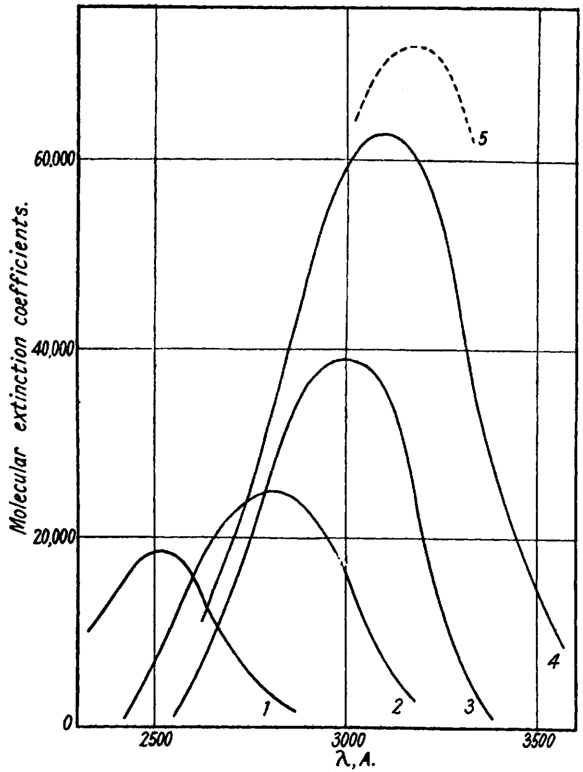
* The term " polyphenyl " is not strictly correct as a generic name for these compounds, but it is short and convenient and, following the German usage, has been adopted here with this reservation.

FIG. 1.



Absorption spectra of para-*polyphenyl compounds in hexane.*
1. *Diphenyl.* 2. *Terphenyl.* 3. *Quaterphenyl.*

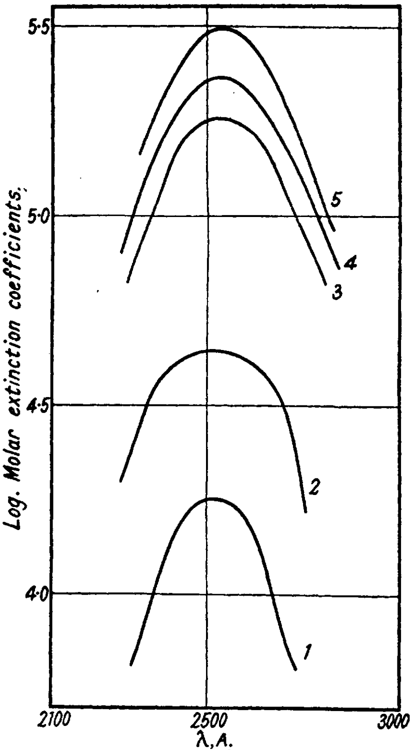
FIG. 2.



Absorption spectra of para-*polyphenyl compounds in chloroform.*

1. *Diphenyl.* 2. *Terphenyl.* 3. *Quaterphenyl.* 4. *Quinquiphenyl.* 5. *Sexiphenyl (qualitative only).*

FIG 3.



Absorption spectra of meta-*polyphenyl compounds in chloroform.*

1. *Diphenyl.* 2. *Terphenyl.* 3. *Noviphenyl.* 4. *Duodeciphenyl.* 5. *Quindeciphenyl.*

exhibited with progressive lengthening of the chain. In fact, the observed intensities are remarkably close to those to be expected from a simple summation of the absorptions due to the unconjugated chromophores present (cf. Table III). The contributions of the individual benzene nuclei to the gross intensity of absorption are much closer to the mean value in the *m*-polyphenyls than they are in the various phenylmethanes (cf. Table I). The increments by which the intensities of absorption change from member to member in these two series are, however, markedly different (cf. Tables I and III).

TABLE III.

