88. *The Ultra-violet Absorption Spectra of* 2 : 2'-, 2 : 4'-, 4 : 4'-*Dihydroxy diphenylmethanes,* 2 : 2'-*Dihydroxy*-5 : 5'-*dimethyldiphenylmethane and its* 3-, 4-, *and* 5-*Ring Polymers, and of* 4 : 4'-*Dihydroxydiphenylethane.*

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There is a small shift in maximum of ultra-violet light absorption towards the region of longer wave-length on passing from 2 : 2'- to 2 : 4'- and 4 : 4'-dihydroxydiphenylmethane, in agreement with similar difference for *o*- and *p*-substitution observed in the cresols and xylenols. The –CH$_2$– link gives more satisfactory " insulation " between phenolic chromophores in 4 : 4'- than in 2 : 2'-dihydroxydiphenylmethane, and the insertion of a second –CH$_2$– link, as in 4 : 4'-dihydroxydiphenylethane, further assists this. The appearance of a second band at 227 mμ. indicates, however, that even here " insulation " is not perfect. Substitution of methyl groups in the *p*-position to the hydroxyl groups in 2 : 2'-dihydroxydiphenylmethane slightly displaces the maximum to longer wave-length, and addition of a further cresol nucleus causes a smaller displacement on passing from the 2- to the 3-ring polymer of 2 : 2'-dihydroxy-5 : 5'-dimethyldiphenylmethane; addition of further cresol nuclei, in the 4- and 5-ring polymers, has however no such effect. There is a steady increment of $\varepsilon_{max.}$ of approx. 3000 for each additional aromatic ring. A solution of the " clathrate " complex of the 4-ring polymer and ethylene dichloride gives the same absorption curve as the 4-ring polymer, indicating that the origin of the complex cannot be attributed to any form of enhanced dipole association.

WITH the exception of the paper of de Boer, Houwink, and Custers (*Rec. Trav. chim.*, 1933, **52**, 710) and the later investigation of Mayer-Pitsch and Tröger (*Z. Electrochem.*, 1941, **47**, 60) little work has been published on the ultra-violet absorption spectra of resins of the phenol–formaldehyde type or their intermediate products. During an examination of the ultra-violet absorption of certain Novolak and oil-modified Novolak resins, attention was directed to the isomeric 2 : 2'- (I), 2 : 4'- (II), and 4 : 4'-dihydroxydiphenylmethanes and to 2 : 2'-dihydroxy-5 : 5'-dimethyldiphenylmethane (III ; $n = 0$) and the higher polymers of the last.

Preliminary measurements by the photographic method showed certain small and interesting differences which it was considered desirable to confirm with the Beckman spectrophotometer. The results obtained for (I), (II), (III ; $n = 0$), and the 3-, 4-, and 5-ring polymers of (III), together with those for *o*- and *p*-cresol, *m*-4- and *m*-2-xylenol, and (IV) are given in the table. The detailed ultra-violet absorption curves for some of these compounds are shown in the figure.

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Compound.	$\lambda_{max.}$ (mμ.).	$\varepsilon_{max.}$.	$\lambda_{min.}$ (mμ.).	$\varepsilon_{min.}$.
o-Cresol	274	2,015	240	71·9
m-2-Xylenol	274	1,500	241	90
p-Cresol	280	1,995	244	70
m-4-Xylenol	280·5	2,148	245·7	98·2
2 : 2′-Dihydroxydiphenylmethane	275·5	5,110	242	262·5
2 : 4′-Dihydroxydiphenylmethane	277·5	4,490	248·3	462
4 : 4′-Dihydroxydiphenylmethane	280	3,790	250·8	444
(III; $n = 0$)	284	5,400	247·3	256
(III; $n = 1$)	288·5	8,480	248·3	450
(III; $n = 2$)	288	11,800	249	727
(III; $n = 3$)	288	14,725	249	1,250
4 : 4′-Dihydroxydiphenylethane	279	3,730	246	275
	227	17,625	—	—

It will be seen that there is a small shift of the maximum to the region of longer wave-length on passing from 2 : 2′- to 4 : 4′-dihydroxydiphenylmethane, the 2 : 4′-isomer occupying an


(I.)   (II.)   (III.)

