Anodic Oxidation of 2,6-Dihydroxynaphthalene[1] and Structural Characterization of the Oligomers

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Potential-controlled electrochemical oxidation of 2,6-dihydroxynaphthalene (**1**) produced two oligomers, which were characterized by spectrometric (^{1}H and ^{13}C NMR, IR, and UV) and electrochemical (CV) methods. The ^{1}H NMR chemical shifts of the peracetyl derivatives, which showed different values for the acetoxy groups attached at the terminal and the internal positions of the chain, were essential for structure determination of the products. Peracetyl derivatives of the monomer **1a**, dimer **2a**, and two stereoisomeric trimers **3a** and **4a** served as models in the spectrometric characterization and structure determination of the oligomers. The product isolated from the anolyte was a mixture of oligomers **5** composed of an average of nine monomer units. The spectroscopic data for the product extracted from the anode **6** suggested that its molecular weight was much higher. In all investigated compounds, the naphthalene rings were proven to be linked at the 1- and 5-positions. The solubility and the spectroscopic data of both oligomers suggested that the chains were not cross-linked. Similar cyclic voltammetric (CV) behavior was found for poly(2,6-dihydroxynaphthalene) films prepared either by the dip-coating technique from a solution of **6** or by the previously reported electrochemical deposition from a solution of **1** by the potential-scanning technique.[2]

Introduction

The study of poly(2,6-dihydroxynaphthalene) reported in this article originated from our search for new polymeric materials with tunable π-electron systems. A polymer with a built-in quinone–quinole functionality satisfies such requirements. Previously, we reported a cyclic voltammetry (CV) study of a poly(2,6-dihydroxynaphthalene) film electrochemically deposited on a glassy carbon electrode (GCE) from a solution of **1**.[2] This study suggested that the expected primary product of the oxidation of **1**, the 2,6-naphthoquinone (2,6-NQ), is not formed, and instead a polymeric film is deposited at the electrode surface. Preparation of 2,6-NQ by oxidation of **1** with PbO_2 in strictly anhydrous medium has been claimed.[3] However, the product was not characterized, and repetition of the procedure in our laboratory was unsuccessful. A dimer and a tetramer were the only products of the chemical oxidation of **1** in a protic medium.[4] The dimer was also reported[5] to be formed by an electrochemical oxidation of **1**. In this case the product was isolated by extracting the carbon-cloth anode with benzene. The ^{1}H NMR data of the trimethylsilyl derivative were consistent with the dimeric structure. On the basis of the CV data, hydroxylation of **1** to afford 1,2,6-trihydroxynaphthalene (1,2,6-THN) was suggested to occur when the scan range was extended toward higher positive potentials.[5] However, the structure of the dimer and the oligomers, the position of the linkage between the naphthalene units in particular, has never been studied.

In two reports[2,5] 2,6-NQ was suggested as a transient intermediate in the oxidative coupling of **1**. Similar behavior has been reported for 5,6-indolequinone. Generated from 5,6-dihydroxyindole, it spontaneously polymerizes to a black melanoid pigment.[6] The destabilized π-electron system is the likely driving force for the polymerization of such highly reactive quinones.

Our study involves preparative electrochemical oxidation of **1** and spectroscopic study of the primary products and their peracetyl derivatives. Compared to the chemical oxidation, the electrochemical oxidation allowed for better control of the experimental conditions and made easier the isolation of the products. This paper also includes detailed spectroscopic studies of **1**, 2,6,2′,6′-tetrahydroxy-1,1′-binaphthalene (**2**), two stereoisomeric 2,6,2′,6′,2″,6″-hexahydroxy-1,1′: 5′,1″-ternaphthalenes (**3** and **4**), and their peracetyl derivatives (**1a, 2a, 3a,** and **4a**) which served as models in the structure determination of the oligomers (Figure 1).

The electrochemical properties of the larger oligomer deposited in the form of a film at a solid electrode were studied using CV. This study allowed comparison of the electrochemical properties of the poly(2,6-ND) prepared using controlled-potential and potential-scanning techniques.[2]

Results and Discussion

Synthesis. The model compounds, dimer **2** and trimers **3** and **4**, were prepared by means of a literature procedure.[4] The reaction of **1** with $FeCl_3$ resulted in a complex mixture of **2** and numerous oligomers as indicated by TLC. Pure **2** was isolated by preparative TLC as an amorphous material, which slowly polymerized in the air. Treatment of **1** with $FeCl_3$ or I_2 (1 equiv) followed by acetylation produced a complex mixture from which a stable peracetyl derivative of the dimer **2a** was isolated

