

Fungus Pigments

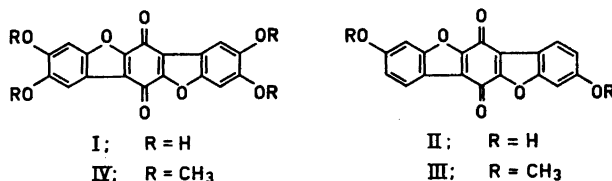
XV.* On the Synthesis of Benzobisbenzofuranquinones

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The condensation of chloranil with certain phenols leads, contrary to earlier views, to a mixture of benzo[1,2-b:4,5-b']bisbenzofuran-6,12-diones and benzo[1,2-b:5,4-b']bisbenzofuran-6,12-diones.

In connection with work¹ on the structure of the so-called "dihydroisothelephoric acid hexaacetate"² we needed some readily available substance related to thelephoric acid (I). One such substance appeared to be 3,9-dihydroxybenzo[1,2-b:4,5-b']bisbenzofuran-6,12-dione (II). Its methyl ether (III) has been described by Acharya *et al.*³ and the synthesis of this compound served as a model for the synthesis of thelephoric acid.²



Acharya *et al.*³ obtained (III) by condensing chloranil with 3-methoxyphenol in the presence of sodium ethylate. Repetition of this system gave a substance, with properties in agreement with those given to it by the Indian researchers. However, its absorption spectrum, with maxima at 390 and 530 $m\mu$, was not compatible with structure (III). One would definitely not expect (III) to absorb at a longer wave-length than thelephoric acid tetramethyl ether (IV), which absorbs at 472 $m\mu$.²

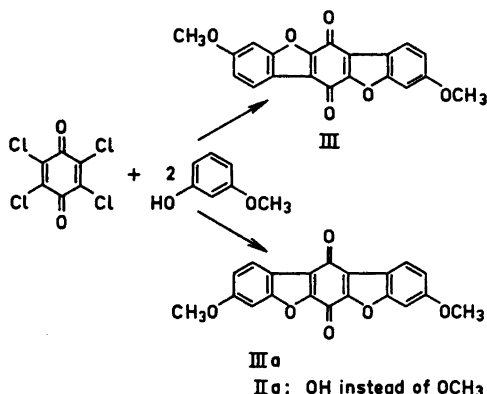
We suspected that the desired compound was mixed with some other substance which caused the absorption above 500 $m\mu$. All attempts to separate the compounds or the derived phenols obtainable by demethylation with

* Part XIV. *Acta Chem. Scand.* 19 (1965) 1051.

pyridinium hydrochloride, were futile. Even thin-layer chromatography on both silica gel and alumina, with several different solvent systems, produces only one spot.

However, when the product was reductively acetylated two compounds could be separated due to their different solubility in acetic acid. They are isomeric and correspond in composition to the expected leucoacetate of (III). The compound which is difficultly soluble in boiling acetic acid has an ultra-violet spectrum which is very similar to that of telephoric acid leucoacetate² and benzo[1,2-b:4,5-b']bisbenzofuran (see Fig. 3) indicating that it is indeed the leucoacetate of quinone (III). Demethylation and deacetylation followed by oxidation gave the desired quinone (II), which has an absorption maximum at 407 $m\mu$ (Fig. 1, curve 1).

The more soluble leucoacetate could be converted similarly into a hydroxyquinone, isomeric with (II). This has absorption maxima at 360 and 538 $m\mu$ (Fig. 2, curve 1), and it is evidently its methyl ether which is responsible for the absorption at 530 $m\mu$ in the original mixture. Reductive acetylation gave a leucoacetate, the ultraviolet spectrum of which resembles that of benzo[1,2-b:5,4-b']bisbenzofuran⁴ (see Fig. 4). The formation of a derivative of benzo[1,2-b:5,4-b']bisbenzofuran in addition to (III), in the reaction of chloranil with 3-methoxyphenol is readily understood if we assume that the initial reaction between the phenoxide anion and chloranil takes place not only in the 2- and 5-positions of chloranil but also in the 2- and 6-positions.

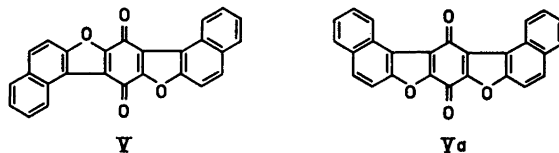


The second quinone is therefore 3,8-dimethoxybenzo[1,2-b:5,4-b']bisbenzofuran-6,12-dione (IIIa).