(IV.)   (V.)
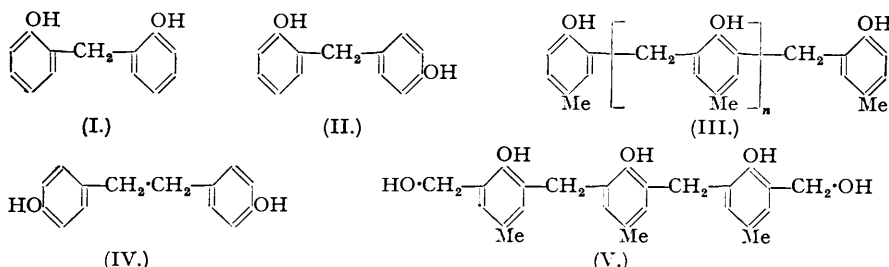
intermediate position in agreement with the similar differences for o- and p-methyl substitution in the cresols and xylenols. However, the substitution of a second methyl group in the xylenols has no effect on the wave-length of the absorption maxima of o- and p-cresol, although there is a curious and substantial drop in extinction coefficient in m-2-xylenol. This may perhaps be explained in terms of steric inhibition of resonance (cf. Braude, Jones, Koch, Richardson, Sondheimer, and Toogood, *J.*, 1949, 1890).

The $\varepsilon_{max.}$ and $\varepsilon_{min.}$ values for 2 : 2′-dihydroxydiphenylmethane, which are both greater than twice the respective values for o-cresol, show that the $-CH_2-$ link between the phenolic chromophores in the latter does not give perfect " insulation " (cf. Ramart-Lucas, *Bull. Soc. chim.*, 1932, 51, 289). Comparison of $\varepsilon_{max.}$ and $\varepsilon_{min.}$ of 4 : 4′-dihydroxydiphenylmethane with those for p-cresol shows that more satisfactory " insulation " occurs in this isomer. The insertion of a second $-CH_2-$ link between the aromatic nuclei in 4 : 4′-dihydroxydiphenylethane (IV) confers still more satisfactory " insulation " of the chromophores (Ramart-Lucas, *loc. cit.*). The appearance of the band at 227 mμ., not shown by p-cresol, indicates, however, that even here "insulation " is not perfect (cf. Braude, *J.*, 1949, 1902).

Substitution of methyl in the p-position to the hydroxyl groups in 2 : 2′-dihydroxydiphenyl-methane causes a slight displacement (7·5 mμ.) of the maximum towards the region of longer wave-length, and the addition of a further p-cresol nucleus causes a smaller displacement on passing from 2 : 2′-dihydroxy-5 : 5′-dimethyldiphenylmethane (III; $n = 0$) to the tricyclic polymer (III; $n = 1$). The addition of further aromatic nuclei in the tetra- and penta-cyclic polymers (III; $n = 2$ and 3 respectively) is unaccompanied by any further displacement of the absorption maximum which remains at 288 mμ.

There is a steady increment in $\varepsilon_{max.}$ of approximately 3000 for each additional aromatic ring in passing from 2 : 2′-dihydroxy-5 : 5′-dimethyldiphenylmethane to the 5-ring polymer, but the $\varepsilon_{max.}$ values for the cresols and m-4-xylenol are about 2000, indicating a roughly 50% increase in the probability of the relevant electronic transition. There is also an interesting rise in $\varepsilon_{min.}$ for each successive additional ring, indicating a steadily increasing probability for another transition with growth of the polymer chain.

	$\varepsilon_{max.}$.	Diff.	$\varepsilon_{min.}$.	Diff.
m-4-Xylenol	2,148	3252	98·2	157·8
(III; $n = 0$)	5,400	—	256	—
(III; $n = 1$)	8,480	3080	450	194
(III; $n = 2$)	11,800	3320	727	277
(III; $n = 3$)	14,725	2925	1250	523
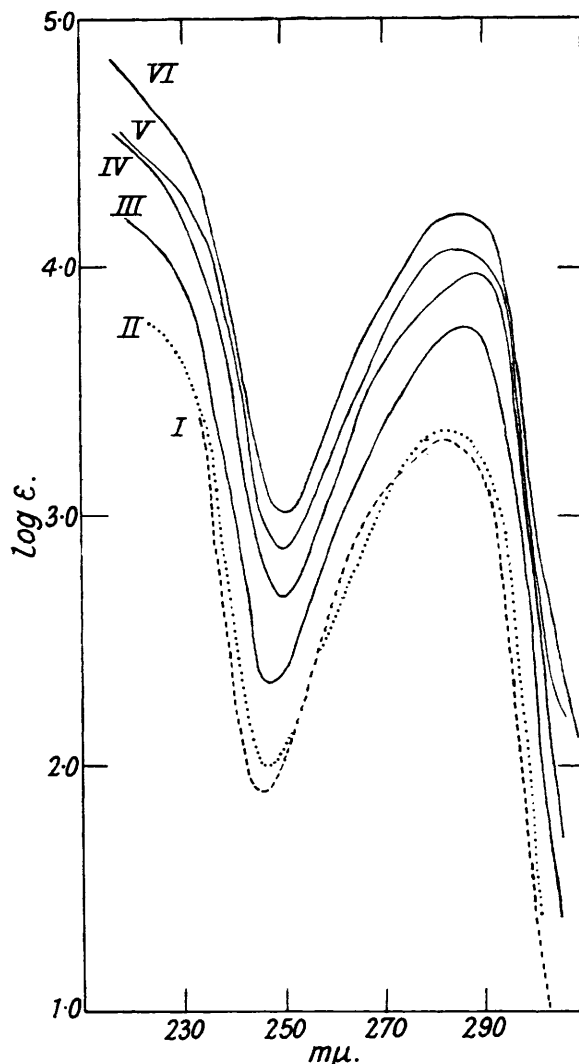
I. p-*Cresol*.   II. m-4-*Xylenol*.   III. 2 : 2′-*Dihydroxy*-5 : 5′-*dimethyldiphenylmethane*.
IV. 3-*Ring polymer*.   V. 4-*Ring polymer*.   VI. 5-*Ring polymer*.

