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Cyclo-oligomerization of Quinones

VI.* The Synthesis and Cyclization of a Furohelicene

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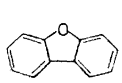
The synthesis of furo[3.2-a:4.5-a′]bisdibenzofuran (*3*) and its cyclization to tetraphenyleno[1.16-bcd:4.5-b′c′d′:8.9-b″c″d″]trifuran (*4*) is described. The spectral properties of these compounds are discussed.

The properties of several complex dibenzofurans, obtained by the action of strong acids on *p*-benzoquinones, have recently been studied in this laboratory. Examples are the compounds *2a* [1] and *5*.[2,3] Compound *3* was



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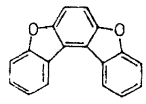

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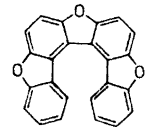

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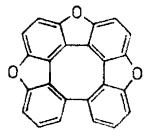
2a: OH instead of H in the positions para to the oxygen atoms



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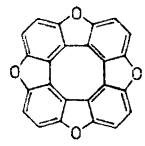

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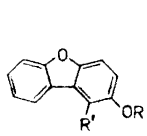
expected to provide valuable information about the steric requirements for the formation of macrocyclic tetramers of the type *5* and has now been synthesized.

* Part V: Ref. 14.

2-Hydroxydibenzofuran (*6*, R = R′ = H) is known to undergo preferential substitution in position 1 [4,5] and reacted with iodine chloride to give a monoiodo derivative whose structure, 2-hydroxy-1-iododibenzofuran (*6*, R = H, R′ = I), was corroborated by its NMR spectrum. The corresponding methyl ether was heated with copper bronze to give compound *7* (R = CH_3). When this dimethyl ether was boiled with hydriodic acid demethylation to phenol *7* (R = H) occurred. Ring closure to compound *3* was eventually effected by prolonged



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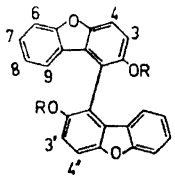

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heating of the phenol with hydrobromic acid at 280°. When this furanobisdibenzofuran was fused with sodium chloroaluminate, cyclization to the tetraphenylenotrifuran *4* occurred. Like the tetraphenylenotetrafurans (*e.g.* compound *5*) the cyclized compound was light yellow and exhibited a greenish yellow fluorescence in UV light.

The UV spectra (Fig. 1) of compounds *1*, *2*, and *3* were very similar to those of various sulphur heterohelicenes which have been discussed by Groen and Wynberg.[6] The α-, *p*-, and β-bands (*cf.* Clar [7]) were therefore easily identified.

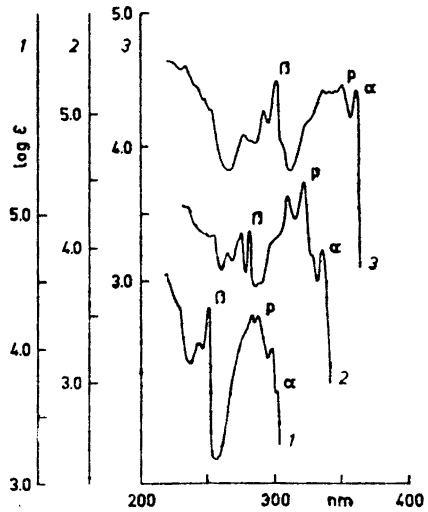


Fig. 1. UV absorption curve of dibenzofuran (*1*) (bottom), benzobisbenzofuran (*2*) (middle) and furobisdibenzofuran (*3*) (top) (all in EtOH).

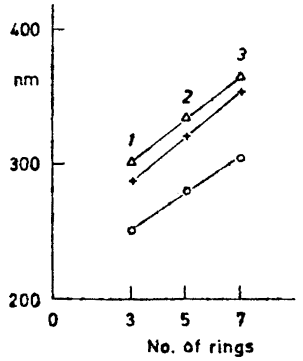


Fig. 2. λ_{max} of the α-, *p*-, and β-band sof compounds *1*, *2*, and *3* *versus* number of rings (△ = α-, + = *p*-, and ○ = β-bands).

As seen from Fig. 2 increasing annelation causes systematic red shifts of the absorption bands. The presence of the furan rings in compounds *1*, *2*, and *3* is reflected in their UV spectra, the α- and β-bands being less split ($\lambda_\alpha/\lambda_\beta = 1.21$, 1.20, and 1.20, respectively) than in the sulphur heterohelicenes ($\lambda_\alpha/\lambda_\beta = 1.25$)[6] and in the series phenanthrene-hexahelicene ($\lambda_\alpha/\lambda_\beta = 1.3$).[7] (For a discussion of this heteroatom effect see Ref. 6).

