316. *The Structure of Cyclotriveratrylene* (10,15-*Dihydro*-2,3,7,8,12,13-*hexamethoxy*-5H-*tribenzo*[a,d,g]*cyclononene*) *and Related Compounds*

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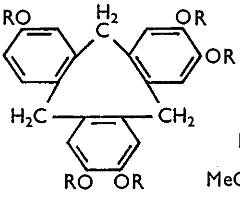
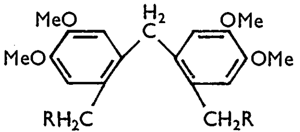
The product of condensation of veratrole and formaldehyde under acid conditions is shown to be a cyclic trimer possessing a novel ring system (I; R = Me). Three general methods of preparing this compound and its analogues are examined and their trimeric nature is established. Certain aspects of the stereochemical conformation of cyclotriveratrylene are discussed.

THE exact structure of the crystalline product $[C_9H_{10}O_2]_n$, m. p. 234°, obtained by condensation of veratrole with formaldehyde in the presence of acids has been in question for some time. This Paper reports chemical evidence and molecular-weight determinations which establish that the condensation product is a cyclic trimer ($n = 3$) of structure (I; R = Me), which for convenience has been named "cyclotriveratrylene."[1] The parent hydrocarbon has similarly been named "cyclotribenzylene" (II) and numbered as shown.

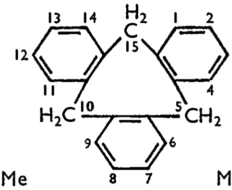
Robinson concluded[2] that the condensation product was 2,3,6,7-tetramethoxy-9,10-dihydroanthracene ($n = 2$), and this structure has been widely accepted in the literature.[3,4] More recent studies by Oliverio and Casinovi and their colleagues[5] have unequivocably established that the product does not possess the dihydroanthracene structure and therefore n must be greater than 2. Their conclusion was based on the following observations: (i) the properties of the condensation product differ from those of 2,3,6,7-tetramethoxy-9,10-dihydroanthracene prepared by an unambiguous route;[6] (ii) although 2,3,6,7-tetramethoxy-9-anthrone is readily oxidised to the corresponding anthraquinone in good yield,[7] oxidation of the $[C_9H_{10}O_2]_n$ product yields a crystalline monoketone, $C_{27}H_{28}O_7$, with only trace amounts of 2,3,6,7-tetramethoxyanthraquinone. Clemmensen reduction of the monoketone leads to substantial regeneration of (I);[5] (iii) 6-(3,4-dimethoxybenzyl)-3,3′,4,4′-tetramethoxydiphenylmethane reacts with formaldehyde in 70% sulphuric acid to give an almost quantitative yield of (I; R = Me).[5]



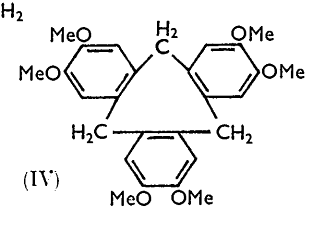
(I)



(III)



(II)



(IV)

Taking cognisance of observation (iii) above and Robinson's report that 3,3′,4,4′-tetramethoxydiphenylmethane reacted with formaldehyde and sulphuric acid to give (I; R = Me) Oliverio and Casinovi concluded that the condensation product was a hexamer ($n = 6$). It was claimed[5] that this structure was supported by *X*-ray crystallography and by the

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[1] Lindsey, *Chem. and Ind.*, 1963, 823.

[2] G. M. Robinson, *J.*, 1915, **107**, 267.

[3] Gadamer, *Arch. Pharm.*, 1915, 253, 274; Bhagwat, Moore, and Pyman, *J.*, 1931, 443; Carre and Lieberman, *Compt. rend.*, 1934, **199**, 791; *Bull. Soc. chim. France*, 1935, 291; Fletcher and Bogert, *J. Org. Chem.*, 1939, **4**, 71; Bide and Wilkinson, *J. Soc. Chem. Ind.*, 1945, 84; Tsatsas, *Compt. rend.*, 1951, **232**, 530.

[4] Mel'nikov and Prilutskaya, *J. Gen. Chem.* (*U.S.S.R.*), 1959, **29**, 3704.

[5] Oliverio and Casinovi, *Ann. Chim.* (*Italy*), 1952, **42**, 168; Bertinotti, Carelli, Liquori, and Nardi, *Ricerca Sci.*, *Suppl.*, 1952, **22**, 65.

[6] Casinovi and Oliverio, *Ann. Chim.* (*Italy*), 1956, **46**, 929.

[7] Vanzetti and Oliverio, *Gazzetta*, 1930, **60**, 620.

calculated weight of the molecular asymmetric unit (925) in the unit cell derived from the *X*-ray-crystallographic data. However, our work shows this value is in error by a factor of 2 (making allowance for the presence of benzene of crystallisation). No direct measurement of the molecular weight of the compound was reported in these Papers.[5]

During the course of our studies of the polycondensation products of *o*- and *p*-diacetoxy- and -dimethoxy-benzenes with formaldehyde [8] it was observed that veratrole in the presence of hydrochloric acid yielded three crystalline products. The main products were cyclotriveratrylene (I; R = Me), and 6,6′-bischloromethyl-3,3′,4,4′-tetramethoxydiphenylmethane (III; R = Cl) together with a small amount of 4,5-bischloromethylveratrole. The structures of the last two named compounds were confirmed by hydrogenolysis to their respective dimethyl derivatives which were directly compared with authentic specimens.

