921. *The Relation between Configuration and Conjugation in Diphenyl Derivatives. Part IX.* Some Tetrachloro-2 : 2′-bridged Compounds.*

By D. MURIEL HALL and FATIMA MINHAJ.

A series of 4 : 6 : 4′ : 6′-tetrachloro-2 : 2′-bridged diphenyls has been prepared from 4 : 6 : 4′ : 6′-tetrachlorodiphenic acid. The ultraviolet absorption spectra of these compounds show increased intensities and red shifts of the conjugation band, in comparison with the corresponding unsubstituted compounds, in spite of the presence of the large chlorine atoms in the *ortho*-positions. In contrast, the conjugation band in 2 : 4 : 2′ : 4′-tetrachlorodiphenyl is present only as an inflection at a shorter wavelength.

These results emphasise the importance of a 2 : 2′-bridge in maintaining conjugation in *ortho*-substituted diphenyls.

SPECTROSCOPIC measurements show that 2 : 2′-bridged diphenyls in which the bridge forms part of a homocyclic or heterocyclic 7-membered ring retain a high degree of conjugation between the two benzene rings.[1,2,3] Investigation of the effect of *ortho*-substituents on the spectra of these compounds has been restricted to compounds with heterocyclic

---

* Part VIII, *J.*, 1957, 651.

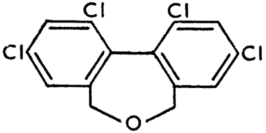
[1] Beaven, Hall, Lesslie, and Turner, *J.*, 1952, 854.

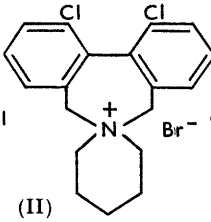
[2] Beaven, Bird, Hall, Johnson, Ladbury, Lesslie, and Turner, *J.*, 1955, 2708.

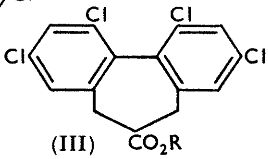
[3] Beaven and Johnson, *J.*, 1957, 651.

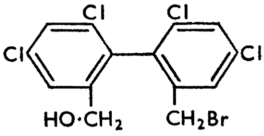
bridging rings and to the substituents methoxyl [1] and methyl.[4] It thus seemed desirable to extend this range by investigating the effect of chlorine atoms in the *ortho*-positions on the ultraviolet absorption spectra of such bridged compounds. For this, 6 : 6′-dichlorodiphenic acid [5] was required as starting material. However, in view of the much shorter synthesis of 4 : 6 : 4′ : 6′-tetrachlorodiphenic acid [6] (in two stages from anthranilic acid), the latter compound was preferred and, accordingly, a series of tetrachloro bridged compounds was prepared.

Methyl 4 : 6 : 4′ : 6′-tetrachlorodiphenate was reduced with lithium aluminium hydride and the resulting diol dehydrated to give the oxepin (I). A solution of the diol in glacial acetic acid was treated with hot hydrobromic acid and gave a dibromide which was a gum. The azepinium bromide (II) was prepared by the condensation of piperidine with the dibromide; the reaction of the latter with sodiomalonic ester gave a cyclic ester from which,


(I)


(II)


(III)


(IV)

after suitable treatment, methyl 2′ : 4′ : 1″ : 3″-tetrachloro-3 : 4-5 : 6-dibenzo*cyclo*hepta-3 : 5-diene-1-carboxylate (III; R = Me) was obtained. Treatment of the dibromide with the sodio-derivative of ethyl ethane-1 : 1 : 2 : 2-tetracarboxylate failed to give any of the ester with an eight-membered ring and 71% of the original ester was recovered (cf. the corresponding reaction with 2 : 2′-bisbromomethyldiphenyl [2]). On the other hand, reaction between the dibromide and ethyl propane-1 : 1 : 3 : 3-tetracarboxylate in the presence of sodium ethoxide led, as with 2 : 2′-bisbromomethyldiphenyl, to fission of the carbon chain of the ester and the formation of the compound with a 7-membered ring, from which the acid (III; R = H) was obtained.

