Concave Dyestuffs: A Triply Bridged Triphenylmethyl Dication

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A triply bridged triphenylmethyl dication {6,13,23,30,39,46-hexaoxaoctacyclo[16.16.16.$2^{2,5}$.$2^{14,17}$.$2^{19,22}$.$2^{31,34}$.$2^{35,38}$.$2^{47,50}$]dohexaconta-2,4,14,16,19,21,31,33,35,37,47,49,51,53,55,57,59,61-octadecaene-8,10,25,27,41,43-hexayne-1,18-diyliumbis(tetrafluoroborate) **4**} and its open-chained analogue 1,6-bis{4-[bis(4-methoxyphenyl)methyl]phenoxy}hexa-2,4-diynediylium bis(tetrafluoroborate) (**9**) are synthesized by using a new variant of the Eglinton reaction. Compound **4** constitutes the first example of concave dyestuffs bearing a large rigid cavity.

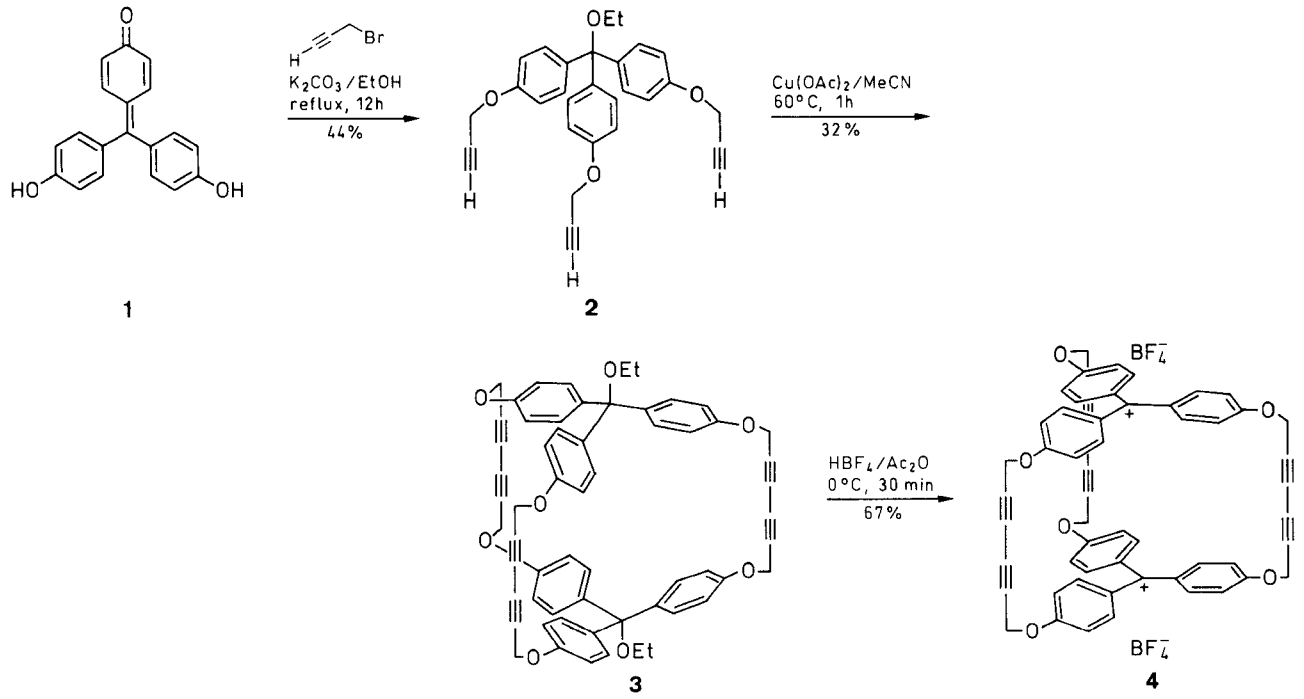
Some years ago we described dyestuff molecules with attached crown rings (chromoionophores).[1] In the meantime compounds of this type have found applications as indicators for chirality,[2] solvatochromy and halochromy.[3]

Here we report on the synthesis of concave dyestuff molecules for the first time, in particular the triply bridged title dication **4**, which bears a relatively rigid large cavity. For comparison we prepared its open-chained analogue **9**. For the preparation of the diyne components we developed a new modification of the Eglinton reaction.[4]

