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Unusual Transformation of the Diarylmethanol Derivative into an Unknown 1,2,3,6,7,10-Hexahydroxylated Anthracene System

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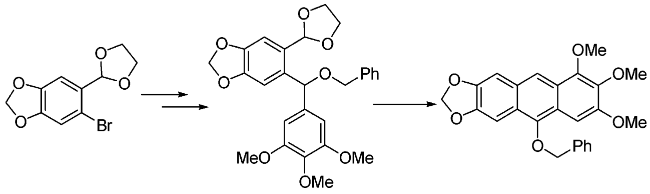
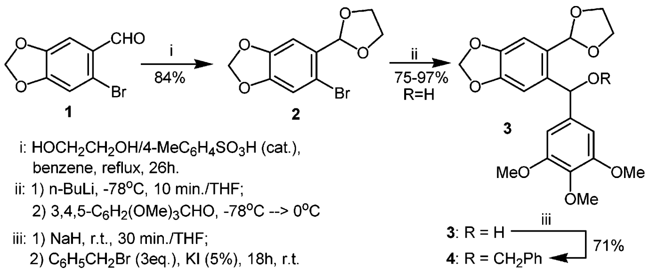
Received December 19, 2005



10-Benzyloxy-1,2,3-trimethoxy-6,7-(methylene-1,3-dioxy)anthracene as a potential material for molecular electronics was synthesized from the *O*-benzyl-protected diarylmethanol derivative containing the 1,3-dioxyethylene acetal function via a one-pot procedure under acidic conditions (1 N HCl, methanol, 60 h) in 60% yield. The replacement of methanol for benzene resulted in hydrolysis of the acetal function in 96% yield.

Increasing interest in ultrapure and structurally perfect crystals and thin layers of π-conjugated molecular semiconductors, such as polycyclic aromatic hydrocarbons (anthracene, tetracene, and pentacene), is connected with their potential application as active elements in new generations of relatively cheap optoelectronic devices, e.g., the field-effect transistors and light-emitting diodes.[1−4] Physical properties of these compounds, unlike traditional inorganic semiconducting materials requiring multiple processing steps, may be simply tailored through chemical modification. Some anthracene derivatives prepared as thin layers, such as 9,10-di-(2-naphthyl)anthracene (ADN),[5−7] 9,-10-diphenylanthracene (DPA) and its derivatives containing *tert*-butyl groups [2-*tert*-butyl-9,10-diphenylanthracene, 2-*tert*-butyl-9,10-di(4-*tert*-butylphenyl)anthracene],[8−10] 9,10-bis(3′,5′-diaryl)-phenylanthracene (JBEM),[11] rotaxane of methyl-*exo*-pyridineanthracene,[12,13] 2,3,6,7-tetramethyl-9,10-dinaphthylanthracene (TMADN),[14] 2,6-bis(4-trifluoromethylphenyl)anthracene,[15] and 2,6-dithienylanthracene,[15] have been intensely investigated as light-emitting materials in multilayer electroluminescence diodes.

SCHEME 1. Synthesis of *O*-Benzyl-Protected Diarylmethanol 4 from 6-Bromopiperonal 1



In investigations on materials for molecular electronics, we needed diarylmethanols with the protected OH function and free benzaldehyde group starting from 6-bromopiperonal **1**. Because an attempt to introduce the 3,4,5-trimethoxyphenyl group in a one-pot procedure using the Kuroda et al. protocol[16] gave a complex mixture of unidentified compounds, a protection of the aldehyde group in **1** with ethylene glycol to give **2** was necessary (Scheme 1).