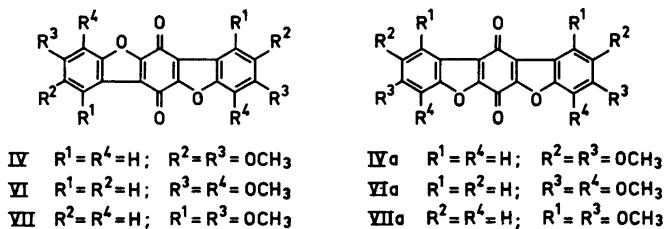
The observation that two isomeric quinones were formed from 3-methoxyphenol prompted us also to investigate the reaction of some other phenols with chloranil in order to see whether this course of the reaction is general or not.

Acharya *et al.*³ had in fact in one case, namely in the reaction with β -naphthol, obtained a by-product. The analysis reported by them, did not comply very well with that of an isomeric compound and they made no comment on its possible nature. We have repeated this synthesis and can confirm

the results of Acharya *et al.*³ with the exception that the analysis of our by-product agrees fairly well with the expected composition. The absorption spectrum of this compound (Fig. 2, curve 3) shows much resemblance to that of (IIIa), particularly in having a maximum above 500 $m\mu$, namely at 526 $m\mu$. Thus we conclude that the reaction between β -naphthol and chloranil also proceeds in two directions giving dinaphtho[1,2-d:1',2'-d']benzo[1,2-b:4,5-b']difuran-8,16-dione (V) and dinaphtho[1,2-d:1',2'-d']benzo[1,2-b:5,4-b']difuran-8,16-dione (Va).



Three more phenols, *i.e.* 3,4-dimethoxy-, 2,3-dimethoxy- and 3,5-dimethoxyphenol, have also been studied. Of these, 3,4-dimethoxyphenol was the one used in the synthesis of telephoric acid tetramethyl ether (IV).² An investigation of the chloroform-soluble portion of the crude reaction product revealed the presence of an isomer in this case also, and the two other phenols gave mixtures of two quinones, which could be separated from one another, either directly (in the case of 3,5-dimethoxyphenol) or through the leucoacetate (in the case of 2,3-dimethoxyphenol). The structures (IVa), (VI), (VIa), (VII), and (VIIa) could readily be assigned to the different isomeric substances on the basis of the absorption spectra of the quinones and their corresponding leucoacetates.



In Fig. 1 are given the spectra of the benzo[1,2-b:4,5-b']bisbenzofuran-quinones and in Fig. 2 those of the isomeric benzo[1,2-b:4,5-b']bisbenzofuran-quinones. The latter always have two maxima in the visible region, whereas the former have only one. Figs. 3 and 4 give the spectra of the relevant leucoacetates, which are all similar to the spectra of the parent unsubstituted compounds, which are also included.

In all the cases studied two products have been obtained. The relative proportions of these are given in Table 1.

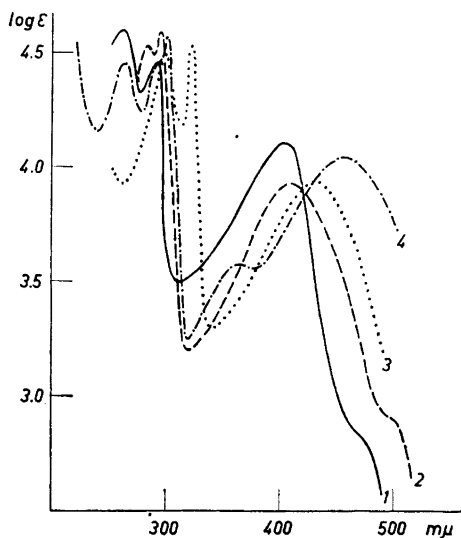


Fig. 1. The spectra of: 1 3,9-Dihydroxybenzo [1,2-b:4,5-b'] bisbenzofuran-6,12-dione (II), 2 1,3,7,9-Tetramethoxybenzo[1,2-b:4,5-b']bisbenzofuran-6,12-dione (VII), 3 Dinaphtho [1,2-d:1',2'-d'] benzo [1,2-b:4,5-b']difuran-8,16-dione (V), 4 2,3,8,9-Tetramethoxybenzo[1,2-b:4,5-b']bisbenzofuran-6,12-dione (IV).

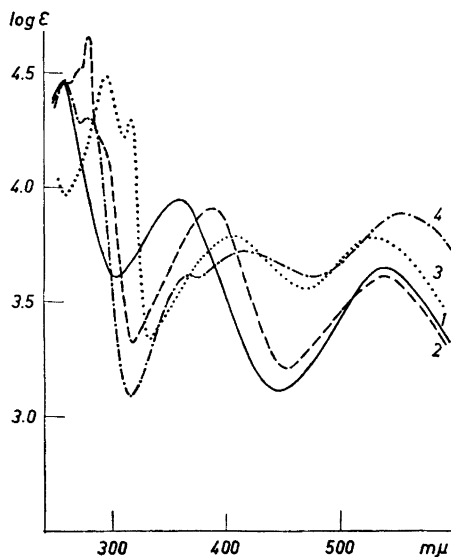


Fig. 2. The spectra of: 1 3,9-Dihydroxybenzo [1,2-b:5,4-b'] bisbenzofuran-6,12-dione (IIa), 2 1,3,9,11-Tetramethoxybenzo [1,2-b:5,4-b']bisbenzofuran-6,12-dione (VIIa), 3 Dinaphtho[1,2-d:1',2'-d']benzo [1,2-b:5,4-b']difuran-8,16-dione (Va), 4 2,3,9,10-Tetramethoxybenzo [1,2-b:5,4-b'] bisbenzofuran-6,12-dione (IVa).