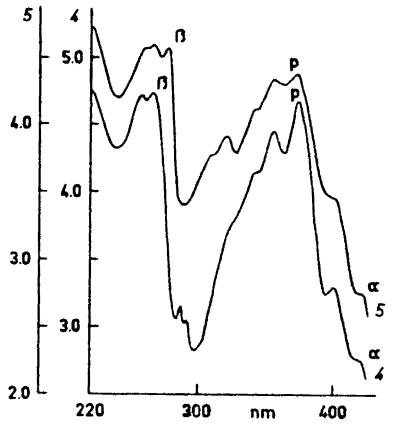


Fig. 3. UV absorption curve of tetraphenylenotrifuran (*4*) (in cyclohexane) (top) and of tetraphenylenotetrafuran (*5*) (in dioxan) (bottom).

A comparison of the very similar UV spectra of the macrocyclic compounds *4* and *5* (Fig. 3) with that of the "open" compound *3* shows that the *p*-bands are shifted to longer wavelengths and that the α- and β-bands have become separated ($\lambda_\alpha/\lambda_\beta = 1.6$). The latter effect is probably due to the higher symmetry of the macrocyclic compounds (*cf.* hexahelicene: $\lambda_\alpha/\lambda_\beta = 1.3$ and coronene: $\lambda_\alpha/\lambda_\beta = 1.4$).[7]

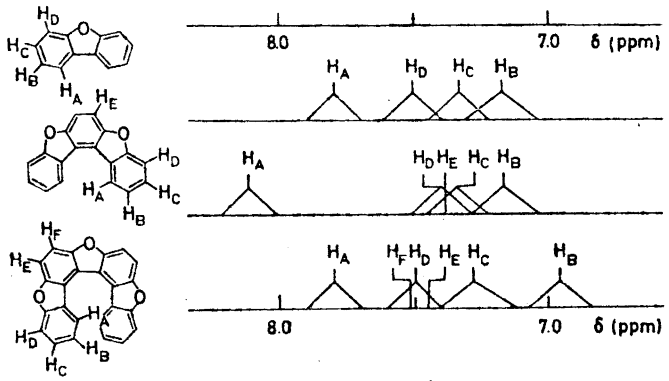


Fig. 4. Schematic NMR spectra of dibenzofuran (*1*), (top), benzobisbenzofuran (*2*) and of furobisdibenzofuran (*3*) (bottom) (all in $CDCl_3$, 60 Mhz).

A diagrammatic representation of the NMR spectra of the compounds *1*, *2*, and *3* is shown in Fig. 4. The chemical shifts assigned to the resonances of the dibenzofuran protons are based upon the detailed discussion in Ref. 8. Those of the protons of compound *2* are assigned on the basis of the close similarity of its NMR spectrum to those of compounds *1* and *3* (Fig. 5). As

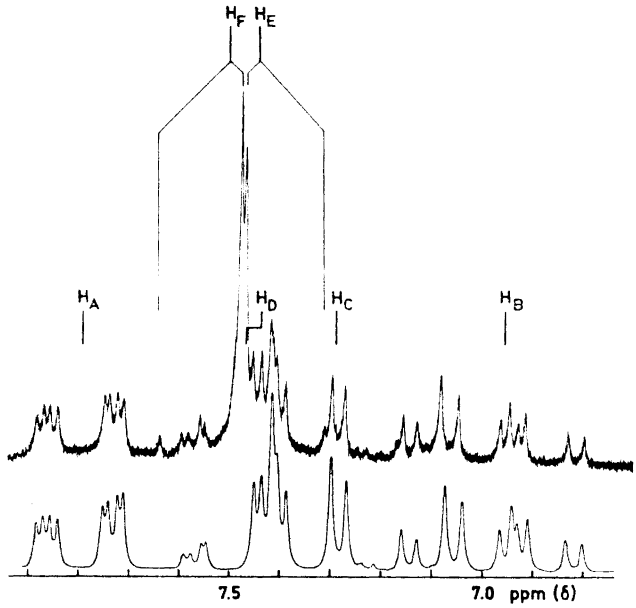
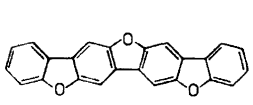


Fig. 5. Experimental (top) and calculated (H_E and H_F not included) (bottom) NMR spectrum of compound *3*. δ (ppm) = 7.79 (H_A); 6.96 (H_B); 7.29 (H_C); 7.47 (H_D); 7.44 (H_E); 7.50 (H_F); $J_{A-B} = 8.2$ cps; $J_{A-C} = 1.6$ cps; $J_{A-D} = 0.6$ cps; $J_{B-C} = 7.2$ cps; $J_{B-D} = 1.2$ cps; $J_{C-D} = 8.6$ cps; $J_{E-F} = 9.6$ cps.