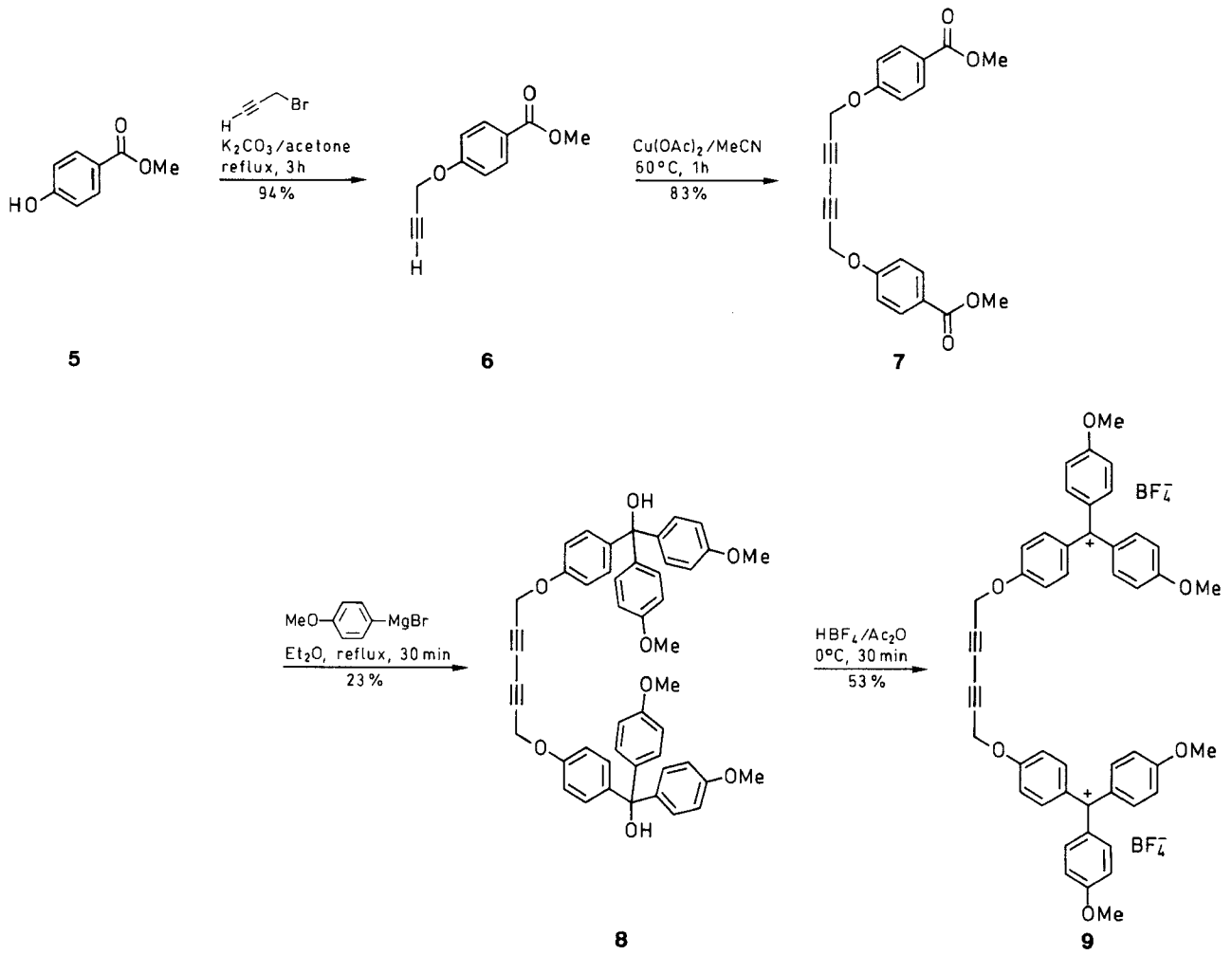
The synthesis of **4** starts with the commercially available red aurin (rosolic acid, **1**, cf. Scheme 1). It was reacted with 3-bromo-1-propyne/potassium carbonate in ethanol to give the colorless trispropargyl ether **2** in 44% yield (after column-chromatographic separation). The trityl unit in this step is protected by the ethoxy group. If dimethylformamide is used as solvent and water for workup, the triarylmethanol analogue of **2** is obtained instead of **2** itself, which is, however, more labile towards acids and more difficult to purify by column chromatography.