A direct comparison of the ultraviolet and infrared absorption spectra of the products of reaction of veratrole and formaldehyde in (*a*) sulphuric acid and (*b*) hydrochloric acid, and (*c*) the product of acid dehydration of 2-(3,4-dimethoxybenzyl alcohol, established that the condensation compounds studied by Robinson,[2] by Oliverio and his co-workers,[5,9] and in the present work were identical. These comparisons also support the orientation of the methylene bridges in compound (I; R = Me) with respect to the methoxyl groups. Similarly our measured ultraviolet spectrum of the monoketone (IV) was closely similar to that reported in the earlier work.[5,9]

Molecular-weight determinations of chromatographically purified cyclotriveratrylene and of its derived monoketone were made using the Rast, Menzies, and vapour pressure osmometric methods.[10] Values close to those calculated for the cyclic trimeric structures were obtained. The majority of measurements were made using the last-named method. Benzene, used initially as solvent for this method, gave erratic results and chloroform was preferred. Both cyclotriveratrylene and the derived monoketone, on crystallisation from benzene readily occluded this solvent, which could be removed completely only by heating the solid under vacuum. Similar formation of occlusion compounds has been reported for other types of cyclic structures such as tri-*o*-thymotide [11] and the *p*-cresol novolac tetramer.[12]

Further compelling evidence for the trimeric cyclic structure was provided by the observation that condensation of 6,6′-bischloromethyl-3,3′,4,4′-tetramethoxydiphenylmethane with an equimolecular amount of veratrole afforded cyclotriveratrylene in good yield. Replacement of veratrole in this experiment by 2-methylanisole, 2-ethoxyanisole, and 1,2-diethoxybenzene, respectively, gave the corresponding unsymmetrically substituted cyclotribenzylenes, all of which had measured molecular weights close to the expected values. This condensation is clearly of general applicability to the preparation of similar substituted analogues of this carbocyclic system.

Demethylation of cyclotriveratrylene afforded the hexahydroxycyclotribenzylene (I; R = H) readily characterised as the hexa-acetate. Silver oxide oxidation of the hexaol under mild conditions gave an unstable yellow compound which was very readily converted into an insoluble polymer, the infrared absorption spectrum of which indicated the presence of *ortho*-quinone groupings (bands at 1730 and 1664 cm.$^{-1}$).[13]

We have not been able to confirm Robinson's observation [2] that 3,3′,4,4′-tetramethoxydiphenylmethane reacts with formaldehyde to give dihydrotetramethoxyanthracene, although it is clear that cyclotriveratrylene cannot be prepared by this route. Thus, we examined the reaction of the chromatographically purified diphenylmethane with formaldehyde in the presence of concentrated sulphuric acid. Only polymer gels from which

[8] Hunt and Lindsey, *J.*, 1962, 1730, 4550.

[9] Arcoleo and Garofano, *Ann. Chim.* (*Italy*), 1956, **46**, 934.

[10] Brady, Huff, and McBain, *J. Phys. Colloid Chem.*, 1951, **55**, 304; see also *The Laboratory*, 1960, **28**, 142.

[11] Baker, Gilbert, and Ollis, *J.*, 1952, 443.

[12] Hunter, Morton, and Carpenter, *J.*, 1950, 441.

[13] Otting and Staiger, *Chem. Ber.*, 1955, **88**. 828.

could be extracted no material soluble in hot benzene were obtained. When acetic acid was used as solvent in this reaction substantial conversion to the diacetate (III; R = OAc) occurred. This reaction is similar to those reported by Vansheidt and co-workers.[14] In concentrated sulphuric acid in the absence of formaldehyde the diphenylmethane was apparently sulphonated quite rapidly.[15] The instability of the diphenylmethane in the presence of sulphuric acid was also confirmed by plotting changes in its ultraviolet absorption spectrum against time. It is noteworthy that many of the compounds described in this Paper give characteristic colorations when dissolved in sulphuric acid.