Because of varying reports[17−19] concerning the reaction time (from 8 to 48 h for reactions of a similar scale), the protection reaction was monitored with ^{1}H NMR. In our hands, it required 26 h for completion to give **2** on a multigram scale and in almost 100% purity. The Br/Li exchange reaction in the latter with *n*-BuLi/*n*-hexane in a THF solution to give **2**−Li followed by condensation with 3,4,5-trimethoxybenzaldehyde afforded the

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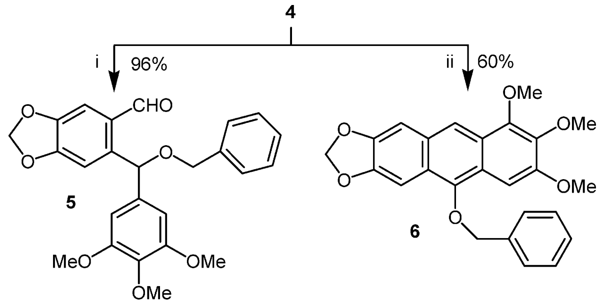
SCHEME 2. Differentiated Reactivity of 4 toward 1 N HCl



i: 1N HCl, benzene, reflux, 18h; ii: 1 N HCl, MeOH, r.t., 60h

diarylmethanol **3** in 75−97% yield. Synthesis of **3** via the corresponding Grignard reagent **2**−MgBr in THF[18] and via **2**−Li in ether/THF[20,21] solutions was also described. Protection of the OH group with benzyl bromide in the presence of KI (5%) afforded **4** in 71% yield. Selective hydrolysis of the acetal function in the latter was carried out in benzene with 1 N HCl at 80 °C within 18 h to give the required diarylmethanol derivative **5** with the free aldehyde group in 96% yield (Scheme 2).

However, when the hydrolysis was carried out with 1 N HCl in MeOH (room temperature, 18 h), 10-benzyloxy-1,2,3-trimethoxy-6,7-(methylene-1,3-dioxy)anthracene **6** as a well-crystallizing solid was unexpectedly formed in nonoptimized 38% yield accompanied by the substrate **4** (33% yield) (Scheme 2). Prolongation of the reaction time to 60 h gave **6** in 60% yield. When MeOH was replaced by *i*-PrOH, only **4** was present in the reaction mixture under the same reaction conditions (60 h, room temperature, 1 N HCl). In acetone (60 h, room temperature, 1 N HCl), the anthracene **6**, the aldehyde **5**, and unidentified impurities were formed in a ratio of 3.7:1:1.5 (**6**: 59% yield). The result in THF (60 h, room temperature, 1 N HCl) was similar to that obtained in refluxing benzene (Scheme 2): **6**/**5**/**4** = 1:8.4:3 (**5**: 67% yield; **6**: 8% yield). Shortening of the reaction time to 1 h was possible in refluxing MeOH (**6**: 50% yield; no **4** and **5**) or *i*-PrOH (**6**: 44% yield; no **4** and **5**).

The compound **6** is the first representative of the 1,2,3,6,7,-10-hexahydroxylated anthracene system protected with three different protecting groups. Formation of 10-hydroxy-1,2,3-trimethoxy-6,7-(methylene-1,3-dioxy)anthracene, based on the mass molecular peak only, was postulated by Galletti et al. as a possible byproduct in the 800 °C pyrolysis reaction leading to an isobenzofuran derivative.[22]

The plausible explanation of this interesting transformation includes a primary formation of benzyl carbocation **7** and its intramolecular Friedel−Crafts-type cyclization to give σ-complex **8**. In the next step, a new benzyl carbocation **10** formed after removal of the glycol molecule from **9** undergoes aromatization to the new anthracene system **6** which was separated as a well-crystallizing solid (Scheme 3). The loss of a proton from **8** can be alternatively effected via 1,4-elimination of ethylene glycol; however, this mechanistic proposal requires a protonation of the glycol moiety oxygen and formation of the doubly charged intermediate.