The successive oxidative cyclodimerization of **2** to the diethoxy-protected macrobicyclic compound **3** was successfully carried out with copper(II) acetate monohydrate in acetonitrile in 32% yield (after separation by column chromatography). Such diyne couplings with copper salts carried out exclusively in *acetonitrile* as solvent seem not to have been described so far.[4,5] In pure *pyridine* we obtained only 18% yield. After addition of 10% acetonitrile the yield increased significantly (to 28%) whereas in a mixture of acetonitrile/pyridine (20:80, v/v) the yield even on further addition of acetonitrile remained nearly constant (32% in pure acetonitrile). The cyclodimerization of **2** to **3** in acetonitrile proceeds more cleanly than in pyridine and the workup is very simple (see experimental part).

The high yield in this new modification of the Eglinton coupling could be due to a template-effect (acetonitrile as template). The bicyclic compound related to **3** bearing two Ar_3CH units instead of the Ar_3COEt moiety crystallizes from acetonitrile as a 1:1-inclusion complex. The X-ray analysis showed that one acetonitrile molecule is



Scheme 1



Scheme 2

enclosed *inside* the cavity; cavities in between the molecules are unoccupied:[6] Possibly the "half cavity" structure **2** has also a certain complexing ability towards acetonitrile, which might lead to a preorganization of the alkyne units and which could favor the cyclodimerization to the desired bicyclic compound **3** compared to the cyclooligomerization. The experimental results might be rationalized by this assumption.

Splitting off the two ethoxy groups from **3** was carried out with tetrafluoroboric acid in acetic anhydride and led to the desired orange colored macrobicyclic dication **4** in 67% yield.

The new concave dyestuff **4** is orange in the solid state. In solution it shows solvatochromic properties. The longest wavelength UV/VIS absorption is λ = 476 nm (in dichloromethane), 481 nm (in acetonitrile) and 487 nm (in tetrahydrofuran).

For comparison we synthesized the bistritylium salt **9** (Scheme 2). Starting from methyl 4-hydroxybenzoate (**5**) we obtained the propyne ether **6** according to standard methods in 94% yield. The successive oxidative dimerization to the diyne **7** was again carried out with copper(II) acetate monohydrate in acetonitrile (83% yield after column chromatography). Here again we found a cleaner reaction when acetonitrile is applied exclusively. Here we also varied the amount of acetonitrile in solvent mixtures of acetonitrile/pyridine and found in contradiction to the cyclodimerization of **2** to the bicyclic compound **3** nearly constant yields in the coupling of **6** to the open-chained diyne **7** when different amounts of acetonitrile were used in the reaction mixture. Based on these experimental results the yield increase in the cyclodimerization **2** to **3** due to solvent dependency only seems less probable. Therefore the observed yield increase because of the application of higher amounts of acetonitrile as mentioned above for the synthesis of **3** could well be due to a template effect.

The diyne **7** was transformed to the dihydroxy compound **8** by fourfold Grignard reaction with 4-bromoanisol (23% yield after column-chromatographic separation). By reaction with tetrafluoroboric acid in acetic anhydride we obtained the red dication **9** in 53% yield. This compound is reversibly decolorized by addition of bases.

The new variant of the Eglinton reaction (acetonitrile as solvent) which was used in both preparations is attractive because of its short reaction times and simple workup. In the case of the cyclodimerization of **2** to **3** the application of acetonitrile instead of pyridine leads to yield increases.

In particular, in the area of supramolecular chemistry this synthetic modification should be interesting, as oxidative cyclodimerizations have already been applied in several cases for the preparation of polycyclic host compounds.[7]

The properties (solvatochromy, halochromy, pH-dependency) of the new dyestuffs in relation to the open-chained analogues will be reported elsewhere in detail.[8]