From all these condensations of the dibromide with esters in the presence of sodium ethoxide appreciable quantities (sometimes as much as 40%, based on the diol used to prepare the dibromide) of the oxepin (I) were isolated. This suggested that the dibromide was contaminated with the bromohydrin (IV), which would readily form the oxepin in the presence of alkali, and, indeed, by heating this " dibromide " (*i.e.*, the gum as used for the above condensations) for about 10 min. with 30% sodium hydroxide, oxepin was obtained. Subsequently, by prolonged boiling of the diol with a larger excess of hydrobromic acid and no acetic acid, the dibromide was obtained as a crystalline solid. Unlike the gum, this was unaffected when heated with 30% sodium hydroxide for 10 min.

Discussion of Spectra.—The ultraviolet absorption spectra (Figs. 1 and 2) of the compounds (I), (II), and (III) show long-wave shifts and increased intensities of the conjugation band, as compared with the corresponding unsubstituted compounds (Table 1). Similar effects are apparent in the long-wave fine structure (which is rather more highly developed in the tetrachloro-compounds), in the minimum on the short-wave side of the conjugation band, and, where data are available, in the shortwave band itself, although here the increases in intensity are proportionately rather small and may hardly be significant.

Introduction of the four chlorine atoms into these bridged compounds clearly does not reduce the conjugation between the benzene rings and, while the *ortho*-chlorine atoms may

---

[4] Wittig and Zimmermann, *Chem. Ber.*, 1953, **86**, 629.
[5] Christie, James, and Kenner, *J.*, 1923, **123**, 1948.
[6] Atkinson, Murphy, and Lufkin, *Org. Synth.*, 1951, **31**, 96.

reduce somewhat the auxochromic influence which the *para*-chlorine atoms would otherwise have, their steric effect on conjugation is nevertheless slight. This is in accordance with our view that fairly large substituents can be accommodated in the *ortho*-positions of 2 : 2′-bridged diphenyls with only slight distortion of the bridging ring, since the angle θ between the planes of the benzene rings is already, in the unsubstituted compounds, of the order of 45—50°. Further, the *ortho*-substituents can undoubtedly approach one another more closely when free rotation of the benzene rings is prevented by bridging than they can in a non-bridged compound, where interactions between such *ortho*-substituents are probably the dominant factor in determining preferred conformation. (For small *ortho*-substituents, therefore, such distortion of the bridging ring is probably negligible.) Calculations of θ with use of normal covalent radii and bond angles give values of 43°, 47° *, and 49° for the unsubstituted oxepin, azepinium bromide, and dibenzo*cyclo*heptadiene, respectively. The angles measured on our (rigid) molecular models have similar values since the models incorporate the same bond lengths and angles. It is less easy to predict the amount of distortion permitted, and here the use of highly flexible models may give misleading results. Braude and Forbes,[7] using " open " scale models, find θ to be about 21° in the unsubstituted oxepin but their model, shown in a photograph, appears to be considerably distorted so that the two benzene rings are no longer collinear.

TABLE 1. *Ultraviolet absorption spectra of* 2 : 2′-*bridged diphenyls.*

	Short-wave band		Minimum		Conjugation band		Long-wave features	
Compound	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$
2 : 7-Dihydro-3 : 4-5 : 6-dibenzoxepin [3]	206·5	40,000	227	4920	250·5	16,500	(*ca.* 277)	1600
2′ : 4′ : 1″ : 3″-Tetrachloro-2 : 7-dihydro-3 : 4-5 : 6-dibenzoxepin (I)	217·5	42,500	239	9500	257	19,000	(*ca.* 290) (*ca.* 280)	1200 3400
2 : 7-Dihydro-3 : 4-5 : 6-dibenzazepinium-1-*spiro*-1‴-piperidinium bromide (in water) [1]	—	—	224	4500	248	15,000	(*ca.* 281·5) (*ca.* 272)	2250 4750
2′ : 4′ : 1″ : 3″-Tetrachloro-2 : 7-dihydro-3 : 4-5 : 6-dibenzazepinium-1-*spiro*-1‴-piperidinium bromide (II)	222	41,500	242·5	9600	259·5	18,100	(*ca.* 293) 283·5	3550 6520
Methyl 3 : 4-5 : 6-dibenzo*cyclo*hepta-3 : 5-diene-1-carboxylate [2]	207·5	42,500	227·5	5700	248·5	15,500	(*ca.* 274)	1700
Methyl 2′ : 4′ : 1″ : 3″-tetrachloro-3 : 4-5 : 6-dibenzo*cyclo*hepta-3 : 5-diene-1-carboxylate (III)	215·5 (*ca.* 223)	46,000 41,500	236	8400	254·4	19,000	(*ca.* 286)	810

Solvent, 96% ethanol, except where otherwise stated; wavelengths in mμ; values in parentheses denote inflections.