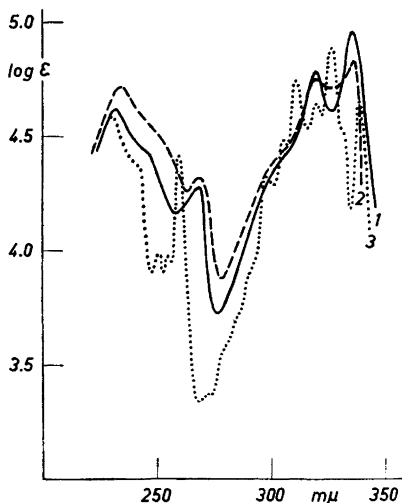


Fig. 3. The spectra of: 1 6,12-Diacetoxy-3,9-dimethoxybenzo [1,2-b:4,5-b']bisbenzofuran, 2 6,12-Diacetoxy-3,4,9,10-tetramethoxybenzo[1,2-b:4,5-b']bisbenzofuran, 3 Benzo[1,2-b:4,5-b']bisbenzofuran (taken from Ref. 2).

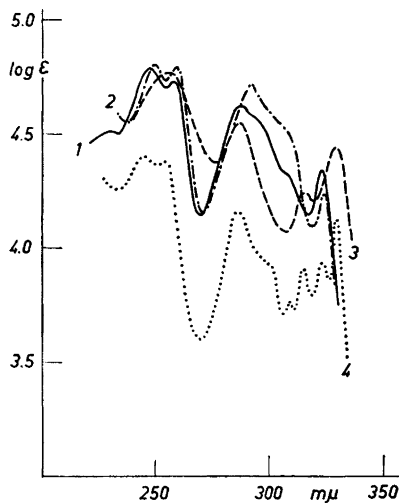


Fig. 4. The spectra of 1 3,6,9,12-Tetraacetoxybenzo[1,2-b:5,4-b']bisbenzofuran, 2 2,3,6,9,10,12-Hexaacetoxybenzo [1,2-b:5,4-b'] bisbenzofuran, 3 6,12-Diacetoxy-3,4,8,9-tetramethoxybenzo [1,2-b:5,4-b'] bisbenzofuran, 4 Benzo[1,2-b:5,4-b']bisbenzofuran (taken from Ref. 4).

Table 1.

Starting phenol	Proportion of benzo[1,2-b:4,5-b']bis-benzofuran-derivative to benzo[1,2-b:5,4-b']bisbenzofuran-derivative
β -Naphthol	1:1
3-Methoxyphenol	1:8
2,3-Dimethoxyphenol	1:8
3,4-Dimethoxyphenol	4:1
3,5-Dimethoxyphenol	1:1,5

Only with 3,4-dimethoxyphenol does the reaction go predominantly in the direction assumed by Acharya *et al.*³ In all other cases at least an equal amount of the isomeric quinone is formed. Presently we are not prepared to offer an explanation for the different behaviour of these phenols.

Great difficulties were encountered in the combustion analyses of the compounds described in this paper and many of them gave low values for carbon. Similar difficulties were also experienced in the work of telephoric acid.²

EXPERIMENTAL

The melting points were determined in a capillary melting point apparatus (Townson & Mercer Ltd.) and are corrected. The U.V. spectra were measured, unless otherwise stated, for dioxane solutions on a Beckman DK-2 apparatus. The I.R. spectra were recorded from KBr-discs on a Beckman IR-5 (marked B), a Perkin-Elmer 237 (marked PE 237) or a Perkin-Elmer 125 (marked PE 125) apparatus. The microanalyses were performed by Dr. A. Bernhardt, Mülheim, Germany.