Aurin (rosolic acid) **1** was purchased from Aldrich. Solvents were purified by standard methods and dried if necessary. Reagents were used in commercial quality if not noted otherwise. Thin layer chromatographic analyses were carried out on DC-aluminum foils, covered with silica gel $^{60}F_{254}$ (E. Merck); the spots were detected by UV (254 nm) and in addition to that by a dipping bath of $SbCl_5/CCl_4$ (1:4, v/v) which leads to characteristic colors. Melting points were determined on a microscope heating unit of Reichert Company, Vienna, and are not corrected. IR spectra were obtained using a UNICAM SP 1100 spectrophotometer, Pye Unicam Ltd. Company, Cambridge, GB and a IFS 11sv spectrophotometer of Bruker-Physik AG, Karlsruhe. The NMR spectra were measured on AC-200 (^{1}H: 200.1 MHz; ^{13}C: 50.3 MHz), AC-250 (^{1}H: 250.1 MHz;^{13}C: 62.7 MHz) and WM-400 (^{1}H: 400.2 MHz; ^{13}C: 100.6 MHz) spectrometers of Bruker-Physik AG, Karlsruhe, with TMS as external standard. Mass spectra were recorded on MS-30 and MS-50 spectrometers, A.E.I. Company, Manchester, with DEI ionization (70 eV). The FAB-MS spectra were measured with a Concept 1 H spectrometer, Cratos Company, Manchester, in *m*NBA (*m*-nitrobenzyl alcohol) as matrix. The UV/VIS spectra were obtained on a spectrophotometer 550 of Perkin–Elmer Company, Überlingen. The elemental analyses were carried out by the microanalytical department of the Institut für Organische Chemie und Biochemie der Universität Bonn.

Ethyl Tris[4-(2-propynoxy)phenyl]methyl Ether (2):

Aurin (*p*-rosolic acid) **1** (14.5 g, 50 mmol) was heated together with finely powdered K_2CO_3 (41.5 g, 300 mmol) and 3-bromo-1-propyne (45 mL, 0.5 mol) in EtOH (1 L) under reflux for 12 h. The mixture was allowed to cool down and after addition of 10% aq NaOH (250 mL) the mixture was extracted with Et_2O (3 × 250 mL). The combined organic phases were washed with 10% NaOH (3 × 100 mL), sat. aq NaCl (3 × 100 ml) and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue obtained (ca. 19 g of a brown sticky oil) was roughly separated from impurities by filtration over a short column (silica gel; cyclohexane/Et_2O, 1:1). The resulting viscous, pale brown oil was purified by column chromatography (silica gel; cyclohexane/Et_2O, 1:1) to give **2** as an analytical pure, colorless solid; yield: 9.9 g (44%); mp 88 °C. R_f = 0.60 (silica gel; hexane/Et_2O, 1:4; orange in $SbCl_5/CCl_4$).

HRMS: *m/z*, $C_{30}H_{26}O_4$ calc.: 450.1831; found: 450.1833.

MS (DEI): *m/z* (%) = 450 (M^+, 14), 422 ($M^+ - C_2H_4$, 3), 405 ($M^+ - OC_2H_5$, 100), 366 (36), 327 (14), 319 (9), 291 (10), 159 (13), 131 (2), 121 (4).

IR (KBr): ν = 3360 s (alkyne CH), 2140 w (alkyne C≡C), 1620 s, 1595 m, 1520 s, 1463 w, 1382 w, 1310 s, 1272 s, 1245 s, (aryl CO), 1198 vs, 1135 m (trityl CO), 1088 s, 1050 vs (alkyl CO), 940 m, 845 s cm^{-1}.

^{1}H NMR (CD_2Cl_2): δ = 1.21 (t, J = 7.0 Hz, 3 H, CH_3), 2.58 (t, J = 2.4 Hz, 3 H, ≡CH), 3.06 (q, J = 7.0 Hz, 2 H, OCH_2CH_3), 4.67 (d, J = 2.4 Hz, 6 H; OCH_2C≡), 6.90 (dd, J_o = 8.8 Hz, J_m = 2.5 Hz, 6 H, HC-3,5), 7.34 (dd, J_o = 8.8 Hz, J_m = 2.5 Hz, 6 H, HC-2,6).

^{13}C NMR (CD_2Cl_2): δ = 15.43 (q, 1 C, CH_3), 56.07 (t, 3 C, OCH_2C≡), 59.45 (t, 1 C, OCH_2CH_3), 75.61 (d, 3 C, ≡CH), 79.00 (s, 3 C, ≡CCH_2), 85.75 (d, 1 C, Ar_3COEt), 114.21 (d, 6 C, C-3,5), 130.00 (d, 6 C, C-2,6), 138.27 (s, 3 C, C-1), 156.67 (s, 3 C, C-4).