These authors regard 2 : 2′-bridged diphenyls as compounds which manifest steric effects predominantly by changes in the absorption intensity and not by wavelength displacements. For such compounds they calculate [8] the approximate mean interplanar angle θ from the expression $\cos^2\theta = \varepsilon/\varepsilon_0$, where ε is the molecular extinction coefficient for the diphenyl band in the particular compounds and ε_0 is the corresponding value for fluorene, which they regard as a planar, *oo*′-disubstituted diphenyl.

Since the two rings in fluorene are planar but not collinear [9] the molecule must be

---

* The C–N⁺ bond length is taken as 1·50 Å.

[7] Braude and Forbes, *J.*, 1955, 3776.

[8] Braude, *Experientia*, 1955, **11**, 457; Braude and Sondheimer, *J.*, 1955, 3754.

[9] Brown and Bortner, *Acta Cryst.*, 1954, **7**, 139; Burns and Iball, *Nature*, 1954, **173**, 635; *Proc. Roy. Soc.*, 1955, *A*, **227**, 200.

somewhat strained and so appears to be rather unsuitable as a standard. A more serious objection, however, to the validity of such calculations of θ is that the intensity and, to a smaller degree, the position of the diphenyl hand in these bridged compounds are affected by the presence (and nature) of substituents in the *para*-, *meta*-, or *ortho*-positions; in the last case a steric effect may be superimposed. These points are illustrated by some of the compounds quoted by Braude and Forbes. (1) *N*-Acetylcolchinol methyl ether (V) has $\varepsilon_{max.}$ 20,000 at 262 mμ,[10] from which Braude and Forbes calculate θ to be zero. However the increased intensity of absorption is almost certainly due to the presence of *pp'*-methoxyl groups, which here more than compensate for the effects of the single *o*- and *m*-methoxyl groups. Additional evidence for the non-planarity of a diphenyl with a three-carbon bridge comes from the preparation by Iffland and Siegel[11] of ethyl 3 : 4-5 : 6-dibenzo*cyclo*hepta-3 : 5-diene-1 : 1-dicarboxylate (VI) in an optically active form, although, of course, the existence of optical isomerism in a compound of this type gives no direct

FIG. 1. FIG. 2. FIG. 3.

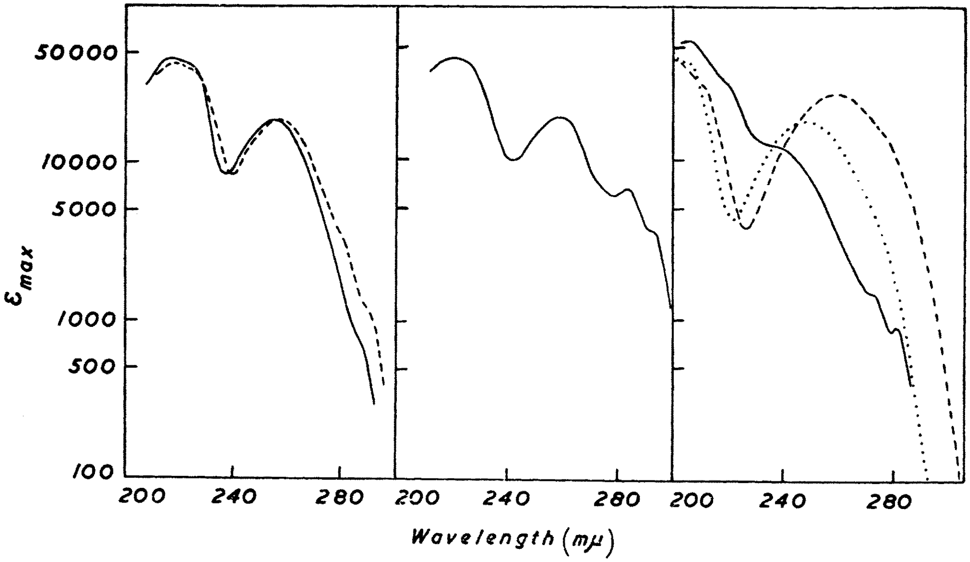


FIG. 1. ——— Methyl 2' : 4' : 1'' : 3''-tetrachloro-3 : 4-5 : 6-dibenzo*cyclo*hepta-3 : 5-diene-1-carboxylate (III; R = Me). - - - - 2' : 4' : 1'' : 3''-Tetrachloro-2 : 7-dihydro-3 : 4-5 : 6-dibenzoxepin (I).