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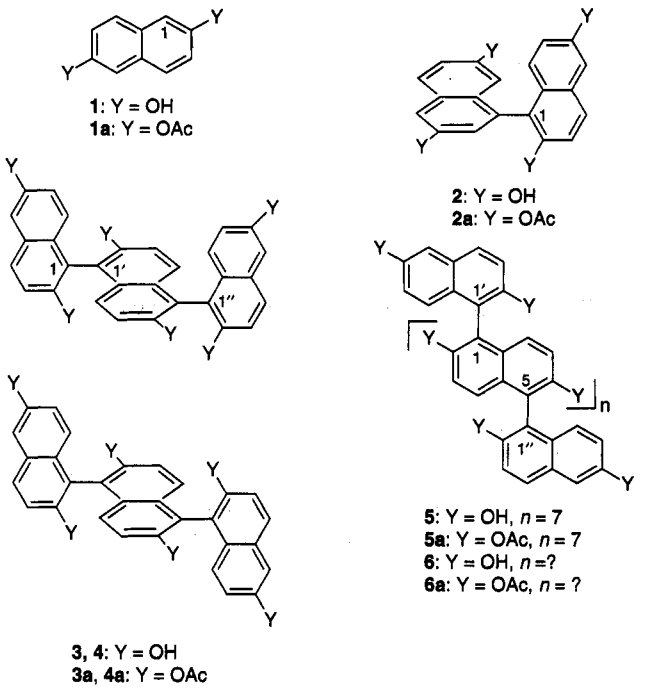

Figure 1.

by means of silica gel column chromatography. From another fraction, a mixture of peracetylated trimers was separated by preparative TLC, and in a repeated run one of the stereoisomers was isolated in pure form.

The CV of **1** in 0.2 M $HClO_4$ presents a well-defined anodic peak at E_p 0.55 V and a cathodic peak whose peak potential and peak current are strongly affected by the initial substrate concentration and other experimental conditions.[7] Similar results were reported from measurements carried out under slightly different conditions.[2,5] In the preparative electrolysis of **1** the potential was controlled at 0.6 V vs SCE. A large carbon-cloth anode and a two-compartment cell filled with a 0.2 M $HClO_4$–t-BuOH (3:1) electrolyte constituted the hardware. The electrolysis was terminated after the consumption of two electron equivalents. A solid (**5**) was precipitated from the anolyte with water in 30% yield (after drying with P_2O_5). The product was white and ethanol soluble and turned slowly dark green on the air. A second product (**6**) was recovered by continuous extraction of the anode with ethanol. Evaporation of this solution produced a green transparent film in a 46% yield. This material was only slightly soluble in ethanol but easily soluble in $(Me)_2SO$ or 1 M NaOH. The low R_f of both products when compared with that of model compounds **2**–**4** and the spectroscopic data (*vide infra*) suggest that **5** and **6** are the homooligomers of **1**.

Spectroscopic Studies. Model compounds **1**–**4**, oligomers **5** and **6**, and their peracetyl derivatives **1a**, **2a**, **3a**, **4a**, **5a**, and **6a** were studied using UV, IR, and ^1H, and ^{13}C NMR. The data for the peracetyl derivatives are summarized in Tables 1 and 2. ^1H NMR chemical shifts of the acetoxy group hydrogens proved to be particularly useful for determining the connectivity of the naphthalene units in the dimer and the oligomers. Whereas CH_3COO- in **1a** shows only one signal at 2.35 ppm, two signals of equal integration are found for **2a**. One of these signals is identical with that in **1a**; the second is shifted 0.46 ppm upfield. For explaining the upfield shift, the conformation of the naphthalene rings plays an essential role. On the basis of studies of the closely related 2,2′-dihydroxy-1,1′-binaphthalene in both the solid phase[10] and in solution,[11] it is assumed that in the largest populated conformation of **2a** the rings are oriented approximately perpendicular to each other. In such a conformation, the acetoxy group hydrogens in positions 2 and 2′ (i.e., adjacent to the 1,1′-linkage) experience the shielding effect of the ring current of the adjacent aromatic π-electron ring system.[9] The aromatic hydrogens of **2a** were assigned through a homonuclear *J*-correlated spectroscopic experiment (^1H ^1H COSY). The observed ABX and AB systems support the structure of a dimer in which the naphthalene units are linked at the 1- and 1′-positions. In qualitative agreement with the conformation assumed for **2a**, the H8 and H7 signals are shifted 0.63 and 0.21 ppm upfield, respectively, whereas