6,12-Diacetoxy-3,9-dimethoxybenzo[1,2-b:4,5-b']bisbenzofuran (leucoacetate of III). The product obtained by condensing 3-methoxyphenol with chloranil according to Acharya *et al.*³ (9 g) was refluxed in acetic anhydride (1500 ml) with sodium acetate (6 g) and zinc powder (15 g). The mixture was filtered hot and the precipitate that formed on cooling was washed with acetic anhydride, acetic acid and water. Yield 11.2 g. This product (26 g) was boiled with acetic acid and filtered while hot. The portion insoluble in hot acetic acid was boiled once more with acetic acid and again filtered. The remaining insoluble 6,12-diacetoxy-3,9-dimethoxybenzo[1,2-b:4,5-b']bisbenzofuran (3 g) was finally recrystallised from acetic acid, m.p. 312–314°. (Found: C 65.82; H 4.05. $C_{24}H_{18}O_8$ requires: C 66.38; H 4.18). U.V.-spectrum: λ_{\max} 232, 246(infl.), 269, 307(infl.), 320, 336 m μ (log ϵ 4.62, 4.43, 4.28, 4.41, 4.78, 4.96); λ_{\min} 258, 277, 327 m μ (log ϵ 4.16, 3.72, 4.60). I.R.-maxima (B): 3020w, 2960w, 2860w, 1780s, 1720w, 1630s, 1595w, 1540s, 1485m, 1440m, 1420m, 1375m, 1340s, 1295m, 1275s, 1235m, 1185s, 1150s, 1085s, 1045w, 1025s, 990m, 945s, 880m, 850w, 825s, 815w, 745w, 735m, 675w, 655m, 630m cm^{-1} .

6,12-Diacetoxy-3,9-dimethoxybenzo[1,2-b:5,4-b']bisbenzofuran (leucoacetate of IIIa) crystallised on cooling from the acetic acid solution obtained as described in the preceding paragraph (21 g). It was further purified by recrystallisation from acetic acid, m.p. 268–271°. (Found: C 66.09; H 4.22. $C_{24}H_{18}O_8$ requires: C 66.38; H 4.18). U.V.-spectrum: λ_{\max} 251, 261, 296(infl.), 300, 305, 325, 335(infl.) m μ (log ϵ 4.77, 4.63, 4.50, 4.51, 4.49, 4.34, 3.75); λ_{\min} 257, 274, 303, 317 m μ (log ϵ 4.61, 3.96, 4.48, 4.13). I.R.-maxima (B): 3020w, 2950w, 2840w, 1775s, 1705w, 1625s, 1585m, 1535w, 1495s, 1465w, 1440m, 1420m, 1370m, 1330m, 1280s, 1190s, 1165m, 1145s, 1095s, 1045s, 1030m, 950m, 930w, 885w, 870w, 825m, 815m, 795w, 740w, 655m cm^{-1} .

3,9-Dihydroxybenzo[1,2-b:4,5-b']bisbenzofuran-6,12-dione (II). 6,12-Diacetoxy-3,9-dimethoxybenzo[1,2-b:4,5-b']bisbenzofuran (260 mg) was boiled with acetic acid (20 ml)

and 63 % hydrobromic acid (20 ml). The dark brown precipitate was filtered off, dried and dissolved in pyridine. Chromic trioxide was added and the mixture refluxed for 2 h. Water was then added and most of the pyridine distilled off. The brown precipitate was filtered (125 mg) and recrystallised from pyridine giving 3,9-dihydroxybenzo[1,2-b:4,5-b']-bisbenzofuran-6,12-dione, m.p. > 350°. (Found: C 66.53; H 2.58. $C_{18}H_8O_6$ requires: C 67.51; H 2.51). U.V.-spectrum: λ_{\max} 262, 292, 407, 475 (infl.) $m\mu$ (log ϵ 4.60, 4.46, 4.11, 2.81); λ_{\min} 277, 310 $m\mu$ (log ϵ 4.32, 3.50). I.R.-maxima (B): 3450m, 3090w, 1670s, 1625s, 1590m, 1535s, 1500m, 1435m, 1385m, 1335m, 1300m, 1240s, 1150m, 1130m, 1090s, 1030s, 950m, 865m, 825s, 770m, 755w, 720m, 715w, 630m cm^{-1} .

3,6,9,12-Tetraacetoxybenzo[1,2-b:4,5-b']bisbenzofuran (*leucoacetate of II*) was prepared by reductive acetylation of the quinone described above with acetic anhydride, pyridine and zinc. The product was recrystallised from acetic acid, m.p. 341–343°. (Found: C 63.28; H 3.71. $C_{28}H_{18}O_{10}$ requires: C 63.67; H 3.70). U.V.-spectrum: λ_{\max} 234, 263, 300 (infl.), 311, 328 $m\mu$ (log ϵ 4.70, 4.22, 4.52, 4.84, 4.86); λ_{\min} 257, 273, 320 $m\mu$ (log ϵ 4.01, 3.73, 4.64). I.R.-maxima (PE 237): 1760s, 1624m, 1600w, 1538m, 1476w, 1434m, 1416m, 1376s, 1344m, 1282m, 1250w, 1200s, 1136m, 1124s, 1088s, 1020s, 990s, 958s, 908m, 874m, 814m, 730w, 678m, 650m cm^{-1} .