FIG. 2. 2' : 4' : 1'' : 3''-Tetrachloro-2 : 7-dihydro-3 : 4-5 : 6-dibenzazepinium-1-*spiro*-1'''-piperidinium bromide (II).

FIG. 3. ——— 2 : 4 : 2' : 4'-Tetrachlorodiphenyl. - - - - 4 : 4'-Dichlorodiphenyl. .... Diphenyl

indication of the value of θ except that it must be greater than zero. (2) The *oo'*-dimethoxy-derivatives[1] of 9 : 10-dihydrophenanthrene and 2 : 7-dihydro-3 : 4-5 : 6-dibenzoxepin show a larger reduction in intensity of the conjugation band than do the corresponding *oo'*-dimethyl derivatives,[4] * although methyl causes much greater steric interference than

---

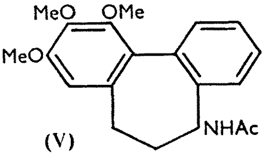
* Bergmann and Pelchowicz[12] have also determined the spectrum of 9 : 10-dihydro-4 : 5-dimethylphenanthrene but their data in the text are at variance with their drawing of the spectrum and we have therefore only considered Wittig and Zimmermann's figures.

[10] Huang, Tarbell, and Arnstein, *J. Amer. Chem. Soc.*, 1948, **70**, 4181; Horowitz, Ullyot, E. C. Horning, M. G. Horning, Koo, Fish, Parker, and Walker, *ibid.*, 1950, **72**, 4330; Rapoport, Williams, and Cisney, *ibid.*, 1951, **73**, 1414.

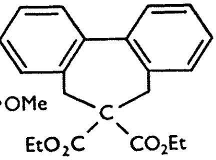
[11] Iffland and Siegel, *J. Org. Chem.*, 1956, **21**, 1056.

[12] Bergmann and Pelchowicz, *J. Amer. Chem. Soc.*, 1953, **75**, 2663.

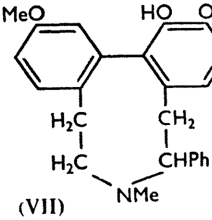
methoxyl (in which the methyl group can be out of the way). (3) In a compound with a large 2 : 2′-bridge as in dihydrophenylthebaine (VII) the molecule is more flexible and a number of conformations are possible. From our models it appears that θ cannot be less than about 50° but could be as large as 110°. Preferred conformations, of which there may be several, probably have intermediate values of θ. It is therefore not surprising that the conjugation band is apparently absent,[13] although evidence from compounds with a four-carbon bridge [2,14] suggests that it might be detectable, at least as an inflection, at a much shorter wavelength. The band at 281 mμ ($\varepsilon_{max.}$ 5600) in dihydrophenylthebaine cannot be a diphenyl band at all and is presumably the normal long-wave band due to absorption by methoxyphenyl partial chromophores. (4) The effect of *meta*-substituents is attributed by Braude and Forbes to " buttressing " of the *o*-hydrogen atoms against in-plane bending away from the diphenyl link. However, on their hypothesis, the steric effect of such " buttressed " hydrogen atoms (in the *mm*′-dimethoxy-compounds) on the spectrum of, for example, the oxepin [15] ($\varepsilon_{max.}$ 11,000) would be as great as that of two *ortho*-methyl groups [4] ($\varepsilon_{max.}$ 11,000).



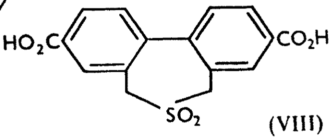
(V)



(VI)



(VII)



(VIII)

The calculation of θ by the above formula, involving as it does the assumption that *all* changes in intensity may be attributed to steric effects, thus leads to inconsistent results. Further evidence comes from our work, since the spectrum of the tetrachloro-oxepin, with $\varepsilon_{max.}$ 19,000, would give θ = 0°, which is clearly impossible on any model.