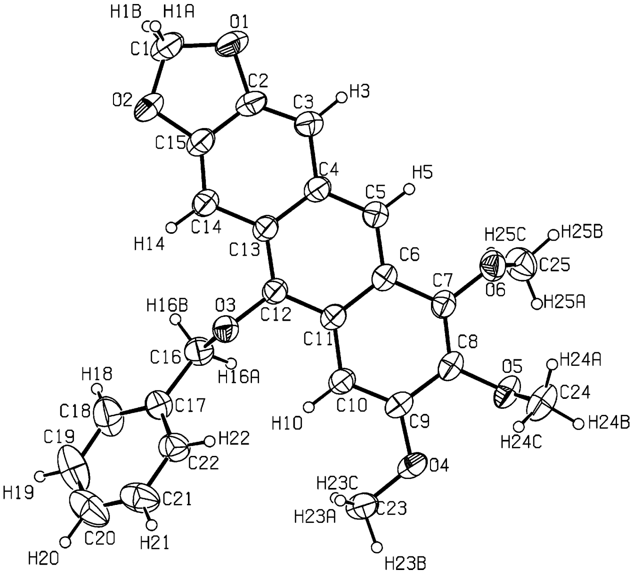
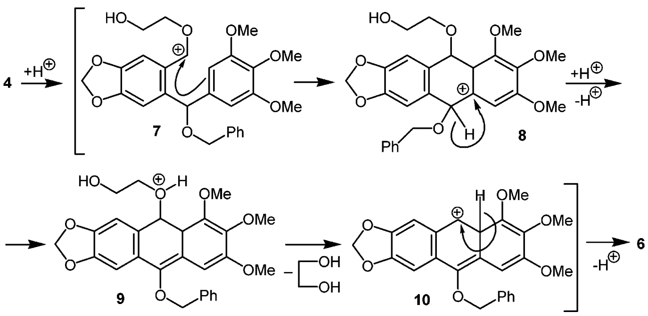


FIGURE 1. Perspective view of **6**, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level, and H atoms are shown as small spheres of arbitrary radii.

SCHEME 3. Mechanistic Proposal for the Formation of the Anthracene 6 from 4



The anthracene **6** crystallizes in the triclinic P$\bar{1}$ space group with two molecules per unit cell. The anthracene and dioxolane rings as a whole are essentially planar with the largest deviations from the best least-squares plane of 0.028(2) Å for atom C5 (Figure 1). Methoxy atoms O4, O5, O6, and C23 and also benzyloxy atom O3 are nearly coplanar. The dihedral angle between the phenyl ring plane and the plane formed by anthracene and dioxolane rings is 51.8(1)°. There are two intramolecular contacts of type C−H···O involving (1) atoms C5−H5 and O6 (C5−H5 = 0.93, H5···O6 = 2.50, and C5···O6 = 2.822(2) Å and C5−H5···O6 = 100.4°) and (2) atoms C25−H25A and O5 (C25−H25A = 0.96, H25A···O5 = 2.49, and C25···O5 = 3.066(3) Å and C25−H25A···O5 = 118.8°). The crystal packing of **6** is stabilized by a C−H···O intermolecular hydrogen bond, with C16−H16A = 0.97, H16A···$O5^{(i)}$ = 2.49, and C16···$O5^{(i)}$ = 3.238(3) Å and C16−H16A···$O5^{(i)}$ = 134.2° (symmetry code: (i) −*x*, −*y*, 1 − *z*) (Figure 2). This intermolecular hydrogen bond forms the $R_2^2(18)$ graph-set[23] dimer. The dimeric units are connected via the intermolecular C−H···π hydrogen bond between C23 and H23A atoms of the molecule at (*x*, *y*, *z*) and a benzene ring formed by atoms C4−C6/C11−C13 (Cg3) of the molecule at (1 − *x*, −*y*, 1 − *z*); the

