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Cyclo-oligomerization of Quinones

III.* The Action of Strong Acids on 1,4-Naphthoquinone

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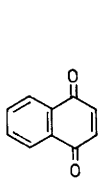
When treated with acids 1,4-naphthoquinone gives a dimer, 5,8-dihydroxydinaphtho(1,2-b:2′,1′-d)furan (*8*), a trimer, 15, 18-dihydroxydinaphtho(2,1-d:2′,1′-d)naphtho(1,2-b:4,3-b′)difuran (*2*) and a tetramer, tetranaphthyleno(5,6-bcd:11,12-b′c′d′:17,18-b″c″d″:23,24-b‴c‴d‴) tetrafuran (*7*). The tetramer probably is formed *via* the dimer and the trimer.

Polymerization of 1,4-naphthoquinone (*1*) in the presence of sulphuric acid was noted by Liebermann in 1883.[3] This reaction was investigated by Erdtman in 1933. When treated with sulphuric acid in acetic acid a mixture of 1,4-naphthoquinone and 1,4-naphthohydroquinone gave two main reaction products, a phenolic trimer to which the structure *2* was assigned and a non-phenolic compound for which the structure *3* was suggested.[4] The latter compound was later obtained by Marschalk in much higher yield by treating 1,4-naphthoquinone with aluminium chloride in nitrobenzene solution.[5] This method, slightly modified, gives a 90 % yield.

Studies by Erdtman and Stjernström [4,6–8] of the action of acids on various 1,4-benzoquinones have shown that treatment with sulphuric acid in dilute acetic acid gives low to moderate yields of the corresponding trimers of general structure *4* from unsubstituted 2-substituted and 2,3-disubstituted 1,4-quinones. The yields depend on the substitution pattern of the quinones, 2,3-disubstitution favouring the formation of trimeric products. Yields are considerably increased when the corresponding dimeric dihydroxydibenzofurans of the general structure *5* are added to the appropriate reaction mixtures.[7] The formation of dibenzofuran derivatives in the condensation reactions also indicates that these may be intermediates in the formation of the trimeric products.[8]

The polymerization of 1,4-naphthoquinone in the presence of pyridine takes a different course. Pummerer *et al.* found that the main product was trinaphthyl-

* Part I: Ref. 1; Part II: Ref. 2.



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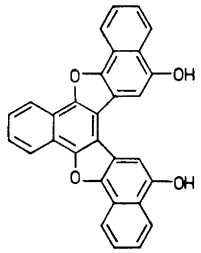

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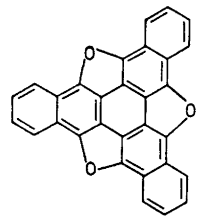

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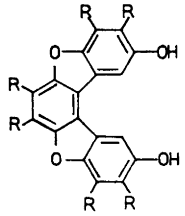

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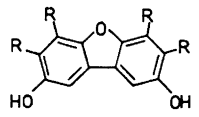

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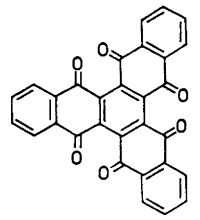

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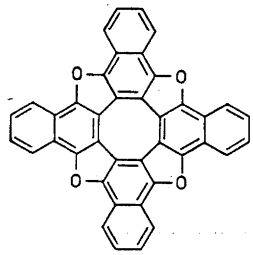
enetriquinone (*6*).[9,10] This is an oxidation product of hexahydroxytrinaphthylene, a possible intermediate in the transformation of 1,4-naphthoquinone into compound *3*. An attempt to convert trinaphthylenetriquinone (*6*) into compound *3* failed. Reductive acetylation of compound *6* gave a hexaacetate which when boiled with hydrobromic acid gave a phenolic product and not compound *3* showing that the ring closure is difficult to achieve.