***out*, *out*-1,18-Diethoxy-6,13,23,30,39,46-hexaoxaoctacyclo[16.16.16.$2^{2,5}$.$2^{14,17}$.$2^{19,22}$.$2^{31,34}$.$2^{35,38}$.$2^{47,50}$]dohexaconta-2,4,14,16,19,21,31,33,35,37,47,49,51,53,55,57,59,61-octadecaene-8,10,25,27,41,43-hexayne (3):**

$Cu(OAc)_2 \cdot H_2O$ (12.3 g, 62 mmol) was warmed in MeCN (500 mL) to 60 °C. Compound **2** (3.08 g, 6.8 mmol) dissolved in MeCN (50 mL) was added at once and the mixture was stirred at 60 °C for 1 h, whereby a yellow solid precipitates. The mixture was allowed to cool down, H_2O (1 L) was added, the precipitate was filtered off, washed with H_2O (500 mL) and dried in the desiccator. The dry solid was purified by column chromatography (silica gel, cyclohexane/Et_2O/CH_2Cl_2/Et_3N, 10:30:1:1). Compound **3** was obtained as a colorless solid in an analytical pure grade. Yield: 0.98 g (32%); mp > 250 °C. R_f = 0.57 (silica gel; hexane/Et_2O, 1:4; orange in $SbCl_5/CCl_4$).

$C_{60}H_{46}O_8$	calc.	C 80.52	H 5.18
(895.0)	found	80.35	5.01

FAB-MS (CI): *m/z* = 895.3 ([M + H]$^+$), 866.3 ($M^+ - C_2H_4$), 849.2 ($M^+ - OC_2H_5$).

IR (KBr): ν = 1618 s, 1595 w, 1515 s, 1460 w, 1380 w, 1310 m, 1266 s, 1235 s (aryl CO), 1195 vs, 1135 m (trityl CO), 1088 m, 1045 s (alkyl CO), 940 w, 843 s cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.19 (t, J = 7.0 Hz, 6 H, CH_3), 3.07 (q, J = 7.0 Hz, 4 H, OCH_2CH_3), 4.75 (s, 12 H, OCH_2C≡), 6.94 (dd, J_o = 8.8 Hz, J_m = 2.5 Hz, 12 H, HC-3,5), 7.39 (dd, J_o = 8.8 Hz, J_m = 2.5 Hz, 12 H, HC-2,6).

^{13}C NMR ($CDCl_3$): δ = 15.40 (q, 2C, CH_3), 55.90 (t, 6C, OCH_2C≡), 58.99 (t, 2C, OCH_2CH_3), 71.16 (s, 6C, ≡CC≡), 74.82 (s, 6C, ≡CCH_2), 85.32 (s, 2C, Ar_3COEt), 113.96 (d, 12C, C-3,5), 130.11 (d, 12C, C-2,6), 137.81 (s, 6C, C-1), 156.19 (s, 6C, C-4).

6,13,23,30,39,46-Hexaoxaoctacyclo[16.16.16.$2^{2,5}$.$2^{14,17}$.$2^{19,22}$.$2^{31,34}$.$2^{35,38}$.$2^{47,50}$]dohexaconta-2,4,14,16,19,21,31,33,35,37,47,49,51,53,55,57,59,61-octadecaene-8,10,25,27,41,43-hexayne-1,18-diylium Bis(tetrafluoroborate) (4):

Compound **3** (89.5 mg, 0.10 mmol) was dissolved in Ac_2O (2.0 mL) and cooled down to 0 °C. 50% HBF_4 (0.12 mL, 1.0 mmol) was added slowly under stirring, whereby the mixture spontaneously turned orange-red. After stirring for 30 min at 0 °C ice-cold Et_2O (25 mL) was added and the mixture was stirred at 0 °C for 1 h. The orange precipitate **4** was filtered off, washed with a little bit of cold Et_2O, and the solvent removed in vacuo. Yield: 65.7 mg (67%); mp > 250 °C. R_f = 0.62 (silica gel; EtOH; orange in $SbCl_5/CCl_4$).