Three general methods are available for the synthesis of substituted cyclotribenzylenes: (i) the reaction of 1,2-disubstituted benzenes with 3,3′,4,4′-tetra-alkoxy-6,6′-bischloromethyldiphenylmethanes, (ii) the condensation of suitable 1,2-disubstituted benzenes with formaldehyde in the presence of 70% sulphuric acid; (iii) the condensation of 3,4-disubstituted benzyl alcohols or halides. Method (i) has already been discussed above, but the other two methods require further consideration since the structures of products obtained by their application have not been clearly established in the literature. Where either chloral hydrate or acetaldehyde replaces formaldehyde in method (ii), cyclic trimers do not appear to be formed but usually substantial amounts of the corresponding substituted dihydroanthracenes appear, together with other products.[16,17] Crystalline condensation products have been obtained from methylenedioxybenzene, 2-ethoxyanisole, and 1,2-diethoxy- and 1,2-dibutoxy-benzenes by application of method (ii), and from 3,4-diethoxybenzyl chloride by method (iii). In the case of the methylenedioxybenzene product a dealkylation-remethylation procedure [18] converted it directly into cyclotriveratrylene, thus establishing the cyclotribenzylene structure. Molecular-weight determinations and comparison of the physical (ultraviolet absorption spectra) and chemical (oxidation to monoketone) properties of the condensation products of 2-ethoxyanisole and of 1,2-diethoxybenzene with those of cyclotriveratrylene offer good evidence in support of a cyclotribenzylene ring system. Three orientational isomers are possible in the case of the compound derived from 2-ethoxyanisole, but establishment of the orientation of the compound examined in the present work was not attempted. The structures of the compounds derived from 1,2-dibutoxybenzene [19] and from 3,4-diethoxybenzyl chloride [4] still remain in doubt. The high melting point (270°) of the latter product differentiates it from the hexaethoxycyclotribenzylene (m. p. 145°) already described. On the other hand, it does not correspond to 2,3,6,7-tetraethoxy-9,10-dihydroanthracene [18] (m. p. 220°). It may possibly be the corresponding tetraethoxyanthracene [18] (m. p. 264°), or a stereoisomer.

A consideration of the stereochemistry of cyclotriveratrylene may now be made. The foregoing work establishes that cyclotriveratrylene possesses a completely novel carbon ring system, consisting of a cyclononatriene ring to which are separately fused three benzene rings carrying methoxyl substituents. The parent ring system, cyclotribenzylene, can, in theory, adopt two possible conformations which correspond to the " crown " and " saddle " conformations of the cyclononatriene ring. Examination of Fisher–Hirschfelder–Taylor molecular models of cyclotribenzylene leads to two important conclusions: firstly, steric requirements favour the " crown " conformation of the cyclononatriene ring and in consequence the molecular structure will be essentially pyramidal, the aromatic rings forming three sides of the pyramid and the methylene hydrogens lying close together at the apex. The alternative " saddle " conformation would be possible however if distortion of the methylene C–H bonds from the normal tetrahedral valency angles occurred. However, in cyclononatriene itself the " saddle " conformation is

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[14] Vansheidt, Mel'nikova, and Gladkovski, *Vysokomol. Soedineniya*, 1962, **4**, 1178, 1303.

[15] Cf. Gillespie and Leisten, *Quart. Rev.*, 1954, **8**, 65.

[16] Arcoleo, Werber, and Lombardo, *Ann. Chim.* (*Italy*), 1960, **50**, 1242.

[17] Garofano and Oliverio, *Ann. Chim.* (*Italy*), 1957, **47**, 876.

[18] Garofano, *Ann. Chim.* (*Italy*), 1958, **48**, 125.

[19] Hughes and Lions, *J. Proc. Roy. Soc., New South Wales*, 1938, **71**, 103.

considered[20] to be the less stable of the two alternatives. It may also be noted that in cyclotriveratrylene the nuclear hydrogen atoms *ortho* to the methylene bridges introduce further steric constraints unfavourable to the " saddle " conformation for this molecule.

On the basis of the crown conformation the following approximate interatomic and inter-ring distances have been calculated: *ortho*-nuclear-H–*ortho*-nuclear-H, 2·36 Å; *ortho*-nuclear-H–methylene-H, 2·58 Å; oxygen–oxygen, 5·90, 7·62, and 9·36 Å; ring centre–ring centre, 4·77 Å. Scaled measurements taken from a molecular model were in general agreement with these values.

The ultraviolet absorption spectrum of cyclotriveratrylene in hexane consists of three band systems with maxima at 2050, 2335, and 2918 Å. These bands exhibit bathochromic and hypsochromic shifts with respect to the corresponding absorption bands of the monomeric and dimeric units (*i.e.*, 4,5-dimethylveratrole and 3,3′,4,4′-tetramethoxy-6,6′-dimethyldiphenylmethane). This behaviour is consistent with the proposed structure of cyclotriveratrylene and is analogous to that observed in the paracyclophane series.[21,22] A more detailed consideration of the electronic spectra of these and related linked π-electron systems is made elsewhere.[23]

The proton magnetic resonance spectrum of cyclotriveratrylene supports the " crown " conformation.[20,22] Thus, at room temperature the spectrum of a deuterochloroform solution of cyclotriveratrylene exhibited three signals with chemical shift values of 3·22, 5·48, and 6·16 τ, arising from ring, methylene bridge, and methyl hydrogens, respectively. After cyclotriveratrylene had been heated at 200°, its resonance spectrum showed no evidence of inversion of the conformation nor of the presence of other forms.[24]