If the values for $\varepsilon_{max.}$ and $\varepsilon_{min.}$ are plotted against the number of aromatic nuclei, there is a good approach to linearity for the former and a less satisfactory one for the latter.

While the results therefore plainly show that the series is as a first-order problem simply additive, the second-order constitutive effects are by no means negligible.

In the course of attempts to purify the 4-ring polymer (III; $n = 2$) by recrystallisation from ethylene dichloride the formation was observed of an extraordinary stable crystalline 1 : 1-addition complex of this compound with the solvent which survived heating to 90° in a high vacuum (molecular distillation conditions). The ultra-violet absorption spectrum of a solution of the addition complex gave the same curve as the 4-ring polymer when molecular extinction coefficients were calculated on the basis of a 1 : 1 mol. ratio of the latter to ethylene dichloride : $\lambda_{max.}$, 288 mμ.; $\varepsilon_{max.}$, 9740; $\lambda_{min.}$, 249 mμ.; $\varepsilon_{min.}$, 572. The origin of the addition complex is therefore not attributable to any form of enhanced dipole association (cf. Hunter, Qureishy, and Samuel, *J.*, 1936, 1576) and it seems probable that this is a further example of the " clathrate " compounds described by Powell (*J.*, 1948, 61).

A molecular model of the 4-ring polymer based on accepted van der Waals radii showed that an ethylene dichloride molecule could be inserted under the more compact configuration of

the polymer. This may also explain the ease of crystallisation from ethylene dichloride in the form of the addition complex in contrast to the difficulty experienced with other solvents.

The properties of the pentacyclic polymer (III; $n = 3$) obtained by condensation of the tricyclic *bishydroxymethyl* derivative (V) with *p*-cresol do not agree with those described by Koebner (*Angew. Chem.*, 1933, **46**, 251) for the " pure " substance obtained by treating 4-methyl-2 : 6-bishydroxymethylphenol with 2 : 2′-dihydroxy-5 : 5′-dimethyldiphenylmethane ; no analysis was, however, given by him. The ultra-violet absorption spectrum of our specimen, which was purified by " molecular " distillation and gave satisfactory analytical data, therefore provides confirmation of its constitution.

It may be noted that the ultra-violet absorption spectrum of the tricyclic polymer (III; $n = 1$) also fails to support the inherently improbable formula suggested by Niederl and McCoy (*J. Amer. Chem. Soc.*, 1943, **65**, 629) for this compound.

<div align="center">EXPERIMENTAL.</div>

Materials [with A. T. CARPENTER].—The specimens of *o*- and *p*-cresol, *m*-4- and *m*-2-xylenol were obtained from the Chemical Research Laboratory, Teddington. *o*- and *p*-Cresol were further purified by distillation under reduced pressure at room temperature (*ca.* 1 mm.), and the *m*-2-xylenol was subjected to 5 recrystallisations from light petroleum (b. p. 80—100°). In view of the low extinction coefficient of the latter ($\lambda_{max.} = 273$ mμ; $\varepsilon_{max.} = 1460$), a new and larger specimen was prepared from *m*-2-xylidine as follows. *m*-2-Xylidine (15 g.) in dilute sulphuric acid (15 g. in 450 c.c. of water) was cooled and gradually treated with sodium nitrite (10 g. in 20 c.c. of water). The mixture was heated on a steam-bath until evolution of nitrogen ceased and then distilled in steam, and the distillate was extracted with light petroleum (b. p. 40—60°) [yield 60% (crude)]. After several recrystallisations from light petroleum, *m*-2-xylenol was obtained in needles which had m. p. 47—48° after prolonged drying in a vacuum. The extinction coefficient of this specimen was only slightly higher than that of the original ($\lambda_{max.} = 274$ mμ.; $\varepsilon_{max.} = 1500$). The 2 : 2′-, 2 : 4′-, and 4 : 4′-dihydroxydiphenylmethane had m. p. 118—119·5°, 118—119°, and 162—163° respectively. The tricyclic polymer (III; $n = 1$) was prepared as described by Koebner (*loc. cit.*) and had m. p. 212—214°.

