A High Yield Easy Method for the Preparation of Alkoxy-Substituted Triphenylenes

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2,3,6,7,10,11-Hexamethoxytriphenylene is prepared by oxidative trimerization of 1,2-dimethoxybenzene (veratrol) with iron(III) chloride/sulfuric acid in nearly quantitative yield. The obtained crude product is almost pure. Other alkoxy-substituted triphenylenes are also synthesized by this method.

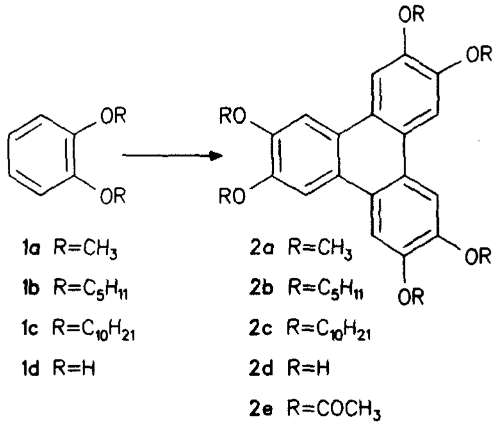
Triphenylene was first described in 1935;[1] it is planar and thermally quite stable as long as it is unsubstituted. Triphenylene is prepared by the reaction of 1,2-dihalo-substituted benzenes with lithium or magnesium in aprotic solvents.[2,3]

Hexaalkoxy-substituted triphenylenes show liquid crystalline properties if the side chains are long enough, therefore triphenylenes are an important model for discotic liquid crystals.[4,5] By cleavage of the methyl groups in 2,3,6,7,10,11-hexamethoxytriphenylene (**2a**) and reaction with suitable substrates other hexaalkoxytriphenylenes were prepared.[6]

Until now the direct synthesis of long chain hexaalkoxy-substituted triphenylenes has not been economical. Even the synthesis of pure **2a** in large quantities is an intensive task for which two routes are reported: electrochemical trimerization of 1,2-dimethoxybenzene (veratrol) (**1a**) on a platinum electrode,[7,8] and oxidative trimerization of **1a** in 70% sulphuric acid with chloranil[9,10] or with iron(III) chloride and water.[11] The trimerization by electrolysis can be carried out in only small amounts, e.g. 0.4 g of **1a** yields 35% of **2a**.[8] The oxidation with chloranil yields 70% of crude product, after purification the total yield decreases to 45%.[9] Compound **2a** was also synthesized in 7% yield by reaction of a mixture of veratrol (**1a**), iron(III) chloride and water at 75 °C.[11]

We report here a simple synthesis of 2,3,6,7,10,11-hexamethoxytriphenylene (**2a**) in large quantities and with almost quantitative yield by stirring 1,2-dimethoxybenzene (**1a**) with 70% sulphuric acid/iron(III) chloride at room temperature for 24 hours (Scheme 1). The product is filtered and washed with water, ethanol, and toluene. Besides an almost quantitative yield, the obtained **2a** is of high purity. There is no difference in the ^{1}H NMR spectrum of this product and a purified sample. The melting point of crude **2a** is only 3 °C below the pure substance (316–318 °C). Compound **2a** can be further purified through sublimation or recrystallization from ethanol/chloroform or dimethylformamide.

Our method can be used in general for the synthesis of alkoxy-substituted triphenylenes. As an example dipentyloxybenzene (**1b**) and didecyloxybenzene (**1c**) were used as starting materials and treated with iron(III) chloride/sulphuric acid. The obtained yields of **2b** and **2c** (35 and 45%, respectively) were, however, lower in comparison to **2a**.



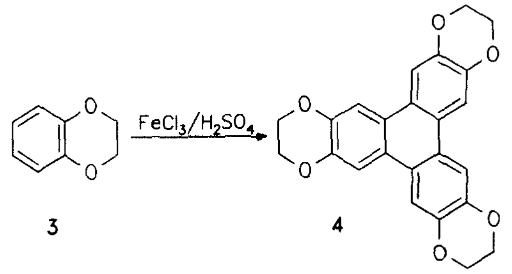
Scheme 1

The triphenylenes **2b** and **2c** have liquid crystalline properties.[9] The transition temperatures of **2b** lie at 69 °C (crystalline–meso phase) and 122 °C (meso phase–liquid phase) and for **2c** at 58 °C and 69 °C, respectively. Compounds **2b** and **2c** are soluble in organic solvents e.g., in chloroform or toluene.