The spectroscopic properties of the monoketone (IV) are also of interest in relation to the structure of cyclotriveratrylene. Thus, the close similarity of the ultraviolet absorption spectra of the ketone and of 3,3′,4,4′-tetramethoxy-6,6′-dimethylbenzophenone confirm that the chromophoric systems are similar. Examination of the infrared carbonyl bands of these compounds, both as solids and in solution, reveals a marked shift to longer wavelengths in comparison to benzophenone. The wavelength at which a ketonic carbonyl group absorbs in the infrared is known to be dependent on inductive, conjugative, and ring-strain effects.[25,26] Thus, electron-donating substituents, increase in aryl conjugation, and increase in ring-size can all, independently, cause a shift to longer wavelengths. The results of these effects are evident in the series acetophenone (1692 cm.$^{-1}$), benzophenone (1669 cm.$^{-1}$), 3,3′,4,4′-tetramethoxy-6,6′-dimethylbenzophenone (1654 cm.$^{-1}$), and the monoketone (IV) (1630 cm.$^{-1}$), all measured in carbon tetrachloride or chloroform solution. From the data available at present it is not possible to evaluate the relative importance of these effects. In general terms, however, the spectroscopic measurements reported here are consistent with the proposed structure of cyclotriveratrylene.

EXPERIMENTAL

Microanalyses were carried out by the Microanalytical Section of this Laboratory. Ultraviolet absorption spectra of compounds in ethanolic solution (except where stated) were measured by means of the Optica CF4 double-beam recording spectrophotometer. Infrared absorption spectra of solids dispersed in potassium chloride discs were measured on a Grubb–Parsons G.S.3 double-beam grating instrument; both strong and medium bands are reported, these being correct to ±3 cm.$^{-1}$ except those above 2700 cm.$^{-1}$ which are correct to ±5 cm.$^{-1}$.

Molecular weights of compounds in chloroform solution were determined by means of the Mechrolab vapour pressure osmometer[10] (designated M(VPO)). In some cases the Rast (camphor) and Menzies (benzene) methods were used. Light petroleum had b. p. 60—80°,

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[20] Boikess and Winstein, *J. Amer. Chem. Soc.*, 1963, **85**, 343.

[21] Cram, Allinger, and Steinberg, *J. Amer. Chem. Soc.*, 1954, **76**, 6132.

[22] Cf. Untch, *J. Amer. Chem. Soc.*, 1963, **85**, 345, 346.

[23] Lindsey, *Spectrochim. Acta* (in preparation).

[24] Cookson, private communication.

[25] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, 1958, p. 137.

[26] Cook, *Canad. J. Chem.*, 1961, **39**, 31 (a referee kindly drew attention to this Paper).

except where indicated. The proton resonance spectrum was measured on an Associated Electrical Industries RS2 spectrometer operating at 60 Mc./sec.

Chloromethylation of Veratrole.—Veratrole (50 g.) was added gradually to a stirred mixture of aqueous formaldehyde (200 ml.; 38%) and concentrated hydrochloric acid (270 ml.) at 0° previously saturated with hydrogen chloride at 0°. Within 30 min. the mixture became pasty. After stirring for 4 hr. at room temperature, the solid product, recovered by filtration, was washed with ice-cold water, dried (desiccator), and, on recrystallisation from benzene, yielded 10,15-*dihydro*-2,3,7,8,12,13-*hexamethoxy*-5H-*tribenzo*[a,d,g]*cyclononene*(*cyclotriveratrylene*) (I; R = Me) (11·2 g.), m. p. 234° (Found: C, 72·0; H, 6·8%; *M* (Rast), 444, 472; (Menzies) 457, (VPO) 451, 454. $C_{27}H_{30}O_6$ requires C, 72·0; H, 6·7%; *M*, 451), $\lambda_{max.}$ 205, 233, and 292 mμ (log ε 4·82, 4·49, and 3·99), $\nu_{max.}$ 2970, 2915, 2825, 1605, 1508, 1460, 1447, 1390, 1346, 1315, 1260, 1220, 1190, 1142, 1085, 1025, 990, 948, 923, 877, 847, 738, 675, and 614 cm.$^{-1}$.

Concentration of the mother-liquors afforded 6,6′-*bischloromethyl*-3,3′,4,4′-*tetramethoxydiphenylmethane* (III; R = Cl) (31 g.), m. p. 130° (from benzene–light petroleum) (Found: C, 59·1; H, 5·9; Cl, 18·1. $C_{19}H_{22}Cl_2O_4$ requires C, 59·2; H, 5·8; Cl, 18·4%), $\nu_{max.}$ 3000, 2955, 2940, 2915, 2850, 2840, 1610, 1584, 1521, 1464, 1450, 1392, 1361, 1310, 1274, 1260, 1225, 1210, 1196, 1144, 1124, 1100, 1036, 1002, 920, 886, 784, 867, 827, 749, 736, 705, 678, 673, and 614 cm.$^{-1}$.

Treatment of the bischloromethyl compound with sodium acetate in acetic acid yielded the *bisacetoxymethyl derivative* as soft needles, m. p. 94—95° (from ethanol) (Found: C, 64·1; H, 6·5. $C_{23}H_{28}O_8$ requires C, 63·9; H, 6·5%).