Absorption spectra of the m-*polyphenyl compounds in chloroform.*

Compound.	Formula.	*M.*	λ, max., A.	ε.	ε/ (no. of benzene nuclei).
(Diphenyl	$C_{12}H_{10}$	154	2515	18,300	9,000)
Terphenyl	$C_{18}H_{14}$	230	2515	44,000	14,700
Noviphenyl	$C_{54}H_{38}$	686	2530	184,000	20,500
Deciphenyl	$C_{60}H_{42}$	762	2530	213,000	21,300
Undeciphenyl	$C_{66}H_{46}$	838	2530	215,000	19,500
Duodeciphenyl	$C_{72}H_{50}$	914	2530	233,000	19,400
Tredeciphenyl	$C_{78}H_{54}$	990	2530	252,000	19,400
Quattuordeciphenyl	$C_{84}H_{58}$	1066	2530	283,000	20,700
Quindeciphenyl	$C_{90}H_{62}$	1142	2540	309,000	20,600
Sedeciphenyl	$C_{96}H_{66}$	1218	2550	320,000 *	20,000
				Average (last 8 only)	20,100

* This value is only approximate owing to the very low solubility of the compound.

These results indicate that, whereas some degree of conjugation is possible throughout the whole molecule in the *p*-series of hydrocarbons, in the *m*-series the optical properties are more consistent with the presence of a number of identical unconjugated chromophoric units.

It is noteworthy that, in contrast to benzene, diphenylmethane, triphenylmethane, naphthalene, anthracene, and similar compounds, solutions of which exhibit absorption bands showing considerable fine structure, all the polyphenyl compounds discussed here exhibit broad absorption bands showing only one maximum completely without fine structure. Pickett, Walter, and France (*J. Amer. Chem. Soc.*, **1936**, **58**, **2296**) studied the absorption spectra of certain substituted derivatives of diphenyl and found that, in the compounds in which free rotation about the internuclear bond is supposedly restricted by the presence of substituent groups, the absorption curve exhibits fine structure. Conversely, when free rotation of the nuclei is possible the fine structure disappears.

A comparison of the optical properties of aromatic and ethylenic compounds by Kuhn and Grundmann (*Ber.*, **1937**, **70**, **1318**) led to the conclusion that the benzene nucleus as a chromophoric unit is approximately equivalent to 1½ conjugated double bonds. In *p*-sexiphenyl, the highest member of the *p*-series studied, the complete chromophoric system might therefore be expected to correspond with nine conjugated double bonds. By analogy with diphenyldodecahexaene (having the equivalent of nine conjugated double bonds) and members of the carotenoid group of compounds having 8—10 double bonds in conjugation, *p*-sexiphenyl should exhibit an absorption maximum in the visible region of the spectrum and so be visibly coloured, but it is practically colourless and its absorption maximum occurs well outside the confines of the visible and into the ultra-violet (max. 3175 A in chloroform). It must therefore be concluded that the measure of conjugation which has been indicated as existing in the *p*-polyphenyl compounds, from the evidence of absorption-spectra data, must be less effective than that which occurs when benzene nuclei are associated with conjugated ethylene linkages as in the diphenylpolyenes.

In order to account for the enormous increase in intensity of absorption which occurs in passing from benzene to diphenyl, as well as for the absorption of the *m*-polyphenyl compounds, it might at first be thought reasonable to postulate the diphenyl structure itself as the chromophore; but from the facts that the location of the absorption band for members of this series having either odd or even numbers of benzene nuclei is remarkably constant, and that the intensity increment for one added benzene nucleus, in the higher members at least, is also remarkably constant, it follows that the diphenyl group itself is unlikely to be the chromophoric unit (cf. Table III). If, on the other hand, the chromophoric group is regarded as a " semidiphenyl " unit (as distinct from a single benzene nucleus) the locations and intensities of absorption of the members of the *m*-series can be visualised as simple summations of such unconjugated semidiphenyl units producing therefore no displacement of the absorption band but a regular increase in intensity. That such a half-diphenyl unit is vastly different from an isolated benzene nucleus is shown by the fact that whereas 15 unconjugated benzene nuclei in *m*-quindeciphenyl give an observed value for the molecular extinction coefficient of over 300,000, the summation of 15 isolated benzene nuclei of the type occurring in di- and tri-phenylmethane would be expected to have an extinction coefficient of the order of 3,000—4,000 (*i.e.*, 1% of the observed value).

It is noteworthy that these polyphenyl compounds, and particularly the higher members of the *m*-series, with their unusually large number of chromophoric groups in one molecule and high molecular weights, are among the few organic compounds having molecular extinction coefficients of the order of one third of a million. It is this high intrinsic absorption (apart from molar weight) which makes it possible to detect and determine these compounds even with their minute solubilities; *e.g.*, 1 part of *m*-quindeciphenyl can be detected and determined quantitatively in about 3·5 million parts of solvent or other transparent medium.

EXPERIMENTAL.