Table 1. ^1H NMR Chemical Shifts (ppm) Relative to Internal TMS ($CDCl_3$)

H	1a	2a	3a	4a	5a[a]	6a[a]
H1	7.56					
H3	7.25	7.43	7.48	7.49		
H4	7.80	7.94	7.98	7.98		
H5	7.56	7.68	7.71	7.70		
H7	7.25	7.04	7.15	7.09		
H8	7.80	7.17	7.36	7.23		
H3′,H7′			7.23	7.23		
H4′,H8′			7.35	7.33		
upfield −OOCMe		1.88[b]	1.85[d]	1.84[d]	1.87[f]	1.88[f]
			1.83[d]	1.94[d]	1.99[f]	2.00[f]
regular −OOCMe	2.35	2.34[c]	2.37[c]	2.36[e]	2.39[g]	

[a] Numbering starts on the central naphthalene unit. Chemical shifts correspond to acetoxy group methyl hydrogens at the carbons listed in *b*–*g*. [b] C2. [c] C6. [d] C2, C2′, C6′, and C2″. [e] C6 and C6″. [f] C2, C6, C2′, and C2″. [g] C6′ and C6″.

Table 2. ^{13}C NMR Chemical Shifts (ppm) Relative to Internal TMS ($CDCl_3$)

carbon	1a	2a	3a	4a	5a[a]	6a[a]
C1	118.6	123.0	123.6	123.6	123.7	123.7
C2	148.3	146.7	146.9	146.9	147.0	147.0
C3	122.0	122.8	122.9	123.0	123.2	123.1
C4	129.1	129.3	129.5	129.5	128.0	128.0
C5	118.6	118.8	119.0	119.0	123.7	123.7
C6	148.3	148.4	148.1	148.6	147.0	147.0
C7	122.0	122.0	122.3	122.3	122.3	123.1
C8	129.1	127.8	127.9	127.7	128.0	128.0
C9	131.5	131.2	131.4	131.5	131.5	131.5
C10	131.5	132.0	132.0	132.1	131.5	131.5
C3′,C7′			123.0	123.0		
C4′,C8′			127.9	127.9		
2-OOCMe	21.2	20.6	20.5[b]	20.5[b]	20.4[c]	20.5[c]
			20.6[b]	20.6[b]	20.6[c]	20.7[c]
6-OOCMe	21.2	21.2	21.3[d]	21.3[d]	21.2[c]	
−CO−	169.5	169.4	169.1	169.5	169.0	169.2
			169.2			
			169.5			

[a] Numbering starts on the central naphthalene unit. [b] −OOCMe at C2, C2′, C6′, and C2″. [c] −OOC*Me* at C2 and C6 (chain units). [d] −OOC*Me* at C6 and C6″. [e] −OOC*Me* at C6′ and C6″ (terminal units).

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the value of the chemical shift for H4 is close to the value corresponding to the H4 and H8 hydrogens in **1a**.

The chemical shift data of the *dimer* were corroborated using the theoretical Boveys model,[9] which has been developed for estimation of the chemical shift of hydrogens interacting with a benzene ring. For the application to 2,2′-dihydroxy-1,1′-binaphthalene, on the basis of crystallographic data,[10] the origin was placed in the center of the ring carrying the hydroxy groups, and a 90° dihedral angle was assumed. In this model H_8 and H_7 reside in the field of only one of the two naphthalene rings. The calculation predicts upfield shifts for H_8 and H_7 of 0.78 ppm (ϱ = 1.34 ru (radii units), z = 1.87 ru) and 0.18 ppm (ϱ = 2.22 ru, z = 3.39 ru), respectively. These values are in reasonable agreement with the observed upfield shift data.

The five dominant peaks in the ^{13}C NMR spectrum of **2a** were assigned to the unsubstituted aromatic carbons through a heteronuclear $^{13}C-^{1}H$ chemical shift correlation experiment (^{1}H ^{13}C COSY) (optimized for $^{1}J_{HC}$, 160 Hz). In comparison with those of **1a** the chemical shifts for C8 and C3 of **2a** (1.3 ppm downfield and 0.8 ppm upfield, respectively) are notably affected. The low-intensity signal at 123.0 ppm is assigned to the quaternary C1 for which a larger relaxation time should be expected. Further support for the assignment of C1 was obtained from a long-range ^{1}H ^{13}C COSY experiment in which the $^{3}J_{HC}$ (optimized for 8.0 Hz) was tuned in. A cross peak between this peak and H3 results from the long-range C−H coupling.