FAB-MS (CI, *m*NBA): *m/z* = 956.3 ([M + *m*-$O_2N(C_6H_6)CH_2O$]$^+$), 805.3 ([M + H]$^+$).

MS (DEI): *m/z* = 68 (BF_3), 49 (BF_2).

IR (KBr): ν = 1595 s, 1382 m, 1280 m, 1190 vs, 1100 w, 1035 m (alkyl CO) 775 w (BF_4^-), 541 m (BF_4^-) cm^{-1}.

UV (CH_2Cl_2): λ_{max} (ε) = 263 (21600), 476 nm (66100).

^{1}H NMR (CD_2Cl_2): δ = 5.08 (s, 12 H, OCH_2), 7.32 (dd, J_o = 9.0 Hz, J_m = 2.5 Hz, 12 H, HC-2,6), 7.54 (dd, J_o = 9.0 Hz, J_m = 2.5 Hz, 12 H, HC-3,5).

^{13}C NMR (CD_2Cl_2): δ = 57.97 (t, 6C, OCH_2), 72.23 (s, 6C, ≡CC≡), 73.93 (s, 6C, ≡CCH_2), 117.40 (d, 12C, C-3,5), 133.13 (s, 6C, C-1), 143.46 (d, 12C, C-2,6), 168.55 (s, 6C, C-4), 193.84 (s, 2C, Ar_3C^+).

Methyl 4-(2-Propynoxy)benzoate (6):

Methyl 4-hydroxybenzoate (**5**; 15.2 g, 100 mmol) was dissolved in acetone (125 mL) under Ar atmosphere. Finely powdered K_2CO_3 (19.3 g, 140 mmol) and 3-bromo-1-propyne (15.0 mL, 200 mmol) were added under stirring and the mixture was heated under reflux for 3 h. The mixture was allowed to cool down, H_2O (125 mL) and $CHCl_3$ (125 mL) were added and the phases separated. The aqueous phase was extracted with $CHCl_3$ (3 × 125 mL) and the combined organic phases were washed with 10% NaOH (3 × 100 mL), H_2O (3 × 100 mL) and sat. aq NaCl (3 × 100 mL). The organic phases were dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. Compound **6** was obtained as a pale yellow, analytical pure solid; yield: 17.9 g (94%); mp 56–57 °C. R_f = 0.54 (silica gel; hexane/Et_2O, 1:4; yellow in $SbCl_5/CCl_4$).

HRMS: *m/z*, $C_{11}H_{10}O_3$ calc.: 190.0630; found: 190.0631.

MS (DEI): *m/z* (%) = 190 (M^+, 29), 175 ($M^+ - CH_3$, 11), 159 ($M^+ - OCH_3$, 31), 131 (159-CO, 100), 121 (10), 103 (16).

IR (KBr): ν = 3307 s (alkyne CH), 2148 m (alkyne C≡C), 1724 s (C=O), 1620 s, 1591 m, 1522 m, 1449 s, 1297 vs (acyl CO), 1257 s (aryl CO), 1195 s, 1128 s, 1040 s, (alkyl CO), 865 s (aryl CH), 782 s cm^{-1}.

UV (CH_2Cl_2): λ_{max} (ε) = 251 nm (17060).

^1H NMR ($CDCl_3$): δ = 2.50 (t, J = 2.5 Hz, 1 H, ≡CH), 3.83 (s, 3 H, OCH_3), 4.70 (d, J = 2.5 Hz, 2 H, OCH_2), 6.97 (dd, J_o = 9.0 Hz, J_m = 2.0 Hz, 2 H, HC-3,5), 8.00 (dd, J_o = 9.0 Hz, J_m = 2.0 Hz, 2 H, HC-2,6).

^{13}C NMR ($CDCl_3$): δ = 51.91 (q, 1 C, OCH_3), 55.79 (t, 1 C, OCH_2), 76.13 (d, 1 C, ≡CH), 77.83 (s, 1 C, ≡$\underline{C}CH_2$), 114.46 (d, 2 C, C-3,5), 123.41 (s, 1 C, C-1), 131.53 (d, 2 C, C-2,6), 161.13 (s, 1 C, C-4), 166.66 (s, 1 C, Ar$\underline{C}O_2CH_3$).