The mother-liquors from the crystallisation of the bischloromethyltetramethoxydiphenylmethane above, were adsorbed on to a column of alumina. Elution with benzene–light petroleum (1 : 1) afforded crystalline material (3·3 g.) which, on further recrystallisation from light petroleum, gave 4,5-bischloromethylveratrole, m. p. 87° (Found: C, 51·4; H, 5·2; Cl, 29·9. $C_{10}H_{12}Cl_2O_2$ requires C, 51·1; H, 5·1; Cl, 30·2%).

Hydrogenolysis of 4,5-*Bischloromethylveratrole*.—The veratrole (280 mg.) in AnalaR ethyl acetate (80 ml.) was shaken with palladised charcoal (100 mg.; 10%) and anhydrous potassium carbonate (100 mg.) under hydrogen until no more gas was taken up. The product, recovered in the usual way, was purified by filtration through alumina and, after recrystallisation from light petroleum (b. p. 40—60°), afforded 4,5-dimethylveratrole (190 mg.), m. p. 43—44°, identified by mixed m. p. and infrared spectrum.

Hydrogenolysis of 6,6′-*Bischloromethyl*-3,3′,4,4′-*tetramethoxydiphenylmethane*.—In a similar way hydrogenolysis of the diphenylmethane (III; R = Cl) gave an almost quantitative yield of 3,3′,4,4′-tetramethoxy-6,6′-dimethyldiphenylmethane (III; R = H), m. p. 122—123°, identified by m. p., mixed m. p., infrared spectrum and elemental analysis with an authentic specimen (see below).

4,5-*Dimethylveratrole*.—6-Amino-3,4-dimethylphenol (5 g.) was oxidised [27] to 3,4-dimethyl-1,2-benzoquinone (2·2 g.). The *ortho*-quinone (2·2 g.) in AnalaR ethyl acetate was shaken with palladised charcoal (1 g.; 10%) under hydrogen until no further absorption occurred. The product, 3,4-dimethylcatechol, was rather susceptible to aerial oxidation, and the solvent was therefore evaporated *in vacuo*.

The recovered dimethylcatechol, in methanol (30 ml.) and dimethyl sulphate (10 g.), was cooled in an ice-bath and potassium hydroxide (6 g.) in water (10 ml.) was added down the reflux condenser. Addition of saturated brine and ether extraction led to recovery of the oily dimethylveratrole, which was purified by passing the solution in light petroleum (b. p. 40—60°) through alumina. 4,5-Dimethylveratrole (1·81 g.) crystallised from the same solvent as needles, m. p. 43—44° (lit.,[28] 43·5°) (Found: C, 72·4; H, 8·5. Calc. for $C_{10}H_{14}O_2$: C, 72·3; H, 8·5%), $\nu_{max.}$ 2980, 2950, 2940, 2845, 1605, 1517, 1464, 1446, 1388, 1332, 1263, 1217, 1197, 1190, 1175, 1149, 1104, 1036, 1010, 996, 854, 828, 730, and 625 cm.$^{-1}$.

Cyclotriveratrylene Prepared by Alternative Routes.—Cyclotriveratrylene was also prepared (*a*) by warming a solution of 3,4-dimethoxybenzyl alcohol in glacial acetic acid containing a few drops of concentrated sulphuric acid (yield, 87%), and (*b*) by reacting veratrole with formaldehyde in 70% sulphuric acid at 0° (yield, 21%). Both products had m. p. 234° (from benzene) and were identical to each other and to the product obtained by chloromethylation of veratrole.

3,3′,4,4′-*Tetramethoxy*-6,6′-*dimethyldiphenylmethane*.—4-Methylveratrole (2 g.) was warmed

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[27] Bardos, Olsen, and Enkoji, *J. Amer. Chem. Soc.*, 1957, **79**, 4704.

[28] Karrer and Schick, *Helv. Chim. Acta*, 1943, **26**, 800.

(40°) with 40% aqueous formaldehyde (20 ml.) and concentrated hydrochloric acid (20 ml.) for 30 min. and set aside at room temperature for 16 hr. The product was crystallised several times from ethanol to give the *diphenylmethane* (III; R = H) (1·1 g.) as colourless prisms, m. p. 122—123° (Found: C, 72·0; H, 7·6. $C_{19}H_{24}O_4$ requires C, 72·1; H, 7·6%), $\nu_{max.}$ 2995, 2953, 2920, 2835, 1600, 1583, 1512, 1457, 1442, 1390, 1330, 1306, 1252, 1212, 1198, 1184, 1155, 1100, 1086, 1035, 998, 990, 939, 888, 877, 856, 834, 765, and 735 cm.$^{-1}$.