Our view is still that in the oxepins, azepinium compounds, and dibenzo*cyclo*heptadienes the steric effect of *ortho*-substituents is small and can easily be over-ridden by the effects of substituents in the *para*-positions (as, for example, in the tetrachloro-compounds described above and in *N*-acetylcolchinol methyl ether) or may be enhanced by other effects of the *ortho*-substituents (as in the *oo*′-dimethoxy-compounds). The large mesomeric effect of methoxyl groups makes them rather unsuitable substituents for the study of steric effects, and a series of other *oo*′-disubstituted bridged diphenyls is in preparation. Qualitatively, the 9 : 10-dihydrophenanthrenes behave in the same way as the compounds with larger bridging rings but in view of the smaller value of θ (15—16°, depending on the length of the central diphenyl bond) it is likely that *large ortho*-substituents, which can readily be accommodated when θ is about 50°, will cause appreciable molecular distortion here. Even so, this is not *necessarily* accompanied by much loss of conjugation but further experimental evidence is required.

Truce and Emrick [16] correlate the position of the conjugation band in seven-membered ring bridged diphenyls with optical stability and suggest that $\lambda_{max.}$ 242 mμ " represents about the borderline in resolvability "; compounds with the band at longer wavelengths would either not be resolvable or would be optically unstable. There is independent evidence from other work [17] that increase in θ leads to increase in optical stability but,

---

[13] Small, Sargent, and Bralley, *J. Org. Chem.*, 1947, **12**, 839.

[14] Cope and Smith, *J. Amer. Chem. Soc.*, 1956, **78**, 1012.

[15] Beaven, Hall, Lesslie, Turner, and Bird, *J.*, 1954, 131.

[16] Truce and Emrick *J. Amer. Chem. Soc.*, 1956, **78**, 6130.

[17] Hall and Turner, *J.*, 1955, 1242; Hall, *J.*, 1956, 3674; Armarego and Turner, *J.*, 1956, 3668; 1957, 13.

while it appears probable that in the absence of all other substituents the position of the conjugation band may be roughly correlated with the value of θ, it cannot be expected that small variations in $\lambda_{max.}$ will be reflected in racemisation rates. Among seven-membered ring bridged diphenyls *without ortho*-substituents optical activity has been demonstrated only in ethyl 3 : 4-5 : 6-dibenzo*cyclo*hepta-3 : 5-diene-1 : 1-dicarboxylate[11] (VI) and 2 : 7-dihydro-3 : 4-5 : 6-dibenzothiepin-2′ : 3″-dicarboxylic acid 1 : 1-dioxide (VIII).[16] The former racemises in about 5 hr. at 32·5° but no information is available about the optical stability of the latter. (Incidentally we find 3 : 4-5 : 6-dibenzo*cyclo*hepta-3 : 5-diene-1 : 1-dicarboxylic acid to have $\varepsilon_{max.}$ 15,000 at 250 mμ, not *ca.* 100,000 as described by Truce and Emrick.)

In contrast to the bridged compounds, unbridged diphenyls are far more sensitive spectroscopically to the presence of *ortho*-substituents. For comparison with the bridged compounds it was desirable to examine 2 : 4 : 2′ : 4′-tetrachlorodiphenyl. This compound proved unexpectedly difficult to prepare. It is described by Ullmann[18] as a solid, m. p. 83°, obtained by heating 2 : 4-dichloro-1-iodobenzene with copper bronze. The only other reference to it describes its isolation[19] from the products of thermal decomposition of 2 : 4 : 2′ : 4′-tetrachlorodibenzoyl peroxide. We failed to prepare it either by Ullmann's method (including considerable variation in the temperature of the reaction) or by the diazo-process (Sandmeyer or Gattermann) from 2 : 2′-dichlorobenzidine.[20] It was finally obtained as a solid, m. p. 41°, in 13% yield by the action of anhydrous cupric chloride on 2 : 4-dichlorophenylmagnesium iodide (Krizewsky–Turner method[21]). Possibly this is a metastable form, but the m. p. has remained unchanged for several months.