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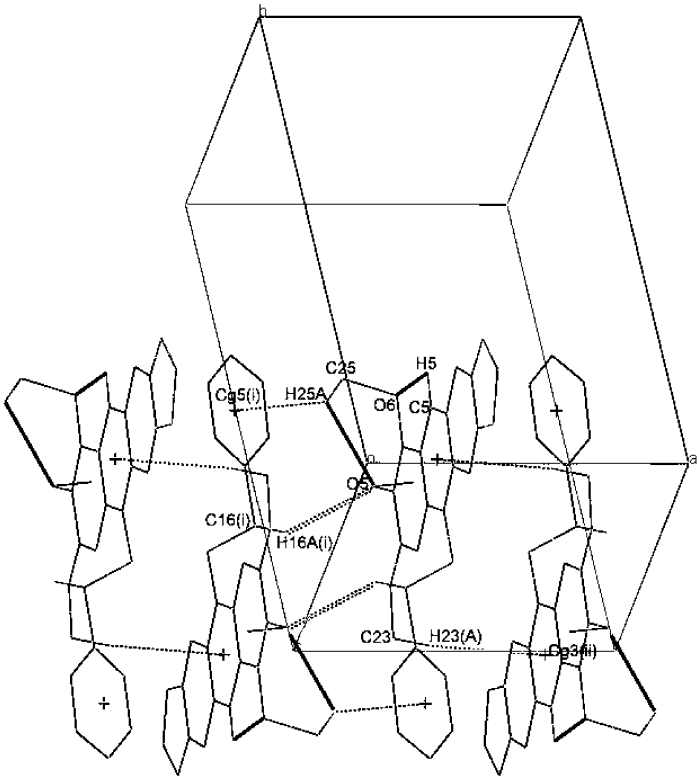

FIGURE 2. Part of the crystal structure of **6**, showing the intermolecular hydrogen bond C−H···O (double dashed line) forming the $R_2^2(18)$ graph-set dimer, the intramolecular C−H···O contacts (bold line), and the intermolecular C−H···π interactions (dashed line). The Cg3 and Cg5 centroids of C4−C6/C11−C13 and C17−C22 benzene rings, respectively, are denoted by crosslets. H atoms, except for atoms H5, H16A, H23A, and H25A have been omitted for clarity.

H23A···Cg3 and C23···Cg3 distances are 2.87 and 3.770(3) Å, respectively, and the C−H···Cg angle is 156°.

As a concluding remark, the first isolated representative of the unknown 1,2,3,6,7,10-hexahydroxylated anthracene system was synthesized in a one-pot unexpected transformation from the diarylmethanol derivative. This compound is a potential material for molecular electronics.

Experimental Section

Crystallographic Data of 6: $C_{25}H_{22}O_6$, $M = 418.43$, triclinic, $P\bar{1}$, $a = 7.985(2)$ Å, $b = 11.404(2)$ Å, $c = 12.996(3)$ Å, $\alpha = 113.74(3)°$, $\beta = 92.24(3)°$, $\gamma = 104.11(3)°$, $V = 1038.0(5)$ Å, $Z = 2$ molecules per unit cell, $D_c = 1.339$ g/cm^3, $F(000) = 440$, crystal size of 0.40 × 0.30 × 0.28 mm. Diffraction data were collected at 293(2) K, using a diffractometer with graphite-monochromated Cu Kα radiation ($\lambda = 1.54178$ Å) and a $\omega/2\theta$ scan mode to $\theta = 67.90°$. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with SHELXL-97.[24] Carbon and oxygen atoms were refined anisotropically, and hydrogen atoms were introduced at calculated positions as riding atoms, with C−H distances in the range 0.93−0.97 Å. The three free variables for U_{iso}(H) were refined according to SHELXL97:[24] R1 = 0.055, wR2 = 0.149, $S = 1.057$ for 3161 with $I > 2\sigma(I)$ unique reflections and 287 parameters. Further details on the crystal structure investigation have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 289080.