A mass spectrometric investigation by Erdtman and Högberg of the non-phenolic product assigned structure *3* has shown that in fact the compound is actually the tetramer of structure *7* [tetranaphthyleno(5,6-bcd:11,12-b′c′d′:17,18-b″c″d″:23,24-b‴c‴d‴)tetrafuran].[2]

The present paper deals with the evidence for the structure *7* and further studies of the reactions leading to the formation of this type of compound.

After treating a mixture of 1 mol of 1,4-naphthoquinone and 0.5 mol of 1,4-naphthohydroquinone in acetic acid with 15 % sulphuric acid, 5,8-di-



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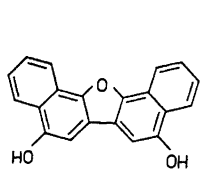
hydroxydinaphtho(1,2-b:2′,1′-d)furan (*8*) was isolated (as the acetate) in 5 % yield together with compounds *2* and *7*. The yield of compound *8* was increased to 35 % when one equivalent of the hydroquinone and only a minute amount of sulphuric acid was used.



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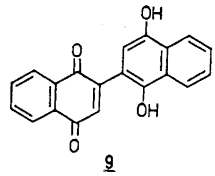

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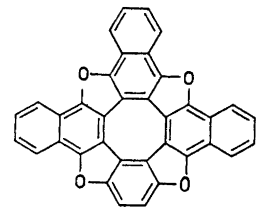

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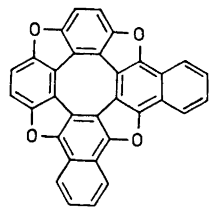

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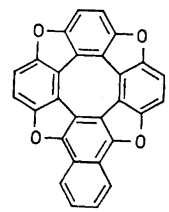

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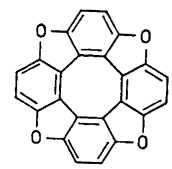

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The structure of compound *8* follows from its formation by dehydration of 1,4,1′,4′-tetrahydroxybinaphthyl-2,2′ and from a zinc dust distillation which furnished dinaphtho(1,2-b:2′,1′-d)furan (*8*, H instead of OH).

Zinc dust distillation of the trimeric product *2* gave dinaphtho(2,1-d:2′,1′-d) naphtho(1,2-b:4,3-b′)difuran (*2*, H instead of OH) identified by mass spectrometry and by its UV spectrum (see Fig. 1). The absorption bands of dinaphtho-

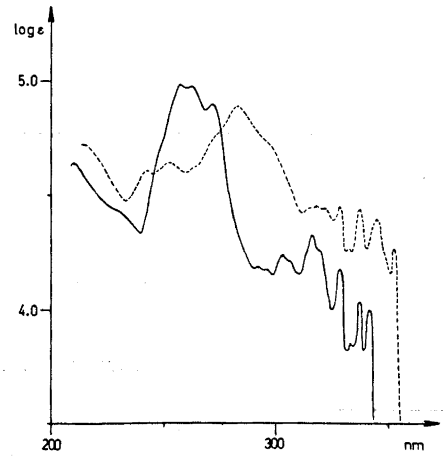

Fig. 1. UV-spectrum of dinaphthofuran (*8*, H instead of OH) ———, and of dinaphthonaphthodifuran (*2*, H instead of OH) - - - - -.

naphthodifuran are shifted bathochromically relative to those of dinaphthofuran. This shift and the similarity of the spectra are in agreement with the structures of these compounds.

Tetranaphthylenotetrafuran (*7*) was also obtained, in a 54 % yield, from the trimer *2* and 1,4-naphthoquinone in the presence of aluminium chloride in nitrobenzene. An equimolar mixture of the dimer *8* and 2,2'-binaphthyl-1,4,1',4' diquinone similarly gave the tetramer *7* in a low yield (5 %). Similar treatment of the diquinhydrone *9* gave compound *7* in a 27 % yield. The oxidation of dimer *8* with tetrachloroquinone in acidified acetic acid solution also gave the tetramer but in low yield (5 %).

In this connection it is of interest that when treated with aluminium chloride in nitrobenzene in the presence of excess 1,4-benzoquinone the trimer *2* gave the unsymmetric compound *10* in a 50 % yield. Under these conditions 1,4-benzoquinone alone did not yield any crystalline condensation product.