TABLE 2. *Ultraviolet absorption spectra of non-bridged diphenyls.*

Compound	Short-wave band		Minimum		Conjugation band		Minimum		Long-wave band	
	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$	$\lambda_{max.}$	$\varepsilon_{max.}$
Diphenyl [a]	203 (*ca.* 205)	46,000 [b] 42,000 [b]	222	4300	249	17,300	—	—	—	—
2 : 2′-Dichlorodiphenyl [c]	208	36,000	—	—	(230)	6600	264	700	273·5 266·5	540 735
2 : 4 : 2′ : 4′-Tetrachlorodiphenyl	205·5 (*ca.* 221)	55,000 28,000	—	—	(*ca.* 237)	12,300	271·5	1445	281 272	900 1450
4-Chlorodiphenyl [d]	203 (210)	40,500 (32,000)	225	3700	253	21,100	—	—	—	—
4 : 4′-Dichlorodiphenyl	201 (*ca.* 211)	42,400 29,100	226	3810	259	25,200	—	—	(*ca.* 283) (*ca.* 275)	9000 16,000

Solvent, 96% ethanol, except where otherwise stated; wavelengths in mμ; values in parentheses denote inflections.

[a] Everitt, Hall, and Turner, *J.*, 1956, 2286. [b] In light petroleum (b. p. 100—120°). [c] Beaven and Hall, *J.*, 1956, 4637. [d] G. H. Beaven, personal communication.

Its spectrum (Fig. 3) shows greater conjugation than that of 2 : 2′-dichlorodiphenyl,[22] as evidenced by long-wave shifts and increased intensities, but the compound is nevertheless very much *less* conjugated than the parent diphenyl (Table 2), the conjugation band being present only as an inflection ($\lambda_{infl.}$ *ca.* 236 mμ) The results for 4-chloro- and 4 : 4′-dichloro-diphenyl show the auxochromic effects of *para*-chlorine atoms on the diphenyl chromophore (Table 2; Fig. 3).

---

[18] Ullmann, *Annalen*, 1904, **332**, 38.

[19] Fichter and Adler, *Helv. Chim. Acta*, 1926, **9**, 279.

[20] Cain and May, *J.*, 1910, **97**, 720.

[21] Krizewsky and Turner, *J.*, 1919, **115**, 559; Turner, *J. Proc. Roy. Soc. New South Wales*, 1920, **54**, 37.

[22] Beaven and Hall, *J.*, 1956, 4637.

EXPERIMENTAL

Methyl 4 : 6 : 4′ : 6′-*Tetrachlorodiphenate*.—4 : 6 : 4′ : 6′-Tetrachlorodiphenic acid,[6] m. p. 264—265°, was heated under reflux with its own weight of concentrated sulphuric acid and 10 times its weight of methanol for 18 hr. Prolonged heating was necessary to complete esterification of both carboxyl groups. The *dimethyl ester*, crystallised from methanol or benzene, had m. p. 160—161° (Found: C, 47·0; H, 3·1; Cl, 35·2. $C_{16}H_{10}O_4Cl_4$ requires C, 47·1; H, 2·5; Cl, 34·8%). The *diamide* was prepared *via* the acid chloride and had m. p. 246—247° (from $CHCl_3$) (Found: C, 44·4; H, 1·9; N, 7·6; Cl, 37·8. $C_{14}H_8O_2N_2Cl_4$ requires C, 44·5; H, 2·1; N, 7·4; Cl, 37·5%).

4 : 6 : 4′ : 6′-*Tetrachloro*-2 : 2′-*bishydroxymethyldiphenyl*.—The above ester was reduced with lithium aluminium hydride in ether, the finely-ground solid ester being washed into the reaction flask with ether. The mixture was heated (water-bath) for 40 min., then decomposed with water and 2N-sulphuric acid. The ethereal layer was separated, the ether removed, and the residue crystallised from carbon tetrachloride, giving the *diol* (98%) as needles, m. p. 136—137° (Found: C, 47·8; H, 2·9; Cl, 40·6. $C_{14}H_{10}O_2Cl_4$ requires C, 47·8; H, 2·9; Cl, 40·3%).

2′ : 4′ : 1″ : 3″-*Tetrachloro*-2 : 7-*dihydro*-3 : 4-5 : 6-*dibenzoxepin* (I) was obtained by heating the above diol (1 g.) with 50% sulphuric acid (20 c.c.) for about ½ hr. with frequent stirring. It crystallised from methanol in long, pointed prisms, m. p. 151—152·5° (Found: C, 50·3; H, 2·5; Cl, 42·2. $C_{14}H_8OCl_4$ requires C, 50·3; H, 2·4; Cl, 42·5%).