Demethylation of Cyclotriveratrylene.—Cyclotriveratrylene (2·0 g.) in anhydrous benzene (150 ml.) was treated with boron tribromide (3 ml.) at room temperature, and the mixture refluxed for 2 hr. After cooling, water (50 ml.) was added, and undissolved solid recovered by filtration. After washing with cold water the solid was recrystallised from water containing a little ethanol to give 10,15-*dihydro*-2,3,7,8,12,13-*hexahydroxy*-5H-*tribenzo*[a,d,g]*cyclononene* (I; R = H) as small colourless prisms, m. p. 375° (decomp.) (Found: C, 68·9; H, 5·1. $C_{21}H_{18}O_6$ requires C, 68·8; H, 4·95%), $\nu_{max.}$ 3360 (broad), 3180, 3070, 2980, 2910, 2860, 1601, 1513, 1473, 1439, *ca.* 1376, *ca.* 1350, 1334, 1280, 1243, 1193, 1168, 1125, 1010, 935, 908, 882, 851, 787, 745, 699, and 614 cm.$^{-1}$. In ethanol the hexaol gave a deep blue-green coloration with neutral ferric chloride solution.

Treatment with acetic anhydride and pyridine gave the *hexa-acetate* as soft needles, m. p. 323—324° (from dioxan–ethanol) (Found: C, 64·0; H, 5·0; Ac, 41·8. $C_{33}H_{30}O_{12}$ requires C, 64·0; H, 4·9; Ac, 41·8%).

Oxidation of the Hexaol (I; R = H).—The hexaol (250 mg.), in anhydrous methanol (50 ml.) to which had been added silver oxide (2 g.) and anhydrous sodium sulphate (200 mg.), was gently refluxed under nitrogen for 4 hr. After filtration, the deep yellow solution was evaporated under vacuum to give a dark brown polymer (130 mg.), infusible when heated to 400°, but decomposing when subjected to a plunge m. p. at 350° (Found: C, 62·2; H, 4·6%), $\nu_{max.}$ 3330 (broad), 2980, 2930, 2900, 1730w, 1664, 1635, 1606, 1500, 1480, 1444, 1370, 1356, 1285, 1250, 1175, 1130, 1070, 1010, 934, 885, 854, 745, 704, and 614 cm.$^{-1}$.

Oxidation of 3,3′,4,4′-*Tetramethoxy*-6,6′-*dimethyldiphenylmethane.*—Chromium trioxide (55 mg.) dissolved in AnalaR acetic acid (10 ml.) and water (1 ml.) was added to a solution of the diphenylmethane (III; R = H) (250 mg.) in AnalaR acetic acid (7 ml.) and left at room temperature for 18 hr. The mixture was poured into water (50 ml.) and after 3 hr. the pale yellow crystalline solid was filtered off. The product, dissolved in benzene–ether (1 : 1), was chromatographed on alumina, the main fraction being eluted with ether. The material recovered from the ethereal eluate crystallised from light petroleum (b. p. 80—100°) to give 3,3′,4,4′-*tetramethoxy*-6,6′-*dimethyldiphenyl ketone* (120 mg.) as clusters of pale yellow needles, m. p. 156—157° (Found: C, 69·4; H, 6·8. $C_{19}H_{22}O_5$ requires C, 69·1; H, 6·7%), $\lambda_{max.}$ 204, 235, 284, and 322 mμ (log ε 4·55, 4·37, 3·98, and 4·01), $\nu_{max.}$ 3012, 2967, 2941, 2849, 2745, 2610, 1649, 1605, 1570, 1515, 1457, 1446, 1387, 1348, 1279, 1258, 1221, 1202, 1192, 1135, 1076, 1036, 1000, 968, 952, 943, 897, 885, 876, 867, 853, 834, 800, and 690 cm.$^{-1}$. The compound gave no coloration with Schiff's reagent, nor did it cause effervescence in aqueous sodium hydrogen carbonate.

10,15-*Dihydro*,2,3,7,8,12,13-*hexamethoxy*-5H-*tribenzo*[a,d,g]*cyclononen*-5-*one* (IV).—This *ketone* was prepared by the reported method [5] and crystallised from benzene as colourless prisms, m. p. 213—214° (Found: C, 69·8; H, 6·1%; *M* (Rast), 459, 469; (VPO) 465. $C_{27}H_{28}O_7$ requires C, 69·8; H, 6·1%; *M*, 464·5), $\lambda_{max.}$ 206, 240, 286, and 326 mμ (log ε 4·81, 4·51, 4·15, and 4·16), $\nu_{max.}$ 2990, 2954, 2930, 2904, 2830, 1628, 1600, 1584, 1517, 1468, 1443, 1406, 1366, 1340, 1289, 1266, 1230, 1220, 1192, 1163, 1126, 1099, 1076, 1042, 1020, 990, 939, 884, 870, 854, 801, 767, 738, and 571 cm.$^{-1}$. With concentrated sulphuric acid the ketone gave a deep orange coloration.

The 2,4-*dinitrophenylhydrazone*, prepared by refluxing the ketone with Brady's reagent for 42 hr., had m. p. 223—224° (from ethanol–ethyl acetate) (Found: C, 61·3; H, 5·25; N, 8·8. $C_{33}H_{32}N_4O_{10}$ requires C, 61·5; H, 5·0; N, 8·7%).