When treated similarly, dihydroxydinaphthofuran (*8*) and excess 1,4-benzoquinone gave a low yield (4 %) of compound *11*. The product also contained compound *7* as a minor impurity.

A mixture of 1,4-naphthoquinone and a large amount of 1,4-benzoquinone, when treated with aluminium chloride, gave three major non-phenolic constituents. Mass spectra indicated the presence of compound *11* (position of one naphthalene unit uncertain) and compounds *10* and *7*. A minor component was probably compound *12*.

The tetramer *7* from 1,4-naphthoquinone is probably formed by coupling of naphthoquinone with naphthohydroquinone giving dihydroxydinaphthofuran (*8*).* Compound *8* can then react with naphthoquinone to produce the trimer *2* which with naphthoquinone will give a phenolic tetrameric product. Oxidation with 1 mol of naphthoquinone will then give naphthohydroquinone and, after dehydration, tetranaphthylenotetrafuran (*7*). The naphthohydroquinone can then reenter the reaction sequence. Dihydroxydinaphthofuran must be formed directly and not *via* 1,4,1',4'-tetrahydroxybinaphthyl-2,2' since the latter does not give compound *8* under the reaction conditions used (*cf.* Ref. 7).

Tetranaphthylenotetrafuran (*7*) is almost insoluble in all common solvents. It melts above 600° with little decomposition. The stability of the compound is also demonstrated by its mass spectrum (Fig. 2). The only important peaks are

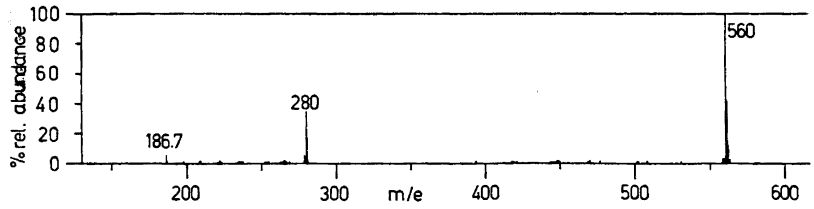

Fig. 2. Mass spectrum of tetranaphthylenotetrafuran (*7*) at 70 eV.

* The acid catalyzed oligomerization of 1,4-naphthoquinone was retarded or inhibited when a strong oxidant such as tetrachloro-1,4-benzoquinone was added to the reaction mixture.

those corresponding to $m/e = 560$ (M^+); 280 (M^{2+}); 186.7 (M^{3+}). No other peaks of abundance greater than 1 % are present. The infrared spectrum is simple, as would be expected for such a rigid, symmetrical compound. No NMR or ultraviolet spectra could be recorded owing to the extremely low solubility of the compound. Pure tetranaphthylenotetrafuran exhibits a greenish-yellow fluorescence in ultraviolet light.

Tetranaphthylenotetrafuran belongs to a new class of compounds, the tetraphenylenotetrafurans. The parent compound, tetraphenylenotetrafuran, *13*, has recently been briefly described by Erdtman and Högberg.[2] These compounds should be planar.

Hellwinkel and Reiff recently described an analogue to tetraphenylenotetrafuran with methylene groups in place of oxygen atoms.[11] They observed the presence of a very high peak in the mass spectrum of their compound corresponding to a doubly charged ion formed by loss of four benzylic hydrogen atoms and pointed out that this ion has $(4n+2)$ π-electrons thus obeying Hückel's rule. The abundant, doubly charged molecular ions observed in the spectra of compounds *7* (see Fig. 2), *10*, *11* and *12* also all have $(4n+2)$ π-electrons.

EXPERIMENTAL

Melting points are uncorrected. Melting points below 360° were determined on a micro hot stage and those above 360° using sealed evacuated capillary tubes heated in an air bath. Instruments: IR, Perkin Elmer No. 421; UV, Beckman DK 2; MS, LKB 9000.