2 : 2′-*Bisbromomethyl*-4 : 6 : 4′ : 6′-*tetrachlorodiphenyl*.—(*a*) The above diol (35·2 g.) was dissolved in hot glacial acetic acid (110 c.c.) and heated with hydrobromic acid (500 c.c., 48%) under reflux for 2½ hr. The mixture was allowed to cool and the acids were decanted from the residual gum. This was dried *in vacuo* over potassium hydroxide for 48 hr., dissolved in ether, and used immediately for condensations with the esters.

(*b*) The diol (5 g.) was dissolved in hot glacial acetic acid (20 c.c.) and heated with hydrobromic acid (150 c.c., 48%) under reflux for 2½ hr. The mixture was allowed to cool, the supernatant liquid discarded, and the residual gum washed with cold water and dissolved in benzene. The benzene solution was then washed with aqueous sodium hydrogen carbonate and with water, and was used for the condensation with piperidine.

(*c*) The diol (7·5 g.) was heated with hydrobromic acid (225 c.c.) under reflux for 2½ hr. More acid (225 c.c.) was added and heating continued for a further 5 hr. The acid was decanted and the remaining oil heated with fresh acid (225 c.c.) for 2 hr. The product was washed with water, dried, and crystallised from light petroleum (b. p. 40—60°), giving 7·5 g. (74%) of the *dibromide*. After recrystallisation from ethanol it had m. p. 101·5—103·5° (Found: C, 34·8; H, 1·6; Hal, 62·3. $C_{14}H_8Br_2Cl_4$ requires C, 35·2; H, 1·7; Hal, 63·1%).

2′ : 4′ : 1″ : 3″-*Tetrachloro*-2 : 7-*dihydro*-3 : 4-5 : 6-*dibenzazepinium*-1-spiro-1‴-*piperidinium Bromide* (II).—The above dibromide, freshly prepared from the diol (5 g.) by method (*b*), was dissolved in benzene, and piperidine (2 g.) in benzene added. A flocculent precipitate, m. p. 141—143° (decomp.) (5·5 g.), separated on warming; after two crystallisations from water the *azepinium bromide* was obtained as a dihydrate, m. p. *ca.* 211—212° (Found: C, 43·7; H, 4·1; Br, 15·4; H_2O, 6·5. $C_{19}H_{18}NBrCl_4,2H_2O$ requires C, 44·0; H, 4·3; Br, 15·4; H_2O, 6·95%). Most of the water of crystallisation was readily lost *in vacuo*; the resulting bromide was extremely hygroscopic. The spectrum was determined on the air-dried dihydrate.

2′ : 4′ : 1″ : 3″-*Tetrachloro*-3 : 4-5 : 6-*dibenzo*cyclo*hepta*-3 : 5-*diene*-1 : 1-*dicarboxylic Acid*.—Sodium (4·6 g.) was dissolved in absolute ethanol (110 c.c.) and ethyl malonate (15 g.) added with stirring. An ethereal solution (300 c.c.) of the dibromide [from 35·2 g. of diol by method (*a*)] was added and the mixture heated for 40 min. Most of the ether was removed by distillation and the reaction mixture then heated under reflux with stirring for 2½ hr. Water was added and a wax separated. This was crystallised from ethanol and then heated under reflux with alcoholic potassium hydroxide. An alkali-insoluble solid was obtained which, after crystallisation from methanol, had m. p. and ultraviolet absorption spectrum identical with those for the oxepin (yield 13·9 g., 42%). Acidification of the alkaline solution, followed by ether-extraction and removal of solvent, gave the *dicarboxylic acid*, m. p. 172—175° (decomp.) (yield 9·5 g., 23%). After crystallisation from aqueous alcohol it had m. p. 188—189° (decomp.) (Found: C, 48·8; H, 2·4; Cl, 34·0. $C_{17}H_{10}O_4Cl_4$ requires C, 48·6; H, 2·4; Cl, 33·8%). From one preparation the pure *diethyl ester*, m. p. 140—141°, was isolated (Found: C, 52·9; H, 3·0; Cl, 29·8. $C_{21}H_{18}O_4Cl_4$ requires C, 53·0; H, 3·8; Cl, 29·8%).