3,9-Dihydroxybenzo[1,2-b:5,4-b']bisbenzofuran-6,12-dione (*IIa*). This was obtained from 6,12-diacetoxy-3,9-dimethoxybenzo[1,2-b:5,4-b']bisbenzofuran by demethylation followed by oxidation in the same manner as described above for the isomeric quinone. Recrystallisation from pyridine gave blue-black crystals, m.p. > 350°. (Found: C 66.78; H 2.44. $C_{18}H_8O_6$ requires: C 67.51; H 2.51). U.V.-spectrum: λ_{\max} 257, 360, 538 $m\mu$ (log ϵ 4.67, 3.95, 3.65); λ_{\min} 305, 446 $m\mu$ (log ϵ 3.61, 3.11). I.R.-maxima (B): 3390m, 3090w, 1670s, 1625s, 1590m, 1570w, 1530s, 1435m, 1420w, 1400w, 1370m, 1360m, 1310s, 1295m, 1235s, 1175w, 1150m, 1105s, 1080w, 1035s, 955w, 945w, 930w, 865m, 855w, 830m, 825m, 795m, 770m, 750w, 720w, 640m cm^{-1} .

3,6,9,12-Tetraacetoxybenzo[1,2-b:5,4-b']bisbenzofuran (*leucoacetate of IIa*) was prepared from the quinone described above by reductive acetylation. Recrystallised from acetic acid giving an m.p. 287–290°. (Found: C 63.84; H 3.98. $C_{28}H_{18}O_{10}$ requires: C 63.67; H 3.70). U.V.-spectrum: λ_{\max} 229, 248, 258, 287, 307 (infl.), 323 $m\mu$ (log ϵ 4.51, 4.79, 4.73, 4.63, 4.33, 4.34); λ_{\min} 234, 255, 270, 317 $m\mu$ (log ϵ 4.50, 4.70, 4.14, 4.14). I.R.-maxima (PE 237): 1774s, 1662w, 1614s, 1540w, 1486s, 1432s, 1420m, 1370s, 1336m, 1288m, 1250w, 1200s, 1132s, 1096s, 1046s, 1012m, 966s, 902m, 890w, 864w, 848w, 814w, 672w, 644w cm^{-1} .

Dinaphtho[1,2-d:1',2'-d']benzo[1,2-b:4,5-b']difuran-8,16-dione (*V*) was prepared according to method B of Acharya *et al.*³ U.V.-spectrum: λ_{\max} 299, 323, 434 $m\mu$ (log ϵ 4.49, 4.53, 3.95); λ_{\min} 262, 315, 339 $m\mu$ (log ϵ 3.93, 4.19, 3.29). I.R.-maxima (B): 1670s, 1625m, 1585m, 1535s, 1515s, 1460m, 1445m, 1425w, 1395w, 1350s, 1340s, 1320m, 1260w, 1230m, 1205m, 1140w, 1120m, 1065m, 1050s, 1030s, 985m, 970m, 950w, 885s, 805s, 785m, 770m, 750s, 735m, 730w, 690w, 670w, 655w cm^{-1} .

Dinaphtho[1,2-d:1',2'-d']benzo[1,2-b:5,4-b']difuran-8,16-dione (*Va*). The benzene solution obtained in the preparation of (*V*) was evaporated almost to dryness and the precipitate was extracted once more with benzene. The residue from the benzene solution was recrystallised first from nitrobenzene and finally from anisole. M.p. 361–362° (Ref. 3, m.p. 361–364°). (Found: C 79.66; H 3.16. $C_{28}H_{12}O_4$ requires: C 80.41; H 3.11). U.V.-spectrum: λ_{\max} 296, 316, 410, 526 $m\mu$ (log ϵ 4.48, 4.29, 3.79, 3.79); λ_{\min} 258, 312, 332, 470 $m\mu$ (log ϵ 3.97, 4.22, 3.34, 3.57). I.R.-maxima (PE 237): 1678s, 1628w, 1588m, 1534s, 1514s, 1448w, 1390m, 1340s, 1220w, 1208m, 1158w, 1116w, 1074s, 1050s, 1030s, 984m, 884w, 812s, 742s cm^{-1} .