Tetracyclic Polymer.—Attempts to prepare this from 2 : 2′-dihydroxy-5 : 5′-dimethyldiphenylmethane and formaldehyde in acetic acid following Koebner, and also from a 10 : 1 mixture of these reactants in the presence of hydrochloric acid, led to unsatisfactory results. It was finally prepared by condensation of 2 : 2′-dihydroxy-5 : 5′-dimethyl-3 : 3′-bishydroxymethyldiphenylmethane (m. p. 146—147·5°) with excess of *p*-cresol as follows. A mixture of the dialcohol (10 g.), *p*-cresol (88 g.), and concentrated hydrochloric acid (8 c.c.) was heated on a water-bath for 2 hours, distilled in steam to remove excess of cresol, and dissolved in benzene (200 c.c.), and the crude polymer (9·7 g.; m. p. 172—178°) precipitated with light petroleum. The mother-liquors furnished a further 0·9 g. (m. p. 173—177°), the total yield being 65%. On recrystallisation from ethylene dichloride, the addition *complex* was obtained in hexagonal plates, m. p. 177—179° (Found : C, 69·7; H, 6·3; Cl, 13·2. $C_{31}H_{32}O_4,C_2H_4Cl_2$ requires C, 68·9; H, 6·3; Cl, 12·5%). The polymer was obtained from this by recrystallisation from benzene and heating of the product (m. p. 177—179° after sintering at 176°) in the " molecular " still at 170°. This specimen, which was used for the spectroscopical measurements, melted at 185—188° (Found : C, 80·2; H, 6·9. Calc. for $C_{31}H_{32}O_4$: C, 79·5; H, 6·8%). When the addition complex was heated in the " molecular " still at 170°, the loss in weight corresponded approx. to the loss of a molecular proportion of ethylene dichloride. Microscopic examination of the product showed that this had the same crystal habit as the complex but that the crystals had become opaque.

Pentacyclic Polymer.—An attempt to prepare this from 4-methyl-2 : 6-bishydroxymethylphenol and 2 : 2′-dihydroxy-5 : 5′-dimethyldiphenylmethane in glacial acetic acid in the presence of alcoholic hydrochloric acid following the directions of Koebner gave only a resinous product, which became brown but was unmelted at 260°. It is difficult to see how Koebner's preparation could lead to substantial amounts of the pentacyclic polymer since the proportions of reactants would be expected to give rise to a tricyclic derivative with a free active position available for further self-condensation. The pentacyclic polymer was finally prepared as follows. A mixture of the tricyclic bishydroxymethyl derivative (Zinke and Hanus, *Ber.*, 1941, **74**, 205) (5·25 g.), *p*-cresol (40 g.), and concentrated hydrochloric acid (5 c.c.) was heated on a water-bath for 2 hours (whereafter absence of free *o*-hydroxymethyl groups was inferred from the ferric chloride test), and excess of cresol removed by distillation in steam. The white amorphous material thus obtained was dissolved in benzene and precipitated with light petroleum. The product (6·5 g.) could not be crystallised from the usual solvents and was therefore purified by molecular distillation, after being subjected to preliminary degassing at 110°. The pentacyclic *polymer* distilled at 170—190°, furnishing a substance which sintered at 94—104° and melted at 112° [Found : C, 79·2; H, 6·7; *M* (Rast), 564, 569. $C_{39}H_{40}O_5$ requires C, 79·6; H, 6·8; *M*, 588].

The 4 : 4′-dihydroxydiphenylethane was prepared by Clemmensen reduction of anisoin and subsequent demethylation (Richardson and Reid, *J. Amer. Chem. Soc.*, 1940, **72**, 413) and had m. p. 198—199°.

Spectroscopic Measurements.—The spectroscopic determinations were carried out on ethyl-alcoholic solutions of the compounds. The absorption curves were first plotted from measurements made by the photographic technique, using an iron–nickel arc and a sector photometer. All the quantitative determinations of maxima and minima were checked using fresh solutions on the Beckman photo-electric instrument with 1-cm. layers of alcoholic solution.

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