1,6-Bis(4-methoxycarbonylphenoxy)hexa-2,4-diyne (7):

Methyl 4-(2-propynoxy)benzoate (**6**; 3.80 g, 20 mmol) was dissolved together with $Cu(OAc)_2 \cdot H_2O$ (20.0 g, 100 mmol) in MeCN (500 mL) under Ar atmosphere and stirred at 60 °C for 1 h. The mixture was allowed to cool down and then diluted with H_2O (750 mL). The precipitate was filtered off, washed with H_2O (250 mL), and dried in the desiccator overnight. The powdered, colorless solid was purified by column chromatography (silica gel; cyclohexane/Et_2O, 1 : 3), whereby **7** was obtained as an analytical pure, colorless solid; yield: 3.13 g (83 %); mp 119 °C. R_f = 0.39 (silica gel; hexane/Et_2O, 1 : 4; yellow in $SbCl_5/CCl_4$).

HRMS: m/z, $C_{22}H_{18}O_6$ calc.: 378.1103; found: 378.1099.

MS (DEI): m/z (%) = 378 (M^+, 5), 347 ($M^+ - OCH_3$, 21), 319 (347-CO, 3), 226 (347-$C_7H_5O_2$, 51), 195 (17), 168 (23), 152 (25), 121 ($C_7H_5O_2$, 100), 93 (14).

IR (KBr): ν = 1724 s (C=O), 1615 s, 1593 w, 1520 w, 1447 m, 1295 s (acyl CO), 1250 vs (aryl CO), 1199 s, 1135 m, 1045 s (alkyl CO), 868 m (aryl CH), 778 s cm^{-1}.

UV (CH_2Cl_2): λ_{max} (ε) = 251 nm (34170).

^1H NMR ($CDCl_3$): δ = 3.87 (s, 6 H, OCH_3), 4.78 (s, 4 H, OCH_2), 6.94 (dd, J_o = 9.2 Hz, J_m = 2.3 Hz, 4 H, HC-3,5), 7.99 (dd, J_o = 9.2 Hz, J_m = 2.3 Hz, 4 H, HC-2,6).

^{13}C NMR ($CDCl_3$): δ = 52.01 (q, 2 C, OCH_3), 56.16 (t, 2 C, OCH_2), 71.34 (s, 2 C, ≡CC≡), 74.15 (s, 2 C, ≡$\underline{C}CH_2$), 114.44 (d, 4 C, C-3,5), 123.67 (s, 2 C, C-1), 131.65 (d, 4 C, C-2,6), 160.95 (s, 2 C, C-4), 166.69 (s, 2 C, Ar$\underline{C}O_2CH_3$).

1,6-Bis{4-[bis(4-methoxyphenyl)hydroxymethyl]phenoxy}hexa-2,4-diyne (8):

Mg shavings (1.22 g, 50 mmol) were treated with 4-bromoanisol (6.25 mL, 50 mmol) in abs. Et_2O (40 mL) under Ar atmosphere and heated 30 min under reflux to obtain the Grignard compound. Then **7** (3.78 g, 10.0 mmol) in solid form was added in small portions (under Ar atmosphere). The mixture was heated again for 30 min under reflux. The mixture was dropped into 20 g ice, treated with sat. aq NH_4Cl (50 mL), diluted with H_2O (200 mL) and shaken with CH_2Cl_2 (100 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 150 mL). The combined organic phases were washed with sat. aq $NaHSO_3$ (3 × 200 mL), sat. aq $NaHCO_3$ (3 × 200 mL), H_2O (1 × 200 mL), sat. aq NaCl (2 × 200 mL), dried (Na_2SO_4) and the solvent was removed under reduced pressure. The crude red oil (ca. 7.2 g) was separated by column chromatography (silica gel; cyclohexane/acetone, 9 : 1, later 4 : 1 and 7 : 3) and yielded 1.74 g (23 %) **8** as a colorless, analytical pure solid with mp 74 °C. R_f = 0.23 (silica gel; hexane/Et_2O, 1 : 4; orange in $SbCl_5/CCl_4$).

FAB-MS (CI): m/z = 747.3 ($[M + H]^+$), 729.3 ($M^+ - OH$).