2,3,9,10-Tetramethoxybenzo[1,2-b:5,4-b']bisbenzofuran-6,12-dione (*IVa*). The condensation of chloranil with 3,4-dimethoxyphenol was carried out as described previously.² The crude product was extracted with chloroform. The residue from the chloroform solution was recrystallised first from nitrobenzene and finally from anisole giving dark violet crystals, m.p. 325–327°. (Found: C 65.00; H 4.21. $C_{22}H_{16}O_8$ requires: C 64.70; H 3.95). U.V.-spectrum: λ_{\max} 261, 283, 367, 416, 554 $m\mu$ (log ϵ 4.47, 4.31, 3.62, 3.72, 3.89); λ_{\min} 273, 315, 379, 476 $m\mu$ (log ϵ 4.27, 3.09, 3.61, 3.61). I.R.-maxima (PE 237): 3025w, 2945w, 2840w, 1662s, 1620m, 1588m, 1524s, 1480s, 1432m, 1372m, 1338m, 1248s, 1230s, 1212s, 1188m, 1176m, 1150m, 1136w, 1102m, 1076m, 1030s, 1010s, 930w, 844s, 810w, 800m, 784w, 760w, 746m, 692w cm^{-1} .

6,12-Diacetoxy-2,3,9,10-tetramethoxybenzo[1,2-b:5,4-b']bisbenzofuran (*leucoacetate of IVa*). This was prepared by reductive acetylation of 2,3,9,10-tetramethoxybenzo[1,2-b:5,4-b']bisbenzofuran-6,12-dione in the manner described above. Recrystallisation from acetic anhydride gave colourless crystals, m.p. 322–323°. (Found: C 62.70; H 4.60. $C_{26}H_{22}O_{10}$ requires: C 63.15; H 4.49). U.V.-spectrum: λ_{\max} 254, 263 (infl.), 311, 315 (infl.), 322 (infl.) $m\mu$ (log ϵ 4.67, 4.61, 4.62, 4.61, 4.58); λ_{\min} 239, 280 $m\mu$ (log ϵ 4.37, 3.86). I.R.-maxima (PE 125): 3010w, 2940w, 2840w, 1770s, 1718w, 1620s, 1534w, 1496s, 1484s, 1446s, 1436m, 1412m, 1376m, 1350w, 1332m, 1304s, 1265w, 1244w, 1218m, 1192s, 1184s, 1164s, 1110s, 1050s, 1018s, 988m, 876w, 840w, 800w, 748m, 660w cm^{-1} .

2,3,6,9,10,12-Hexaacetoxybenzo[1,2-b:5,4-b']bisbenzofuran. 2,3,9,10-Tetramethoxybenzo[1,2-b:5,4-b']bisbenzofuran-6,12-dione (500 mg) was refluxed for 24 h in 63 % hydrobromic acid in acetic acid. The precipitate which was obtained when water was added was extracted with pyridine. An insoluble precipitate which was formed during the extraction was removed and the solution evaporated at room temperature. The residue was dissolved in alcohol and precipitated by addition of light petroleum. The crude 2,3,9,10-tetrahydroxybenzo[1,2-b:5,4-b']bisbenzofuran-6,12-dione thus obtained, was reductively acetylated giving 2,3,6,9,10,12-hexaacetoxybenzo[1,2-b:5,4-b']bisbenzofuran, m.p. 307–309°; yield 60 mg. (Found: C 58.35; H 3.09. $C_{30}H_{22}O_{14}$ requires: C 59.41; H 3.66). U.V.-spectrum: λ_{\max} 250, 260, 292, 324 $m\mu$ (log ϵ 4.80, 4.79, 4.72, 4.23); λ_{\min} 238, 255, 271, 319 $m\mu$ (log ϵ 4.55, 4.73, 4.15, 4.09). I.R. maxima (PE 125): 1776s, 1656w, 1618m, 1534w, 1470s, 1460s, 1452s, 1430m, 1408w, 1370s, 1332m, 1322m, 1288w, 1262m, 1198s, 1154s, 1142s, 1112m, 810w, 782w, 708w, 662w, 650w, 634w, 614w, 592m, 586m, 506m, 494w, 472w, 462w cm^{-1} .

6,12-Diacetoxy-3,4,9,10-tetramethoxybenzo[1,2-b:4,5-b']bisbenzofuran (*leucoacetate of VI*). The condensation of 2,3-dimethoxyphenol with chloranil was carried out analogous to the condensation of 3,4-dimethoxyphenol. From 64 g 2,3-dimethoxyphenol 1.24 g (1.5 %) of a quinone mixture was obtained. This mixture (1.15 g) was reductively acetylated as described above. The hot solution was filtered and allowed to stand. Almost pure 6,12-diacetoxy-3,4,9,10-tetramethoxybenzo[1,2-b:4,5-b']bisbenzofuran crystallised (120 mg). It was further purified by recrystallisation from acetic anhydride, m.p. 313–315°. (Found: C 63.35; H 4.56. $C_{26}H_{22}O_{10}$ requires: C 63.15; H 4.49). U.V.-spectrum: λ_{\max} 234, 249 (infl.), 2.69, 304 (infl.), 320, 336 $m\mu$ (log ϵ 4.72, 4.53, 4.32, 4.41, 4.76, 4.83); λ_{\min} 264, 279, 325 $m\mu$ (log ϵ 4.26, 3.87, 4.71). I.R.-maxima (PE 237): 3015w, 2950m, 2850m, 1770s, 1636m, 1598w, 1538s, 1508s, 1470m, 1426s, 1378m, 1340s, 1300s, 1276s, 1230s, 1200s, 1186s, 1150s, 1090s, 1036m, 1024m, 986m, 966m, 912w, 876m, 800s, 772w, 700w, 676m cm^{-1} .