3,3′,4,4′-*Tetramethoxydiphenylmethane.*—This was prepared by reaction of formaldehyde with veratrole,[5] and was purified first by distillation (b. p. 240—260°/1 mm.) and then by chromatography in benzene–light petroleum (1 : 1) on an alumina column. Recrystallisation from light petroleum gave 3,3′,4,4′-tetramethoxydiphenylmethane as needles, m. p. 74° (Found: C, 70·8; H, 7·0%; *M* (VPO), 293. Calc. for $C_{17}H_{20}O_4$: C, 70·8; H, 7·0%; *M*, 288), $\lambda_{max.}$ (hexane) 204, 230, and 282 mμ (log ε 4·78, 4·20, and 3·79), $\nu_{max.}$ 3010, 2965, 2935, 2890, 2840, 1604, 1587, 1514, 1468, 1448, 1418, 1343, 1330, 1292, 1274, 1263, 1240, 1201, 1187, 1153, 1134, 1024, 960, 933, 916, 907, 851, 815, 800, 769, 746, 720, and 638 cm.$^{-1}$.

Reaction of 3,3′,4,4′-*Tetramethoxydiphenylmethane with Formaldehyde.*—Using chromatographically purified tetramethoxydiphenylmethane the following experiments were carried out.

(i) 3,3′,4,4′-Tetramethoxydiphenylmethane (200 mg.), dissolved in concentrated sulphuric acid (1·4 ml.), was treated by dropwise addition with aqueous formaldehyde (0·6 ml.; 35%) at room temperature and set aside at room temperature for 2·5 hr. Water (10 ml.) was added and the dark resinous gel removed by filtration. After washing with hot water and drying, the ground solid was extracted with hot benzene in a Soxhlet apparatus. No material soluble in benzene was found.

(ii) A repetition of experiment (i) using similar quantities of materials but maintaining the mixture at 0° led to a similar result.

(iii) Concentrated sulphuric acid (5 g.) in glacial acetic acid (10 ml.) was added dropwise to a solution of 3,3′,4,4′-tetramethoxydiphenylmethane (1·0 g.) in glacial acetic acid (30 ml.) and aqueous formaldehyde (5 ml.; 40%) with stirring, under nitrogen, at room temperature. The mixture was stirred for 7 hr., set aside for 15 hr., and poured on·to ice. The sticky flocculent yellow precipitate was taken up in benzene and, after drying, was diluted with an equivalent volume of light petroleum (b. p. 40—60°). Chromatography on alumina gave a colourless gum, eluted with ether, the infrared spectrum of which corresponded closely to that of 6,6′-bisacetoxymethyl-3,3′,4,4′-tetramethoxydiphenylmethane.

Cyclotriveratrylene by Cyclisation.—A solution of 6,6′-bischloromethyl-3,3′,4,4′-tetramethoxydiphenylmethane (385 mg.) and veratrole (120 mg.) in glacial acetic acid (20 ml.) was gently refluxed for 4 hr. After evaporation of the acetic acid under reduced pressure with addition of benzene, the solid residue, dissolved in anhydrous benzene (10 ml.), was chromatographed on an alumina column to yield 6,6′-bisacetoxymethyl-3,3′,4,4′-tetramethoxydiphenylmethane (185 mg.), m. p. and mixed m. p. 94—95°, and cyclotriveratrylene (205 mg.), m. p. and mixed m. p. 234°. The identities of the two products were also confirmed by means of their infrared spectra.

10,15-*Dihydro*-3,7,8,12,13-*pentamethoxy*-2-*methyl*-5H-*tribenzo*[a,d,g]*cyclononene.*—A solution of 6,6′-bischloromethyl-3,3′,4,4′-tetramethoxydiphenylmethane (1·16 g.) and 2-methylanisole (380 mg.) in glacial acetic acid (200 ml.) was gently refluxed 4 hr. in a nitrogen atmosphere. The product crystallised from ethanol to give the *pentamethoxy-compound* (860 mg.) as colourless needles, m. p. 199° (Found: C, 74·3; H, 7·0%; *M* (VPO), 449. $C_{27}H_{30}O_5$ requires C, 74·6; H, 7·0%; *M*, 435), $\lambda_{max.}$ 205, 233, and 291 mμ (log ε 4·87, 4·52, and 3·96), $\nu_{max.}$ 2985, 2924, 2831, 1608, 1585, 1515, 1462, 1449, 1389, 1340, 1316, 1263, 1220, 1190, 1139, 1086, 1026, 990, 980, 870, 845, 739, and 614 cm.$^{-1}$.