Hydrocarbons.—Tetraphenylmethane (m. p. 274—275°, from toluene) was obtained by the decomposition of phenylazotriphenylmethane in benzene solution (Hey, J., 1934, 1968). *p*-Terphenyl (m. p. 212°, from alcohol) was obtained by the interaction of either (*a*) 4-nitrosoacetamidodiphenyl or (*b*) dinitrosodiacetyl-1 : 4-phenylenediamine with benzene (France, Heilbron, and Hey, J., 1938, 1370). *p*-*Q*uaterphenyl (m. p. 312°, from boiling benzene) was prepared in like manner from the interaction of dinitrosodiacetylbenzidine with benzene (Dr. J. W. Haworth, unpublished work). For a further sample of this hydrocarbon we are indebted to Dr. S. T. Bowden, University College of South Wales and Monmouthshire, Cardiff, who obtained it by heating 4-iododiphenyl with copper-bronze as well as by the action of anhydrous cupric chloride on a magnesium 4-diphenylyl halide (J., 1931, 1111). *p*-*Q*uinquiphenyl was prepared from a specimen of the quinhydrone of quinquiphenyl–dihydroquinquiphenyl (kindly supplied by Dr. Eugen Müller of the University of Jena), which was dehydrogenated with selenium in boiling quinoline solution (cf. Müller and Töpel, *loc. cit.*). The hydrocarbon, purified by sublimation in a vacuum (*ca.* 200°/0·01 mm.), was obtained as a white microcrystalline powder, m. p. 380° (uncorr.). *p*-Sexiphenyl was prepared by heating either (*a*) 4-iodo-*p*-terphenyl (France, Heilbron, and Hey, *loc. cit.*) with silver powder, or (*b*) 4 : 4′-di-iododiphenyl with copper-bronze, as described by Pummerer and his co-workers (*Ber.*, 1924, **57**, 84; 1931, **64**, 2477). The latter method gave the better product : the hydrocarbon finally sublimed at 340—350°/0·01 mm. as a very pale cream powder, m. p. >400° (Found : C, 93·8; H, 5·8. Calc. for $C_{36}H_{26}$: C, 94·3; H, 5·7%). *m*-Terphenyl (m. p. 89°, from methyl alcohol) was obtained either (*a*) by the dehydrogenation of 1 : 3-diphenyl*cyclo*hexene, or (*b*) by the interaction of 3-nitrosoacetamidodiphenyl with benzene (Dr. H. France, unpublished work). The members of the *m*-series containing 9—16 benzene nuclei were received from Prof. Dr. Max Busch, University of Erlangen.

Determination of Absorption Spectra.—The lower members of the *m*-series are very sparingly soluble in pure benzene-free hexane, so this solvent was abandoned in favour of chloroform. Even here the solubility is very small and falls progressively as the series is ascended. With the higher members (C_{72}—C_{96}) it was only possible to obtain satisfactory solutions (of the order of 0·0002%) by weighing out about 1 mg. on a microbalance and refluxing it with chloroform (500 ml.) until dissolved, but 1·14 mg. of *m*-sedeciphenyl failed to dissolve completely even when refluxed with 500 ml. of chloroform, although 0·81 mg. dissolved almost completely in this volume; the extinction coefficient recorded for this compound is therefore only approximate but probably within 5% of the true value. In the *p*-series the compounds are even less soluble, and the relatively simple *p*-sexiphenyl is only sufficiently soluble in hexane to obtain the location of the maximum but not its intensity. In chloroform the compound is more soluble, but not sufficiently so to enable the extinction coefficient to be obtained with accuracy (solution 0·00037%).

The absorption-spectra determinations were carried out on a Hilger E3 quartz spectrograph which photographs the region 2200—4000 A on a strip 14 cm. long. The light source was a tungsten-steel spark giving a spectrum of closely packed lines approximating to a continuous spectrum in the sense that it provides a background with relatively few gaps. The Hilger Spekker photometer was used exclusively for the determination of extinction coefficients. The molecular extinction coefficient (ε) is obtained from the relation $\log I_0/I$ = density = εcd, where I_0 is the intensity of the incident light, I that of the transmitted light, c the concentration of the solution (in g.-mols./l.), and d the thickness of the layer of solution (in cm.).

The authors express their grateful thanks to Prof. Dr. Max Busch of the University of Erlangen for the gift of specimens of the *m*-polyphenyl compounds from noviphenyl to sedeciphenyl inclusive.

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