3,4,6,9,10,12-Hexaacetoxybenzo[1,2-b:4,5-b']bisbenzofuran. The foregoing compound was demethylated with hydrobromic acid as described above and the crude product acetylated in the presence of zinc. The 3,4,6,9,10,12-hexaacetoxybenzo[1,2-b:4,5-b']bisbenzofuran was recrystallised from acetic anhydride, m.p. 310–312°. (Found: C 58.51; H 3.73. $C_{30}H_{22}O_{14}$ requires: C 59.41; H 3.66). U.V.-spectrum: λ_{\max} 235, 265, 297 (infl.), 308, 324 $m\mu$ (log ϵ 4.70, 4.10, 4.48, 4.78, 4.77); λ_{\min} 260, 273, 318 $m\mu$ (log ϵ 3.90, 3.69, 4.59). I.R.-maxima (PE 237): 1780s, 1636w, 1602w, 1538m, 1500w, 1432s, 1414m, 1374s, 1340m, 1300m, 1262m, 1210s, 1190s, 1140m, 1044s, 1020s, 980m, 876s, 826m, 800w, 760m, 726w, 670m cm^{-1} .

6,12-Diacetoxy-3,4,8,9-tetramethoxybenzo[1,2-b:5,4-b']bisbenzofuran (*leucoacetate of VIa*). The acetic anhydride solution from which 6,12-diacetoxy-3,4,9,10-tetramethoxybenzo[1,2-b:4,5-b']bisbenzofuran had crystallised (see above) was hydrolysed with water, whereby 6,12-diacetoxy-3,4,8,9-tetramethoxybenzo[1,2-b:5,4-b']bisbenzofuran precipitated. Yield 1.0 g. Recrystallisation from acetic acid gave colourless crystals with m.p. 262–263°. (Found: C 62.59; H 4.68. $C_{26}H_{22}O_{10}$ requires: C 63.15; H 4.49). U.V.-spectrum: λ_{\max} 255, 288, 315, 329 $m\mu$ (log ϵ 4.87, 4.57, 4.24, 4.44); λ_{\min} 277, 308, 320 $m\mu$ (log ϵ 4.37, 4.07, 4.20). I.R.-maxima (PE 237): 3010w, 2940m, 2840m, 1776s, 1642m, 1626m, 1596m, 1534w, 1512s, 1468m, 1450m, 1420s, 1372m, 1334m, 1302m, 1284s, 1228m, 1188s, 1152m, 1114w, 1086s, 1028s, 1008m, 966m, 940w, 880m, 820w, 800m, 776m, 710m cm^{-1} .

1,3,7,9-Tetramethoxybenzo[1,2-b:4,5-b']bisbenzofuran-6,12-dione (*VII*). 3,5-Dimethoxyphenol (15 g) was condensed with chloranil in the manner already described. The yield of quinone mixture was 1.9 g (10 %). The mixture was treated with chloroform and the chloroform-insoluble portion (550 mg) recrystallised from *o*-dichlorobenzene giving 1,3,7,9-

tetramethoxybenzo[1,2-b:4,5-b']bisbenzofuran-6,12-dione, m.p. > 365°. (Found: C 63.13; H 3.96. $C_{22}H_{16}O_8$ requires: C 64.70; H 3.95). U.V.-spectrum (chloroform): λ_{\max} 284, 294, 407, 496(infl.) $m\mu$ (log ϵ 4.53, 4.59, 3.93, 2.91); λ_{\min} 289, 320 $m\mu$ (log ϵ 4.49, 3.21). I.R.-maxima (PE 237): 3090w, 3010m, 2980w, 2945m, 2840w, 1682s, 1662w, 1622s, 1596s, 1528s, 1508s, 1470m, 1450m, 1436m, 1418m, 1380w, 1360m, 1284s, 1220s, 1200s, 1158s, 1150m, 1128m, 1090s, 1050s, 1028m, 980w, 944m, 824s, 802m, 760m, 724m, 630m cm^{-1} .