Attempted synthesis of compound 3. Reductive acetylation of trinaphthylenetriquinone (*6*) afforded hexaacetoxytrinaphthylene,[9,10] m.p. 280 – 283° (lit.[9] 278 – 280°). When boiled with hydrobromic acid under nitrogen this gave a green product, probably identical with the "anhydroquinhydrone" of trinaphthylenetriquinone described by Pummerer *et al.*[9,10] The IR and MS ($m/e = 454$ (M^+, 100 %)) were quite different from those of compound *7*.

Tetranaphthyleno(5,6-bcd:11,12-b'c'd':17,18-b''c''d'':23,24-b'''c'''d''')tetrafuran (*7*). A solution of aluminium chloride (3.5 g) in nitrobenzene (100 ml) was added rapidly to a stirred solution of 1,4-naphthoquinone (*1*) (3.0 g) in nitrobenzene (150 ml) at 60°. Stirring and heating was continued for 1 h. Ethanol (1 l) was then added and the resulting mixture was filtered and washed successively with ethanol, 2 M HCl (to remove traces of aluminium chloride), ethanol and finally with pyridine (to remove phenolic impurities). The yield of almost pure tetranaphthylenotetrafuran (*7*) was 2.2 g (91 %). The compound was sublimed (400°/0.1 mm) and could be recrystallized from boiling dibenzofuran (solubility approximately 1 mg/ml) as light yellow needles. M.p. approximately 625°. (Found: C 85.7; H 2.9. Calc. for $C_{40}H_{16}O_4$: C 85.8; H 2.9). The IR (KBr) was simple. The most important peaks were: 640 m, 660 s, 760 s (four adjacent "aromatic" H), 920 s, 1030 m, 1060 m, 1110 m, 1350 m, 1430 s, 1460 m, 3030 w ("aromatic" H). $M^+ = 560.108$ corresponds to $C_{40}H_{16}O_4$. With hot concentrated sulphuric acid the compound gave a brown solution. Cold oleum gave an intense green colour reaction. Dilution with water gave an almost colourless solution probably containing sulphonic acids. The UV spectrum of this solution (log ε values are based on the amount of compound *7* used): λ_{max} (nm/log ε); 225/4.96; 292/4.95; 383/4.45; 406/4.58. λ_{min} (nm/log ε): 248/4.72; 373/4.39; 394/4.35. No singificant change was observed on rendering the solution alkaline indicating that the ring system was unaffected.

Treatment of 1,4-naphthoquinone and 1,4-naphthohydroquinone with strong sulphuric acid. 1,4-Naphthohydroquinone (15 g) was dissolved in acetic acid (150 ml) and the solution mixed with a solution of sulphuric acid (50 ml) in acetic acid (100 ml). A solution of 1,4-naphthoquinone (30 g) in acetic acid (300 ml) was then added at 50°. After about 10 sec the colour deepened and a greyish precipitate appeared. After 10 min the mixture was poured into hot water (1.5 l) and filtered (filtrate A). The solid was boiled with methanol (2 l) and filtered (filtrate B). The dried product was boiled with acetic anhydride