expected the resonance frequency of the proton H_A is shifted to a lower field in the spectrum of compound *2* as compared with that of dibenzofuran (*1*). However, in the spectrum of compound *3* the resonance frequency of the corresponding proton is shifted to a higher field instead of a lower as would be anticipated had compound *3* had a planar structure. Therefore it should have a non-planar helical structure, the proton H_A being located more or less within the shielding zone of the neighbouring terminal benzene ring. This effect is typical for the helicenes and heterohelicenes.[9,10]

Further support for a non-planar structure for the open compound *3* is provided by the fact that anomalous peaks (M − 1, M − 2, and M − 15) occur in its mass spectrum but not in those of compounds *8*,[11] *2*, and *4* (see experimental). The successive loss of 2 H atoms from the molecular ion of *3* gives a fragment ion M − 2, the molecular ion of compound *4*.

The M – 15 peak is probably due to the loss of a methyl radical with formation of the ion *9* as judged by the presence of a metastable peak at $m/e = 318.4$. (Calc. for the transition $m/e = 348 - 333$, $m/e = 318.64$). Similar complex fragmentations and rearrangements have been observed in the helicene and heterohelicene series.[10,12]



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The cyclic compound *2* does not undergo such abnormal fragmentations.

The facile cyclization of compound *3* to give compound *4* and the spectroscopic results discussed above indicate a close proximity of the carbon atoms of compound *3* involved in the formation of the biphenyl linkage in compound *4*. Macrocyclic compounds such as *4* and *5* therefore seem to differ little in strain from dibenzofuran or compound *8*. The ease with which tetramers of type *5* are formed from suitably substituted *p*-benzoquinones is perhaps not surprising as the reaction leads to highly conjugated products of low energy.

EXPERIMENTAL

Melting points were measured on a micro hot stage. The mass spectra were run at 70 eV, ion source temperature 290° (LKB 9000). The NMR spectra were run at 60 MHz and chemical shifts are given relative to TMS (Varian A60).

1-Iodo-2-hydroxydibenzofuran (*6*, R = H; R′ = I). A solution of 2-hydroxydibenzofuran [4] (18.4 g) in acetic acid (100 ml) was treated with a mixture of conc. hydrochloric acid (25 ml) and iodine chloride (19 g) in acetic acid (50 ml). The iodo compound slowly precipitated in the form of long colourless needles. After 24 h the crystals were collected and washed with a little acetic acid, then with water containing sodium bisulphite and finally with water. The product (25 g) melted at 150 – 155°. Recrystallization from acetic acid gave long colourless needles (19 g, 59 %). M.p. 161 – 162°. (Found: C 46.4; H 2.2. Calc. for $C_{12}H_7IO_2$: C 46.5; H 2.3. Mw = 310). MS, $m/e = 310$ ($M^{+\cdot}$, base peak); 281 ($M^{+\cdot} - CO - H\cdot$); 183 ($M^{+\cdot} - I\cdot$); 155 ($M^{+\cdot} - CO - I\cdot$); 127; 126. NMR (acetone d_6): δ (ppm) = 7.19 (H_3, doublet); 7.48 (H_4, doublet); $J_{3-4} = 8.6$ cps; 7.35 – 8.65 (H_6, H_7, and H_8, complex multiplets); 8.65 – 9.00 (H_9 plus phenolic H, complex multiplet).

1-Iodo-2-methoxydibenzofuran (*6*, R = CH_3; R′ = I) was obtained in almost quantitative yield by methylation of the phenol *5* (R = H; R′ = I) with dimethyl sulphate and alkali. Distillation (160 – 167°, 2 mm) and recrystallization from acetic acid gave colourless prisms melting at 124.5 – 125°. (Found: C 48.2; H 2.8; I 39.0. Calc. for $C_{13}H_9IO_2$: C 48.2; H 2.8; I 39.2. Mw = 324). MS, $m/e = 324$ ($M^{+\cdot}$, base peak); 309 ($M^{+\cdot} - CH_3\cdot$); 281 ($M^{+\cdot} - CH_3\cdot - CO$); 182 ($M^{+\cdot} - CH_3\cdot - I\cdot$); 139; 126.