The reaction of 1,2-dihydroxybenzene (catechol) (**1d**) to form the corresponding 2,3,6,7,10,11-hexahydroxytriphenylene (**2d**) using the same method is more complicated. Although the triphenylene **2d** was formed, it could not be isolated in pure form. The iron is complexed by the six ortho-positioned OH groups in **2d** and the isolated black product is not soluble in organic solvents. The Mössbauer spectrum of the black solid shows only one doublet, indicating that all iron centres have the same non-cubic environment. The Mössbauer parameters ($\delta = 1.26$ mm/s, $\Delta E_Q = 2.71$ mm/s) are clearly indicative of high spin Fe(II).[12] It was not possible to remove the complexed iron completely, e.g., by boiling with hydrochloric acid/ethylenediaminetetraacetic acid.

However, the hexahydroxytriphenylene **2d** can be obtained by cleavage of the ether groups in **2a** with boron tribromide and subsequent hydrolysis[13] even at room temperature. The acetate **2e** is easily obtained if the reaction mixture of **2a** and boron tribromide is treated with acetic anhydride before hydrolysis. As an additional example 1,4-benzodioxane (**3**) was trimerized under the described conditions (Scheme 2) to the corresponding triphenylene **4**[8] in 35% yield.

The trimerization reaction probably proceeds via a radical mechanism. The alkoxy substituents in **1a**–**e** can stabilize a radical intermediate.



Scheme 2

A similar mechanism was described for the oxidative dimerization of phenols with iron(III) chloride in the solid state.[14] To check for an ionic mechanism aluminum(III) chloride was used to induce the trimerization of **1a**. Even at higher temperatures no reaction occurred.

Substitutents other than alkoxy groups do not promote trimerization under the described conditions: e.g., *o*-xylene, 1,2-dihalobenzenes or phthalodinitrile yield only a mixture of unspecific polymeric products.

In summary, we have found an improved and easy method for the preparation of alkoxy-substituted triphenylenes, a class of compounds which are able to form discotic meso phases.

2,3,6,7,10,11-Hexamethoxytriphenylene (2a):
To a stirred mixture of 70% H_2SO_4 (500 mL) and anhydr. $FeCl_3$ (120 g, 0.74 mol) at 0 °C was added **1a** (31 mL, 0.23 mol) slowly, warmed to 25 °C and stirred for 24 h. The mixture was poured onto ice (500 g) and filtered through a sintered glass funnel. The residue was washed with H_2O (1 L), EtOH (500 mL), and toluene (300 mL). The colour changes from near black to pale violet. The product was dried at 50 °C/50 mbar to obtain **2a**; yield: 32.2 g (96%), mp 313–314 °C. The material can be further purified as follows: method 1: sublimation at 185 °C/0.04 mbar; method 2: recrystallization from DMF or $CHCl_3$/EtOH.

MS: m/z (%) = 408.3 (M^+, 100), 393 (b), 365 (10), 350 (20), 204 (41).

IR (KBr): ν = 1520, 1620 (C=C, aromatic), 1263 (aromatic ether), 833, 779 cm^{-1} (aromatic substitution pattern).

^{1}H NMR ($CDCl_3$): δ = 7.74 (s, 6 H_{arom}), 4.06 (s, 18 H, CH_3).

2,3,6,7,10,11-Hexapentyloxytriphenylene (2b):
To a stirred mixture of 70% H_2SO_4 (250 mL) and anhydr. $FeCl_3$ at 0 °C was added **1b** (23.8 g, 0.095 mol) slowly, warmed to 25 °C and stirred for 24 h. The mixture was poured onto ice (250 g) and filtered through a sintered glass funnel. The residue was washed with H_2O (500 mL) and cold EtOH (250 mL). The violet product was recrystallized from EtOH to give **2b**; yield: 10.7 g (45%); mp crystalline–meso phase: 69 °C; meso phase–liquid phase: 122 °C.