(200 ml) and pyridine (50 ml) for 10 min and then filtered. The filtrate contained no crystalline material and was discarded. The solid was boiled with quinoline (200 ml) and the mixture filtered hot. This treatment was repeated once. (Combined filtrates C). The remaining solid was almost pure tetraphenylenotetrafuran (*7*), yield 18 g (45 %). The solution A was extracted with ether and the ether-soluble product subject to reductive acetylation (acetic anhydride, a little pyridine and zinc dust). The product obtained in the usual way was 1,4-diacetoxynaphthalene, yield 3.9 g (6 %). The methanol solution B was evaporated to 200 ml. The grey phenolic material which separated (1.7 g) was collected and acetylated. The acetate was identified as the furan derivative *2* (OAc instead of OH). The solid obtained on further evaporation of the methanol solution was reductively acetylated as above. After cooling, the reaction mixture was poured onto ice. The product was recrystallized from acetic acid (charcoal) yielding 5,8-diacetoxydinaphthofuran (*8*, OAc instead of OH) (2.5 g, 5 %) as slightly pink needles, m.p. 252 – 254°, identical to a sample prepared from 1,4,1′,4′-tetrahydroxydinaphthyl-2,2′ (see below). Filtrate C gave 15,18-diacetoxydinaphtho-naphthodifuran (*2*, OAc instead of OH) (12 g, 33 %). On recrystallization from quinoline and sublimation under reduced pressure this yielded long colourless needles, m.p. 347 – 350°, dec. (lit[4] 340 – 343°). When 1,4-naphthoquinone was treated alone with a 25 % solution of sulphuric acid in acetic acid for 10 min a product was obtained which on acetylation gave tetranaphthylenotetrafuran (*7*) (52 %) and the diacetate of compound *2* (15 %). When this experiment was repeated with the addition of one mole of tetrachloro-1,4-benzoquinone no reaction occurred and the starting material was recovered unchanged.

15,18-Dihydroxydinaphtho(2,1-d:2′,1′-d)naphtho(1,2-b:4,3-b′)difuran (*2*). 15,18-Diacetoxydinaphtho-naphthodifuran (*2*, OAc instead of OH) (60 mg, finely ground) was refluxed with 5 % ethanolic sulphuric acid (100 ml) for 48 h. Unchanged acetate (6 mg) was removed by filtration, and water was added to the hot filtrate until crystallization began. After cooling, the precipitate (40 mg) was collected. It formed grey needles which turned blue when kept in air. M.p. above 360°, dec. (Found: C 78.4; H 4.0. Calc. for $C_{30}H_{16}O_4.H_2O$: C 78.6; H 4.0. Material obtained from an evaporated pyridine solution gave the following analytical results. Found: C 81.7; H 4.1. Calc. for $C_{30}H_{16}O_4$: C 81.8; H 3.7). The compound was sparingly soluble in ethanol, ether, and acetone, but easily soluble in pyridine. It gave a blue colour reaction with conc. sulphuric acid. The compound was crystallized from dilute ethanol. λ_{max} (nm/log ε) (EtOH): 219/4.75; 263/4.69; 288/4.80; 351/4.36; 367/4.36 and λ_{min} (nm/log ε) 241/4.41; 268/4.69; 329/4.23; 360/4.26. MS: $m/e = 440$ (M^+, 100 %); 220 (M^{2+}, 30 %).

15,18-Dimethoxydinaphto(2,1-d:2′,1′-d)naphtho(1,2-b:4,3-b′)difuran (*2*, OMe instead of OH). 15,18-Dihydroxydinaphtho-naphthodifuran (*2*) (200 mg), methanol (20 ml) and dimethyl sulphate (5 ml) were stirred under nitrogen. Sodium hydroxide (4.4 g) in water (10 ml) was added slowly and the mixture was boiled for 1 h, then poured into water. The product was recrystallized several times from quinoline giving the pure methyl ether which formed long colourless needles. M.p. 339 – 341°. (Found: C 82.3; H 4.4. Calc. for $C_{32}H_{20}O_4$: C 82.1; H 4.4). MS: $m/e = 468$ (M^+, 100 %); 453 ($M^+ - CH_3\cdot$, 25 %); 438. ($M^+ - 2CH_3\cdot$, 13 %); 410 ($M^+ - 2CH_3\cdot - CO$, 70 %); 234 (M^{2+}, 9 %); 226.5 ($M^{2+} - CH_3\cdot - CO$, 12 %); 219 ($M^{2+} - 2CH_3\cdot$, 15 %); 205 ($M^{2+} - 2CH_3\cdot - CO$, 9 %); 191 ($M^{2+} - 2CH_3\cdot - 2CO$, 19 %).