5-[Benzyloxy(3,4,5-trimethoxyphenyl)-methyl]-6-[1,3]dioxolan-2-yl-benzo[1,3]dioxole 4. To a suspension of NaH (0.155 g, 3.89 mmol, 60% in mineral oil) and KI (0.181 mmol, 30 mg) in dry THF (5 mL) was added a solution of **3** (1.38 g, 3.54 mmol) in THF (10 mL) at room temperature. The resulting mixture was stirred for 30 min. Then benzyl bromide (1.82 g, 10.62 mmol) in THF (2 mL) was added, and stirring was continued for 18 h at the same temperature. After evaporation of the solvent, the residue was diluted with ethyl acetate (100 mL) and washed with water (2 × 20 mL). The organic layer was dried ($MgSO_4$) and then filtered, and the solvent was removed to leave a pale yellow oil which was purified by column chromatography (petroleum ether/EtOAc in a gradient as an eluent) (yield 71% (1.27 g)). **4**: $R_f = 0.45$ (*n*-hexane/ethyl acetate 1:1 v/v); ^{1}H NMR (C_6D_6, 200 MHz) δ 3.23−3.58 (m, 4H), 3.39 (s, 6H), 3.81 (s, 3H,), 4.52 (d$_{AB}$, $^2J_{HH} = 12.1$ Hz, 1H), 4.62 (d$_{AB}$, $^2J_{HH} = 12.1$ Hz, 1H), 5.17−5.24 (m, 2H), 5.97 (s, 1H), 6.07 (s, 1H), 6.97 (s, 2H), 7.02−7.37 (m, 5H), 7.29 (s, 1H), 7.36 (s, 1H); ^{13}C NMR (CD_2Cl_2, 50 MHz) δ 56.2, 60.6, 65.37, 65.42, 70.8, 77.3, 101.1, 101.7, 104.2, 106.5, 107.4, 127.8, 128.1, 128.6, 128.8, 129.7; 135.3; 137.8; 138.8 147.4; 148.8; 153.5. MS (EI, 70 eV) − *m*/*z*(%): 389 (M(−$PhCH_2$), 40); 372 (M(−$PhCH_2$-OH), 56), 344 (M(−$PhCH_2OH$, −CH_2CH_2), 75), 327 (M(−$PhCH_2$-OH, −CH_2CH_2OH), 35), 313 (M(−$C_6H_2(OCH_3)_3$), 19), 221 (M(−$C_6H_2(OCH_3)_3$, −$PhCH_3$), 47), 177 (M(−$C_6H_2(OCH_3)_3$, −$PhCH_3$, −CH_2CH_2OH), 100); MS (CI, isobutane) − *m*/*z* (%) 481 (M + 1, 6), 420 (M + 1(−OCH_2CH_2OH), 9), 374 (M + 1(−$PhCH_2O$), 100), 314 (M + 1(−$PhCH_2O$, −OCH_2CH_2O), 3); HR MS (EI, 70 eV) −480 (M, 24); calcd for $C_{27}H_{28}O_8$ 480.17842, found 480.17872.

6-[Benzyloxy-(3,4,5-trimethoxyphenyl)-methyl]-benzo[1,3]-dioxole-5-carbaldehyde 5. The compound **4** (0.617 g, 1.285 mmol) was dissolved in benzene (35 mL), and then an aqueous solution of 1 N HCl (15 mL) was added. The mixture was vigorously stirred in a Schlenk tube at 80 °C in an inert atmosphere (argon) for 18 h. After addition of additional an amount of benzene (50 mL), the solution was washed with water (3 × 10 mL). The organic layer was dried, and the benzene was removed in vacuo. Column

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[24] Sheldrick, G. M. *SHELXL97*; University of Göttingen: Germany, 1997.