IR (KBr): ν = 3550 s (br, OH ass.), 1620 s, 1595 m, 1522 s, 1472 w, 1370 w, 1308 m, 1254 vs (aryl CO), 1195 vs, 1131 w (trityl CO), 1047 s (alkyl CO), 925 w, 843 s cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.71 (s, 2 H, Ar_3COH), 3.76 (s, 12 H, OCH_3), 4.71 (s, 4 H, OCH_2), 6.81 (dd, J_o = 9.0 Hz, J_m = 2.5 Hz, 4 H, HC-3',5'), 6.84 (dd, J_o = 8.8 Hz, J_m = 2.5 Hz, 8 H, HC-3,5), 7.14 (dd, J_o = 9.0 Hz, J_m = 2.5 Hz, 4 H, HC-2',6'), 7.17 (dd, J_o = 8.8 Hz, J_m = 2.5 Hz, 8 H, HC-2,6).

^{13}C NMR ($CDCl_3$): δ = 55.23 (q, 4 C, OCH_3), 56.15 (t, 2 C, OCH_2), 71.04 (s, 2 C, ≡CC≡), 74.69 (s, 2 C, ≡$\underline{C}CH_2$), 81.06 (d, 2 C, $Ar_3\underline{C}OH$), 113.12 (d, 8 C, C-3,5), 113.97 (d, 4 C, C-3',5'), 129.05 (d, 8 C, C-2,6), 129.15 (d, 4 C, C-2',6'), 139.55 (s, 4 C, C-1), 140.84 (s, 2 C, C-1'), 156.32 (s, 2 C, C-4'), 158.51 (s, 4 C, C-4).

1,6-Bis{4-[bis(4-methoxyphenyl)methyl]phenoxy}hexa-2,4-diynediylium Bis(tetrafluoroborate) (9):

Compound **8** (74.7 mg, 0.10 mmol) was dissolved in Ac_2O (2.0 mL) and cooled down to 0 °C. 50 % HBF_4 (0.12 mL, 1.0 mmol) was added slowly under stirring, whereby the mixture turned spontaneously orange-red. After stirring for 30 min at 0 °C ice-cold Et_2O (25 mL) was added and the mixture was stirred at 0 °C for 1 h. The red precipitate, **9**, was filtered off, washed with a little bit of cold Et_2O and the solvent was removed in vacuo. Yield: 47.3 mg (53 %); mp 147 °C. R_f = 0.66 (silica gel; EtOH; red in $SbCl_5/CCl_4$).

FAB-MS (CI, *m*NBA): m/z = 864.4 ($[M + m\text{-}O_2N(C_6H_6)CH_2O]^+$), 713.4 ($[M + H]^+$), 356 (cation^{2+}).

MS (DEI): m/z = 68 (BF_3), 49 (BF_2).

IR (KBr): ν = 1620 s, 1451 m, 1380 s, 1285 s, 1188 vs, 1100 m, 1028 m (alkyl CO), 865 m, 775 w (BF_4^-), 539 m (BF_4^-) cm^{-1}.

UV (CH_2Cl_2): λ_{max} (ε) = 263 (37000), 486 nm (110000).

^1H NMR (CD_2Cl_2): δ = 4.09 (s, 12 H, OCH_3), 5.09 (s, 4 H, OCH_2), 7.28 (dd, J_o = 8.5 Hz, J_m = 2.5 Hz, 8 H, HC-2,6), 7.33 (dd, J_o = 9.0 Hz, J_m = 2.5 Hz, 4 H, HC-2',6'), 7.57 (dd, J_o = 9.0, J_m = 2.5 Hz, 4 H, HC-3',5'), 7.58 (dd, J_o = 8.5 Hz, J_m = 2.5 Hz, 8 H, HC-3,5).

^{13}C NMR (CD_2Cl_2): δ = 57.39 (q, 4 C, OCH_3), 57.68 (t, 2 C, OCH_2), 71.93 (s, 2 C, ≡CC≡), 73.94 (s, 2 C, ≡$C\underline{H}C_2$), 116.82 (d, 8 C, C-3,5), 116.92 (d, 4 C, C-3',5'), 132.32 (s, 4 C, C-1), 132.98 (s, 2 C, C-1'), 142.52 (d, 4 C, C-2',6'), 143.47 (d, 8 C, C-2,6), 167.53 (s, 4 C, C-4), 171.21 (s, 2 C, C-4'), 193.01 (d 2 C, $Ar_3\underline{C}^+$).

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