Dinaphtho(2,1-d:2′,1′-d)naphtho(1,2-b:4,3-b′)difuran (*2*, H instead of OH). 15,18-Dihydroxydinaphtho-naphthodifuran (*2*) (1.9 g) was subjected to zinc dust distillation (100 g Zn, hydrogen atmosphere). The distillate (0.9 g) was crystallized from toluene (charcoal) giving 0.5 g (28 %) of dinaphtho-naphthodifuran. After repeated sublimation and recrystallization it furnished long colourless needles. M.p. 316 – 318°, resolidifying and remelting at 335 – 336°. (Found C 88.1; H 4.0. Calc. for $C_{30}H_{16}O_2$: C 88.2; H 3.9). MS: $m/e = 408.117$ (M^+, 100 % corresponding to $C_{30}H_{16}O_2$; 379 ($M^+ - CO - H\cdot$, 12 %); 350 ($M^+ - 2CO - 2H\cdot$, 20 %); 204 (M^{2+}, 3 %).

5,8-Diacetoxydinaphtho(1,2-b:2′,1′-d)furan (*8*, OAc instead of OH). 1,4,1′,4′-Tetraacetoxybinaphthyl-2,2′[9] (10 g) was dissolved in boiling acetic acid (150 ml) and concentrated hydrobromic acid (100 ml) added slowly. A strong blue colour appeared after the addition of only a few drops of the acid. After reflux for 6 h under nitrogen, the reaction mixture was diluted with water. The collected material was triturated with cold methanol and the insoluble blue-black powder (1 g) was removed by filtration. Water was added to the filtrate and the precipitated crude phenol was acetylated. The

crude acetate (4.75 g, 62 %) crystallized in two forms from acetic acid. M.p. 252–254° (needles); 259–260° (prisms). Colour reaction with sulphuric acid: intense violet. (Found: C 75.3; H 4.2. Calc. for $C_{24}H_{16}O_5$: C 75.0; H 4.2). λ_{max} (nm/log ε) (MeOH): 263/4.80; 330/4.10; 344/4.11; 357/3.65 and λ_{min} (nm/log ε): 241/4.19; 313/4.01; 336/4.02. MS: $m/e = 384$ (M^+, 13 %); 342 ($M^+ - CH_2CO$, 18 %); 300 ($M^+ - 2CH_2CO$, 100 %); 271 ($M^+ - 2CH_2CO - CO - H\cdot$, 9 %); 215 ($M^+ - 2CH_2CO - 3CO - H\cdot$, 18 %).

5,8-Diacetoxydinaphthofuran (*8*, OAc instead of OH) *from 1,4-naphthoquinone and 1,4-naphthohydroquinone.* To 1,4-naphthoquinone (3 g) dissolved in acetic acid (25 ml) was added a solution of 1,4-naphthohydroquinone (4 g) in acetic acid (25 ml) followed by 2 M sulphuric acid (1.5 ml). The quinhydrone which precipitated, disappeared on stirring the mixture for three days. The reaction mixture was filtered (filtrate A). The precipitate was acetylated and the boiling reaction mixture filtered (filtrate B). The solid obtained was diacetoxydinaphtho-naphthodifuran (*2*, OAc instead of OH) (1.0 g, 13 %). Addition of acetic anhydride and zinc dust to the filtrate A gave 1,4-diacetoxynaphthalene (2.5 g, 23 %). The filtrate B was boiled with zinc dust, filtered and poured into water. The solid obtained was recrystallized from acetic acid yielding diacetoxydinaphthofuran (2.9 g, 35 %), m.p. 252–255° and 259–260°.

5,8-Dihydroxydinaphtho(1,2-b:2',1'-d)furan (*8*). Diacetoxydinaphthofuran (*8*, OAc instead of OH) (0.63 g) was refluxed with 4 % methanolic sulphuric acid (25 ml) for 2 h. The clear solution was poured into water and the precipitate collected and washed with water (0.48 g, 98 %). Recrystallization from chlorobenzene and sublimation furnished needles, m.p. 290–293° (sealed evacuated tube). Colour reaction with sulphuric acid: intense violet. (Found: C 79.9; H 4.2. Calc. for $C_{20}H_{12}O_3$: C 80.0; H 4.0). λ_{max} (nm/log ε) (EtOH): 264/4.69; 277/4.65; 329/4.30; 343/4.14; 357/4.16. λ_{min} (nm/log ε): 213/4.06; 273/4.64; 318/4.23; 332/4.29; 351/4.01. MS: $m/e = 300$ (M^+, 100 %), 272 ($M^+ - CO$, 7 %), 215 ($M^+ - 3CO - H\cdot$, 14 %), 150 (M^{2+}, 13 %).