2′ : 4′ : 1″ : 3″-*Tetrachloro*-3 : 4-5 : 6-*dibenzo*cyclo*hepta*-3 : 5-*diene*-1-*carboxylic acid* (III; R = H) was obtained by heating the dicarboxylic acid in a bath at *ca.* 200° until evolution of carbon dioxide ceased. It crystallised from ethanol in needles or plates, m. p. 219—221° (Found: C, 51·5; H, 2·8; Cl, 37·3. $C_{16}H_{10}O_2Cl_4$ requires C, 51·1; H, 2·7; Cl, 37·7%). The *methyl ester* crystallised from methanol in needles, m. p. 159—160° (Found: C, 52·7; H, 3·2; Cl, 36·1. $C_{17}H_{12}O_2Cl_4$ requires C, 52·3; H, 3·1; Cl, 36·4%).

Attempted Condensation of the Dibromide with Ethyl Ethane-1 : 1 : 2 : 2-*tetracarboxylate.*—Sodium (3·1 g.) was dissolved in absolute ethanol (45 c.c.) and powdered ethyl ethane-1 : 1 : 2 : 2-tetracarboxylate (21·2 g.) added with stirring, followed by the dibromide [prepared from 23·5 g. of diol by method (*a*)] in ethereal solution. The mixture was heated under reflux for ½ hr. Most of the ether was distilled off and heating continued for another 2 hr. Water was added and the wax obtained was crystallised from *n*-hexane and then from ethanol, giving ethyl ethane-1 : 1 : 2 : 2-tetracarboxylate, m. p. and mixed m. p. 73—75° (15 g., 71%), and the oxepin, m. p. 151—152° (7 g., 31%). No other product was detected.

Attempted Condensation of the Dibromide with Ethyl Propane-1 : 1 : 3 : 3-*tetracarboxylate.*—Similar condensation of the dibromide (from 23·5 g. of diol) with ethyl propane-1 : 1 : 3 : 3-tetracarboxylate (22·1 g.) in the presence of sodium ethoxide (from 3·1 g. of sodium) gave a solid which was heated with aqueous potassium hydroxide for 12 hr. The product was separated into oxepin, m. p. 149—150° after crystallisation (4·4 g., 20%), and a mixture of di- and mono-carboxylic acids (partial decarboxylation having occurred). The acids were heated to complete decarboxylation and the resulting 2′ : 4′ : 1″ : 3″-tetrachloro-3 : 4-5 : 6-dibenzo*cyclo*hepta-3 : 5-diene-1-carboxylic acid crystallised from benzene: m. p. and mixed m. p. 218—219° (4·8 g., 19%).

2 : 4 : 2′ : 4′-*Tetrachlorodiphenyl.*—Anhydrous cupric chloride (67 g., 1·25 mol.) was added gradually to a Grignard reagent prepared from 2 : 4-dichloro-1-iodobenzene [18] (109 g., 1 mol.) and magnesium (9·7 g.) in ether. The mixture was heated under reflux for 2 hr., then poured into water, and the whole acidified and filtered through a pad of kieselguhr. The ethereal layer was separated, washed with brine, and dried. After removal of the ether the residue was distilled under reduced pressure; *m*-dichlorobenzene and unchanged 2 : 4-dichloro-1-iodobenzene came over first, followed by an oil which, after redistillation, had b. p. 146°/2 mm. and solidified on treatment with ethanol. It was crystallised from ethanol and had m. p. 41—42° (Found: Cl, 48·4. $C_{12}H_6Cl_4$ requires Cl, 48·6%) (yield 7·8 g., 13%).

Absorption spectra were measured on a Unicam S.P. 500 photoelectric spectrophotometer. Inflections were confirmed photographically by Dr. G. H. Beaven by the logarithmic-cam, moving-plate method [23] but the wavelengths given in the Tables for the inflections are those obtained by direct examination of large-scale plots.

We thank Dr. G. H. Beaven for helpful discussions and for checking inflections in the spectra. We also thank the Council of Bedford College for a Postgraduate Studentship (to F. M.), the University of Aligarh for study leave (to F. M.), and the Central Research Funds Committee of the University of London for a grant (to D. M. H.) for the purchase of a spectrophotometer.

BEDFORD COLLEGE, UNIVERSITY OF LONDON. [*Received, June* 11*th*, 1957.]

[23] Holiday, *J. Sci. Instr.*, 1937, **14**, 166.