MS: m/z (%) = 744.6 (M^+, 100), 674.5 (27), 604.0 (7), 534.0 (5), 463.2 (17), 393.1 (20), 323.1 (46) (gradual scission of the pentyl groups).

IR (KBr): ν = 1618, 1518 (C=C aromatic), 1263 (aromatic ether), 835, 767 cm^{-1} (aromatic substitution pattern).

^{1}H NMR ($CDCl_3$): δ = 8.19 (s, 6 H_{arom}), 4.10 (m, 12 H, OCH_2), 1.82, 1.49, 1.34 (m, 36 H, CH_2), 0.91 (t, J = 6.9 Hz, 18 H, CH_3).

2,3,6,7,10,11-Hexadecyloxytriphenylene (2c):
Compound **2c** was prepared under the same conditions as for **2b** starting from **1c** (39 g, 0.1 mol); yield 16.4 g (42%), mp crystalline–meso phase: 58 °C; meso phase–liquid phase: 69 °C.

MS: m/z (%) = 1165.2 (M^+, 100), 1025.0 (47), 884.8 (8), 745 (3), 603.4 (5), 463.3 (14), 323.1 (26) (gradual scission of the decyl groups).

IR (KBr): ν = 1616, 1518 (C=C aromatic); 1263 (aromatic ether); 837, 798 cm^{-1} (aromatic substitution pattern).

^{1}H NMR ($CDCl_3$): δ = 8.21 (s, 6 H_{arom}), 4.15 (m, 12 H, OCH_2), 1.88, 1.57, 1.31 (CH_2), 0.93 (t, J = 6.8 Hz, 18 H, CH_3).

2,3,8,9,14,15-Hexahydrotriphenyleno[2,3-*b*: 6,7-*b*′: 10,11-*b*″]tris[1,4]dioxin (4):
To a stirred mixture of 70% H_2SO_4 (125 mL) and anhydr. $FeCl_3$ (15 g, 0.1 mol) at 0 °C was added **3** (6.8 g, 0.05 mol) slowly, warmed to 25 °C and stirred for 24 h. The mixture was poured onto ice (150 g) and filtered through a sintered glass funnel. The residue was washed with H_2O (200 mL) and cold EtOH (100 mL). The crude product was purified by flash chromatography with $CHCl_3$ to give pure **4**; yield: 2.5 g (37%), mp > 320 °C.

MS: m/z (%) = 402.2 (M^+, 100), 346.2 (31), 318.1 (14), 262.2 (15), 234.1 (14), 201.2 (43).

IR (KBr): ν = 1508, 1610 (C=C, aromatic), 1256 cm^{-1} (aromatic ether).

^{1}H NMR ($CDCl_3$): δ = 7.73 (s, 6 H), 4.31 (s, 12 H).

2,3,6,7,10,11-Hexaacetoxytriphenylene (2e):
To a mixture of **2a** (11.5 g, 0.28 mol) and anhydr. CH_2Cl_2 (800 mL) under N_2 at 0 °C was added dropwise a solution of BBr_3 (33 mL, 0.35 mol) in CH_2Cl_2 (80 mL). The mixture was stirred 4 h and then the solvent was removed under vigorous stirring. To the brown residue was added Ac_2O (250 mL) and conc. H_2SO_4 (2 mL) and refluxed for 30 min. The liquid was poured with care onto ice (300 g), filtered through a sintered glass funnel, washed with H_2O and sat. $KHCO_3$ solution. It was washed again with H_2O till pH = 7. The product was dried to give **2e**; yield: 15.3 g (95%); mp 325–326 °C.

MS: m/z (%) = 576.3 (M^+, 7), 534.3 (16), 492.3 (25), 450.2 (42), 408.0 (68), 366.2 (48), 324.2 (100) (gradual scission of the carboxymethyl groups).

IR (KBr): ν = 1767 (aromatic ester), 1624, 1506 cm^{-1} (C=C aromatic).

^{1}H NMR ($CDCl_3$): δ = 8.23 (s, 6 H_{arom}), 2.39 (s, 18 H, CH_3).

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