5,8-Dimethoxydinaphtho(1,2-b:2',1'-d)furan (*8*, OMe instead of OH). 5,8-Dihydroxydinaphthofuran (*8*) (100 mg) was methylated with dimethyl sulphate and alkali. The methyl ether (90 mg) was recrystallized from acetic acid. M.p. 216–217°, resolidifying and remelting at 222–223°. Colour reaction with sulphuric acid: intense red. (Found: C 80.3; H 4.9. Calc. for $C_{22}H_{16}O_3$: C 80.5; H 4.8). λ_{max} (nm/log ε) (EtOH): 211/4.42; 263/4.60; 323/4.12; 338/4.35; 346/4.26. λ_{min} (nm/log ε): 242/3.92; 313/3.97; 328/4.05; 341/3.97. MS: $m/e = 328$ (M^+, 100 %); 313 ($M^+ - CH_3\cdot$, 60 %); 298 ($M^+ - 2CH_3\cdot$, 20 %); 270 ($M^+ - 2CH_3\cdot - CO$, 7 %); 164 (M^{2+}, 18 %).

Dinaphtho(1,2-b:2',1'-d)furan (*8*, H instead of OH). 5,8-Dihydroxydinaphthofuran (*8*) (600 mg) was distilled with zinc dust (10 g) in a stream of hydrogen. Recrystallization of the collected material (100 mg) from benzene-ethanol (charcoal) gave pure dinaphthofuran, m.p. 185°, identical with a sample prepared according to Ref. 12.

Acid treatment of 1,4,1',4'-tetrahydroxybinaphthyl-2,2'. 1',4'-Tetrahydroxybinaphthyl [13] (30 mg) was mixed with acetic acid (1.5 ml) and a solution of sulphuric acid in acetic acid (1:1, 1 ml) was added. The resulting mixture was stirred at 50° for 2 h and then poured into water and filtered. The solid obtained was acetylated, m.p. 218–225° (35 mg). The acetylated starting material gave m.p. 228–230° (lit.[9] 227°). IR and TLC showed no difference between the product and acetylated starting material.

Tetranaphthylenotetrafuran (7) from dihydroxydinaphtho-naphthodifuran (2) and 1,4-naphthoquinone. 15,18-Dihydroxydinaphtho-naphthodifuran (220 mg) was dissolved in a solution of $AlCl_3$ (0.6 g) in nitrobenzene (15 ml). The solution turned intensely blue. It was added to a stirred solution of 1,4-naphthoquinone (158 mg) in nitrobenzene (20 ml) at 60°. After stirring for 1 h the reaction mixture was poured into ethanol. The solid was filtered, washed with ethanol, 2 M HCl and pyridine and then sublimed giving pure tetranaphthylenotetrafuran (213 mg, 52 %, calc. on compound *2*).

Tetranaphthylenotetrafuran (7) from 2,2'-binaphthyl-1,4,1',4'-diquinhydrone (9). Binaphthyl diquinhydrone [13] (266 mg) was stirred with nitrobenzene (15 ml) at 60° and $AlCl_3$ (0.3 g) in nitrobenzene (10 ml) was added. After stirring for 1 h the mixture was worked up to give tetranaphthylenotetrafuran (63 mg, 27 %).

Tetranaphthylenotetrafuran (7) from dihydroxydinaphthofuran (8) and 2,2'-binaphthyl-1,4,1',4'-diquinone. Stirring for 1 h at 60° of 5,8-dihydroxydinaphthofuran (168 mg), binaphthyldiquinone [14] (175 mg), $AlCl_3$ (0.4 g) and nitrobenzene (35 ml) gave tetranaphthylenotetrafuran (10 mg, 3 %).