chromatography (*n*-hexane/ethyl acetate) of the residue gave 0.54 g (96%) of the aldehyde **5** as a pale yellow oil. **5**: $R_f = 0.55$ (hexane/ethyl acetate 2:1 v/v), $R_f = 0.75$ (petroleum ether/ethyl acetate 1:1 v/v in a gradient as an eluent); ^{1}H NMR (C_6D_6, 200 MHz) δ 3.38 (s, 6H), 3.79 (s, 3H), 4.46−4.47 (m, 2H), 5.14−5.18 (m, 2H), 6.44 (s, 1H), 6.83 (s, 2H), 7.04−7.38 (m, 5H), 7.19 (s, 1H), 7.35 (s, 1H), 10.08 (s,1H); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.81 (s, 6H), 3.83 (s, 3H), 4.53 (d_{AB}, $^2J_{HH} = 11.7$ Hz, 1H), 4.60 (d_{AB}, $^2J_{HH} = 11.7$ Hz, 1H), 6.05−6.06 (m, 2H), 6.22 (s, 1H), 6.62 (s, 2H), 7.10 (s, 1H), 7.26−7.35 (m, 6H), 10.11 (s, 1H); ^{13}C NMR (C_6D_6, 50 MHz) δ 56.5, 61.1, 71.9, 78.6, 102.7, 105.7, 109.0, 111.2, 129.0, 129.4, 129.7, 138.0, 139.3, 139.6, 142.6, 148.6, 153.3, 155.0, 190.2; ^{13}C NMR (CD_2Cl_2, 50 MHz) δ 56.2, 60.6, 71.3, 78.0, 102.7, 104.5, 108.4, 109.6, 128.0, 128.1, 128.7, 128.8, 137.2, 138.3, 141.5, 147.9, 152.8, 153.7; the signal due to the *C*-CHO is covered by signals of the $OCH_2C_6H_5$ group both in CD_2Cl_2 and C_6D_6; MS (CI, isobutane) *m*/*z*(%) 437 (M+1, 1), 419 (M + 1(−H_2O), 5), 345 (M(−$PhCH_2$), 30), 329 (M(−$PhCH_2OH$), 100); MS (CI, isobutane) *m*/*z*(%) 437 (M + 1, 1), 419 (M + 1(−H_2O), 5), 345 (M(−$PhCH_2$), 30), 329 (M(−$PhCH_2OH$), 100); HR MS (CI, isobutane) 437 (M + 1, 1), 436 (M, 1); calcd for $C_{25}H_{25}O_7$ (M + H) 437.16002, found 437.15840.

10-Benzyloxy-1,2,3-trimethoxy-6,7-(methylene-1,3-dioxy)anthracene 6. The compound **4** (0.05 g, 0.104 mmol) was dissolved in MeOH (5 mL), and then an aqueous solution of 1 N HCl (1 mL) was added. The mixture was stirred at ambient temperature for 60 h. The reaction mixture was extracted with ethyl acetate (20 mL), and the organic layer was washed with water (5 mL), $NaHCO_3$ aq (5 mL), and again with water (5 mL) and then dried over anhydrous $MgSO_4$. After filtration, the solvents were removed in vacuo to give a pale orange solid. The crude product was purified with column chromatography (*n*-hexane/ethyl acetate or petroleum ether/acetone) to give 26 mg of pure anthracene **6** (yield 60%). **6**: $R_f = 0.55$ (petroleum ether/ethyl acetate 3:1 v/v); $R_f = 0.85$ (petroleum ether/ethyl acetate 1:1 v/v); mp = 146−148 °C; ^{1}H NMR (C_6D_6, 200 MHz) δ 3.40 (s, 3H), 3.86 (s, 3H), 3.96 (s, 3H), 4.98 (s, 2H), 5.26 (s, 2H), 7.06−7.45 (m, 5H), 7.32 (s, 1H), 7.77 (s, 1H), 8.51 (s, 1H); ^{1}H NMR (CD_3CN, 200 MHz) δ 3.86 (s, 3H), 3.90 (s, 3H), 4.04 (s, 3H), 5.10 (s, 2H), 6.04 (s, 2H), 7.17 (s, 1H), 7.26 (s, 1H), 7.36−7.64 (m, 5H), 8.17 (s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 55.7, 61.2, 61.4, 76.4, 95.4, 97.0, 101.0, 103.3, 115.0, 121.7, 122.4, 124.0, 127.9, 128.2, 128.7, 128.9, 137.6, 140.3, 147.2, 147.4, 148.0, 148.9, 152.5; MS (CI, isobutane) − *m*/*z* (%) 419 (M + 1, 100), 327 (M(−$PhCH_2$), 79); HR MS (CI, isobutane) 419 (M + 1, 100); calcd for $C_{25}H_{23}O_6$ (M + H) 419.14946, found 419.14919.

Supporting Information Available: Characterization data for compounds **2** and **3**, ^{1}H/^{13}C NMR spectra of compounds **2**−**6**, crystallographic data of **6** (CIF), and full crystallographic discussion on **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO052599X