2,2′-Dimethoxybidibenzofuranyl-1,1′ (*7*, R = CH_3). 1-Iodo-2-methoxydibenzofuran (4.0 g) was mixed with copper bronze (30 g) and slowly heated to 220° when an exothermic reaction started. The mixture was then heated to 250° for 0.5 h. The ether extract (4 l) from 10 batches gave a sticky product (18.2 g) which was triturated with cold ethanol to give a solid (A, 12.7 g) and a solution which contained 2-methoxydibenzofuran (5.5 g). Recrystallization of product A from acetic acid gave crystals (9.8 g, yield 50 %) melting at 207 – 208°. (Found: C 79.1; H 4.6. Calc. for $C_{26}H_{18}O_4$: C 79.2; H 4.6. Mw = 394). MS, $m/e = 394$ ($M^{+\cdot}$, base peak); 379 ($M^{+\cdot} - CH_3\cdot$); 364 ($M^{+\cdot} - 2CH_3\cdot$); 348 ($M^{+\cdot} - CH_3OCH_3$, the largest fragment peak, corresponding to the formation of compound *3*). NMR,

δ(ppm) = 3.70 (6 H, two OCH_3 groups); 7.22 (doublet, H_3 and $H_{3'}$); 7.73 (doublet, H_4 and $H_{4'}$); J_{3-4} = 9.0 cps; the two doublets were clearly distinguished from the peaks in the region 6.60 – 7.50 (complex multiplets, H_6 and $H_{6'}$, H_7 and $H_{7'}$, H_8 and $H_{8'}$, and H_9 and $H_{9'}$).

2,2'-Dihydroxybidibenzofuranyl-1,1' (*7*, R = H) 2,2'-Dimethoxybidibenzofuranyl-1,1' (9.0 g) in a solution of conc. hydriodic acid in acetic acid (1:1, 200 ml) was refluxed for 24 h. After cooling, water was added. The yield of the precipitated diphenol was almost quantitative. Recrystallization from acetic acid/water gave colourless needles. M.p. 238 – 240°. (Found: C 78.7; H 3.8. Calc. for $C_{24}H_{14}O_4$: C 78.5; H 3.8. Mw = 366). MS, m/e = 366 ($M^{+\cdot}$, base peak); 348 ($M^{+\cdot} - H_2O$, corresponds to compound *3*); 337 ($M^{+\cdot} - CO - H^{\cdot}$); 311; 309; 291; 289; 183 (M^{2+}).

Furo[3.2-a:4.5-a']bisdibenzofuran (3). A mixture of 2,2'-dihydroxybidibenzofuranyl-1,1' (440 mg), conc. hydrobromic acid (4 ml) and red phosphorus (100 mg) was heated with shaking at 285° for 60 h in a sealed glass tube under nitrogen. After cooling the reaction product was finely ground and washed with 2 M sodium hydroxide to remove any phenolic products. The alkali-insoluble product was sublimed (190°/0.1 mm) and the sublimate (224 mg, 54 %) was recrystallized from acetic acid giving long colourless needles melting at 189 – 190°. (Found: C 82.9; H 3.5. Calc. for $C_{24}H_{12}O_3$: C 82.8; H 3.5. Mw = 348). MS, *m/e* (rel. intensity) = 348(100) ($M^{+\cdot}$); 347(23); 346(19); 333(4); 320(4); 319(11); 317(3); 290(4); 263(2); 261(4); 174.0)12) (M^{3+}). Efforts to resolve this compound into optical enantiomers have so far been unsuccessful.

Furo[2.3-b:5.4-b']bisdibenzofuran (8) [11] gave the following MS, *m/e* (rel. intensity) = 348(100) ($M^{+\cdot}$); 319(3); 292(4); 263(3); 261(2); 174.0(10) (M^{2+}).

Tetraphenyleno[1.16-bcd:4.5-b'c'd':8.9-b''c''d'']trifuran (4). Furanobisdibenzofuran (*3*) (100 mg) was added to a sodium aluminium chloride melt [13] kept at 140°. After 5 min the reaction mixture was cautiously poured into 2 M hydrochloric acid and the precipitate was collected. Sublimation (250°/0.1 mm) gave a small amount of starting material and a less volatile yellow material (30 mg, 30 %). Recrystallization from pyridine afforded yellow needles, exhibiting a greenish yellow fluorescence in ultraviolet light. M.p. 317 – 320°. (Found: C 83.2; H 3.0. Calc. for $C_{24}H_{10}O_3$: C 83.3; H 2.9. Mw = 346). MS; *m/e* (rel. intensity) = 346(100) ($M^{+\cdot}$); 317(9) ($M^{+\cdot} - CO - H^{\cdot}$); 290(2); 288(3); 261(4); 259(3); 173.0(20) (M^{2+}); 158.5(3); 145.0(4); 230.5(7).

Benzo[2.1-b:3.4-b']bisbenzofuran (2). This compound was prepared as described by Erdtman and Stjernström.[1] MS; m/e (rel. intensity) = 258(100) ($M^{+\cdot}$); 229(8) ($M^{+\cdot} - CO - H^{\cdot}$); 202(9) ($M^{+\cdot} - 2CO$); 200(12) ($M^{+\cdot} - 2CO - 2H^{\cdot}$); 176(5); 150(2); 129(8) (M^{2+}).

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