1,3,7,9-Tetrahydroxybenzo[1,2-b:4,5-b']bisbenzofuran-6,12-dione. The foregoing (500 mg) was heated with pyridinium hydrochloride at 205–210° for 1.5 h. Water was then added and the precipitate recrystallised from pyridine giving 1,3,7,9-tetrahydroxybenzo[1,2-b:4,5-b']bisbenzofuran-6,12-dione (160 mg), m.p. > 365°. (Found: C 60.74; H 2.56. $C_{18}H_8O_8$ requires: C 61.37; H 2.29). U.V.-spectrum: λ_{\max} 270(infl.), 285(infl.), 294(infl.), 299, 446, 580(infl.) $m\mu$ (log ϵ 4.36, 4.43, 4.51, 4.52, 4.02, 2.85); λ_{\min} 350 $m\mu$ (log ϵ 3.33). I.R.-maxima (PE 237): 3340m, 1660m, 1630s, 1616s, 1596s, 1532m, 1516m, 1404m, 1376w, 1288s, 1180w, 1130s, 1056s, 1036s, 980w, 844m, 830m, 760m, 718m, 630w cm^{-1} .

6,12-Diacetoxy-1,3,7,9-tetramethoxybenzo[1,2-b:4,5-b']bisbenzofuran (leucoacetate of VII). Reductive acetylation of 1,3,7,9-tetramethoxybenzo[1,2-b:4,5-b']bisbenzofuran-6,12-dione gave 6,12-diacetoxy-1,3,7,9-tetramethoxybenzo[1,2-b:4,5-b']bisbenzofuran, which after recrystallisation from acetic anhydride had an m.p. 341–343°. (Found: C 62.49; H 4.48. $C_{26}H_{22}O_{10}$ requires: C 63.15; H 4.49). U.V.-spectrum: λ_{\max} 229, 249, 272, 298, 312, 321, 337 $m\mu$ (log ϵ 4.72, 4.51, 3.99, 4.39, 4.73, 4.69, 4.96); λ_{\min} 247, 266, 276, 301, 317, 328 $m\mu$ (log ϵ 4.50, 3.84, 3.84, 4.37, 4.63, 4.54). I.R.-maxima (PE 237): 3020w, 2990w, 2930w, 2840w, 1770s, 1628s, 1602s, 1538m, 1472m, 1454m, 1410m, 1372m, 1354m, 1336s, 1318m, 1278m, 1226s, 1198s, 1156s, 1128w, 1088s, 1046s, 1022m, 994w, 974w, 942m, 890m, 872w, 820s, 796m, 750w cm^{-1} .

1,3,6,7,9,12-Hexaacetoxybenzo[1,2-b:4,5-b']bisbenzofuran. Reductive acetylation of 1,3,7,9-tetrahydroxybenzo[1,2-b:4,5-b']bisbenzofuran-6,12-dione gave 1,3,6,7,9,12-hexaacetoxybenzo[1,2-b:4,5-b']bisbenzofuran, which after recrystallisation from acetic anhydride had an m.p. 289–293°. (Found: C 59.50; H 4.01. $C_{30}H_{22}O_{14}$ requires: C 59.41; H 3.66). U.V.-spectrum: λ_{\max} 239, 266, 300(infl.), 310, 326 $m\mu$ (log ϵ 4.69, 4.04, 4.43, 4.75, 4.73); λ_{\min} 261, 274, 317 $m\mu$ (log ϵ 3.78, 3.63, 4.60). I.R.-maxima (PE 237): 1774s, 1636s, 1600m, 1536m, 1420m, 1404m, 1376s, 1342m, 1310w, 1274m, 1196s, 1128s, 1110s, 1058s, 1022s, 984w, 908s, 884w, 860w, 840w, 824w, 752w, 690m, 666w cm^{-1} .

1,3,9,11-Tetramethoxybenzo[1,2-b:5,4-b']bisbenzofuran-6,12-dione (VIIa). The chloroform-soluble part of the original quinone mixture obtained from 3,5-dimethoxyphenol and chloranil, as described above, was recrystallised first from benzene and finally from nitrobenzene giving 1,3,9,11-tetramethoxybenzo[1,2-b:5,4-b']bisbenzofuran-6,12-dione, m.p. 314–315°. (Found: C 64.26; H 4.17. $C_{22}H_{16}O_8$ requires: C 64.70; H 3.95). U.V.-spectrum: λ_{\max} 260, 273(infl.), 270, 388, 538 $m\mu$ (log ϵ 4.47, 4.52, 4.66, 3.91, 3.61); λ_{\min} 265, 318, 454 $m\mu$ (log ϵ 4.46, 3.32, 3.21). I.R.-maxima (PE 237): 3020w, 2950w, 2840w, 1696s, 1672s, 1620s, 1592s, 1526s, 1502s, 1450m, 1410w, 1346m, 1276s, 1266s, 1216s, 1194m, 1150s, 1116m, 1090s, 1042s, 1028m, 970w, 946m, 814m, 774w, 746m, 702w, 630w cm^{-1} .

This work has been supported by grants from the *State Commission for Technical Sciences (Valtion Teknillistieteellinen Toimikunta)*.

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Received March 10, 1965.