2,3-*Diethoxy*-10,15-*dihydro*-7,8,12,13-*tetramethoxy*-5H-*tribenzo*[a,d,g]*cyclononene.*—A solution of 6,6′-bischloromethyl-3,3′,4,4′-tetramethoxydiphenylmethane (1·2 g.) and 1,2-diethoxybenzene (500 mg.) in glacial acetic acid (30 ml.) was refluxed for 8 hr. under nitrogen. The crude crystalline product, recovered as described previously, was dissolved in hot benzene and chromatographed on alumina. Hot benzene eluted the *diethoxy-compound* (1·4 g.) which crystallised from benzene as bunches of soft needles, m. p. 184—185° (Found: C, 72·6; H, 7·4%; *M* (VPO), 489. $C_{29}H_{34}O_6$ requires C, 72·8; H, 7·2%; *M*, 479), $\lambda_{max.}$ 209, 234, and 292 mμ (log ε 4·84, 4·50, and 4·01), $\nu_{max.}$ 3035, 2980, 2930, 2905, 2875, 2835, 2820, 1609, 1589, 1519, 1512, 1476, 1467, 1446, 1394, 1341, 1258, 1220, 1193, 1146, 1089, 1040, 997, 954, 944, 904, 876, 851, 741, and 619 cm.$^{-1}$.

2-*Ethoxy*-10,15-*dihydro*-3,7,8,12,13-*pentamethoxy*-5H-*tribenzo*[a,d,g]*cyclononene.*—A solution of 6,6′-bischloromethyl-3,3′,4,4′-tetramethoxydiphenylmethane (1·2 g.) and 2-ethoxyanisole (460 mg.) in glacial acetic acid (50 ml.) was refluxed for 7 hr. under nitrogen. The product (1·6 g.) in hot benzene (30 ml.) was filtered through alumina to remove coloured impurities, and crystallised on addition of light petroleum. Recrystallisation from light petroleum (b. p. 100—120°) afforded the *ethoxy-compound* as dimorphic needles, m. p.s 184—185° and 195—196°. A very slow rate of heating caused the transformation to occur in the solid state since in this case only the upper m. p. was observed (Found: C, 72·1; H, 6·8%; *M* (VPO), 482. $C_{28}H_{32}O_6$ requires C, 72·4; H, 6·95%; *M*, 465), $\lambda_{max.}$ 204, 233, and 292 mμ (log ε 4·86, 4·52, and 4·00), $\nu_{max.}$ 3035, 2975, 2930, 2905, 2840, 2830, 1610, 1590, 1523, 1512, 1474, 1467, 1445, 1396, 1343, 1263, 1218, 1192, 1145, 1086, 1036, 996, 944, 930, 909, 877, 782, 849, 740, and 617 cm.$^{-1}$.

10,15-*Dihydro*-2,3,7,8,12,13-*hexaethoxy*-5H-*tribenzo*[a,d,g]*cyclononene* (I; R = Et).—1,2-Diethoxybenzene (4 g.), in glacial acetic acid, and aqueous formaldehyde (5 ml.; 40%) were cooled in an ice-bath, 98% sulphuric acid (3·5 g.) in acetic acid (10 ml.) was added dropwise with stirring, and stirring continued for several hours. After being set aside for 24 hr. the mixture was added to ice, and the precipitated solid recovered by filtration. The dry product, in hot light petroleum–benzene, was filtered through alumina. On cooling the eluate, the *hexaethoxy-compound* crystallised as rosettes of needles (3·4 g.), m. p. 145—146° (Found: C, 74·3; H, 7·8%; *M* (VPO), 533. $C_{33}H_{42}O_6$ requires C, 74·1; H, 7·9%; *M*, 535), $\lambda_{max.}$ 207, 233, and 289 mμ (log ε 4·85, 4·51, and 3·97), $\nu_{max.}$ 3035, 2975, 2920, 2900, 2865, 1606, 1590, 1548, 1516, 1480, 1440, 1400, 1365, 1345, 1288, 1256, 1216, 1195, 1147, 1110, 1091, 1081, 1050, 1036, 955, 917, 902, 873, 851, 825, 743, and 623 cm.$^{-1}$.

Triethoxytrimethoxy-derivative.—By reacting 2-ethoxyanisole with formaldehyde, as in the preceding experiment, one of the isomeric *triethoxytrimethoxy-compounds* was isolated as small needles, m. p. 174—175° (from benzene–light petroleum) (Found: C, 73·0; H, 7·2%; *M* (VPO), 486. $C_{30}H_{36}O_6$ requires C, 73·1; H, 7·4%; *M*, 493), $\lambda_{max.}$ 204, 234, and 293 mμ (log ε 4·86, 4·52, and 3·99), $\nu_{max.}$ 3035, 2980, 2935, 2895, 2880, 2855, 2830, 1610, 1590, 1523, 1512, 1479, 1467, 1445, 1396, 1343, 1316, 1261, 1219, 1193, 1146, 1110, 1090, 1045, 1013, 944, 916, 877, 853, 744, 742, and 620 cm.$^{-1}$.

I thank Mr. H. M. Paisley for measurement of the infrared spectra, Dr. I. J. Lawrenson for measuring the nuclear magnetic resonance spectra, and Mr. N. G. Savill for determining the molecular weights by means of the vapour pressure osmometer. Mr. F. Rackley kindly prepared the sample of 6-amino-3,4-dimethylphenol and Coalite and Chemical Products Ltd. kindly provided a sample of 4-methylcatechol.

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[*Received, June* 11*th*, 1964.]