Tetranaphthylenotetrafuran (7) by oxidation of 5,8-dihydroxydinaphthofuran (8). 5,8-Dihydroxydinaphthofuran (300 mg), tetrachloro-1,4-quinone (250 mg) and acetic acid (30 ml) were stirred at 50°. Sulphuric acid (5 ml) in acetic acid (10 ml) was added and stirring and heating continued for 1 h. The solid obtained on filtration and washing with acetic acid, ethanol and pyridine was tetranaphthylenotetrafuran (14 mg, 5 %).

Tribenzo(a,f,k)tetraphenyleno(5,6-bcd:9,10-b'c'd':13,14-b''c''d'':17,18-b'''c'''d''')tetrafuran (10). 15,18-Dihydroxydinaphtho-naphthodifuran (440 mg) was dissolved in a solution of $AlCl_3$ (0.6 g) in nitrobenzene (15 ml). The intensely blue solution was added to a stirred solution of 1,4-benzoquinone (436 mg) in nitrobenzene (15 ml) and stirring continued at 60° for 1 h. Work-up as above gave crude compound *10* (260 mg, 50 %, calc. on compound *2*). Sublimation gave light yellow needles, m.p. approximately 540° (Found: C 84.5; H 2.7. Calc. for $C_{36}H_{14}O_4$: C 84.7; H 2.8). MS: $m/e = 510$ (M^+, 100 %); 255 (M^{2+}, 57 %). There were no other important peaks.

Dibenzo(a,f)tetraphenyleno(5,6-bcd:9,10-b'c'd':13,14-b''c''d'':17,18-b'''c'''d''') tetrafuran (11). Dihydroxydinaphthofuran (*8*) (600 mg) and 1,4-benzoquinone (550 mg) in nitrobenzene (25 ml) at 60° were treated with aluminium chloride (1.2 g) in nitrobenzene (15 ml). Stirring and heating was continued for 1 h. Work-up as above gave crude compound *11* (40 mg, 4 %). Repeated gradient sublimations furnished pure compound *11*. (A less volatile component was present as a minor impurity in the product. MS of this component showed that it was identical with compound *7*). Compound *11* crystallized as light yellow needles from quinoline. M.p. approx. 470°. (Found: C 83.3; H 2.7. Calc. for $C_{32}H_{12}O_4$ C 83.5; H 2.6). MS: $m/e = 460$ (M^+, 100 %); 230 (M^{2+}, 33 %).

Acid treatment of 1,4-naphthoquinone and 1,4-benzoquinone. After adding aluminium chloride (5 g) in nitrobenzene (30 ml) to a solution of 1,4-naphthoquinone (0.5 g) and 1,4-benzoquinone (2 g) in nitrobenzene (30 ml) and stirring for 1 h the resulting mixture was poured into ethanol. Washing the collected material with 2 M HCl and pyridine yielded 0.2 g of a grey powder which was moistened with sodium hydroxide solution and subjected to gradient sublimation (400°/0.1 mm). Three separate zones were obtained. The first one containing the fastest travelling compound was very small. Its mass spectrum indicated the presence of a dibenzotetraphenylenotetrafuran, *e.g. 11* [$m/e = 460$ (M^+, 100 %); 230 (M^{2+}, 50 %)] and about 15 % of benzotetraphenylenotetrafuran (*12*) [$m/e = 410$ (M^+, 15 %); 205 (M^{2+}, 7 %)]. The second, somewhat larger, zone contained compound *10* [$m/e = 510$ (M^+, 100 %); 255 (M^{2+}, 60 %)] together with compound *11* (15 %) and tetranaphthylenotetrafuran (*7*) (1 %). The third, major zone contained compound *7* [$m/e = 560$ (M^+, 100 %); 280 (M^{2+}, 40 %)] together with compound (*10*) (20 %).

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