Peaks at 20.6 and 21.2 ppm in **2a** are assigned to the methyl carbons of the acetoxy groups in the positions 2,2′ and 6,6′, respectively. The ^{13}C spectrum is similar to the ^{1}H NMR spectrum, in that the upfield-shifted signal corresponds to the acetoxy group methyl carbon atoms in the 2 and 2′ positions, which are affected by the adjacent aromatic ring magnetic field; the 6 and 6′ acetoxy carbons are identical in chemical shift to those of **1a**. Both the ^{1}H and ^{13}C NMR spectral data, especially those involving the acetoxy groups, support structure **2a** in which the naphthalene moieties are linked at the 1- and 1′-positions.

^{1}H NMR spectrum of the peracetylated *trimer* presents three groups of singlets in the aliphatic region (at 2.36 and 2.37, at 1.94, and at 1.85, 1.84, and 1.83 ppm) in an approximately 2:1:3 ratio. The 2.36- and 2.37-ppm signals correspond to the acetoxy groups of the terminal naphthalene units, and there are two rather distinct groups of signals that belong to the acetoxy groups attached to the central ring. These data, combined with the results from the TLC, suggest that the sample is a mixture of two atropisomeric trimers that differ in the relative orientation of the terminal naphthalene rings with respect to the plane of the central ring. Repeated separation using a preparative TLC silica gel plate and a benzene−chloroform mixture (3:2) allowed isolation of the isomer with a higher R_f (**3a**) in pure form. The second isomer **4a** could not be isolated in pure form, and its spectrum was obtained by subtracting the peaks of **3a** from those of the mixture. Similar to those of **2a**, the chemical shifts for the ring hydrogen and carbon atoms of **3a** and **4a** were assigned through ^{1}H ^{1}H COSY and ^{1}H ^{13}C COSY experiments.

In agreement with the postulated C1 and C5 linkage between the naphthalene rings, the hydrogens of the central ring, H3′, H7′ and H4′, H8′ were found to be magnetically equivalent for both stereoisomers. Whereas both **3a** and **4a** showed identical chemical shifts for H3′, marginally different chemical shifts (δ = 0.02 ppm) were found for H4′.[12] In both trimers, H7 and H8 of the terminal rings are more deshielded than the corresponding hydrogens in **2a**, with the largest downfield shift (0.19 ppm) observed for **3a**. Most likely, this effect results from different dihedral angles between the central and the terminal rings in **3a** and **2a**. The Bovey model calculated for these trimers predicts maximum upfield shifts for H8 and H7 (90° dihedral angle).

In **3a** the hydrogens of the internal acetoxy groups in positions 2, 2′, 6′, and 6″ appear as two singlets (1.85 and 1.83 ppm) that correspond to those for C2 in **2a** (1.88 ppm). Unlike those of **3a**, the chemical shifts of these hydrogens in **4a** are more different (1.84 and 1.94 ppm). The expected 2:1 integrated signal ratio for the shielded and unshielded acetyl group hydrogens (near 2.36 ppm for the latter) is found in both species. ^{13}C NMR spectra of both trimers are quite similar. As expected, C3′, C7′ and C4′, C8′ show identical chemical shifts for both isomers. In each isomer, C3′ and C4′ appear as single signals around 122.9 and 127.9 ppm, respectively. In general, the ^{1}H and ^{13}C NMR data are consistent with the postulated structures for **3a** and **4a** with the naphthalene rings coupled in 1- and 5-positions. The data, however, do not allow identification of the individual stereoisomers.

For determining their structure, it is necessary to consider **5** and **6** as a mixture of oligomers of unknown population of individual species. The structural information available from the ^{1}H NMR spectra of **5** and **6** in DMSO is very limited because of the broad unresolved peaks in the aromatic region that are typical for macromolecular species.[12] The peaks corresponding to water and protic organic solvents observed even after extensive drying suggest a notable capacity of these compounds to strongly adsorb small polar molecules.

For structure determination of **5a** and **6a** the spectral data were correlated with those of **1a, 2a, 3a,** and **4a**. The ^{1}H NMR spectrum of **5a** in $CDCl_3$ (Table 1) shows three broad peaks in the aliphatic region. The peak at 2.39 ppm (compared to 2.34 ppm in **1a**) is assigned to the external acetoxy group protons at the C6 positions of the terminal naphthalene rings. The peaks at 1.88 and 2.00 ppm attributed to the hydrogens of the internal acetoxy groups are similar to those found for the acetoxy groups in **3a** and **4a**. This observation suggests that the oligonaphthalene chain is built randomly with no respect to the tacticity.

An 8.5 ± 0.5 ratio (obtained from five measurements) of integrated ^{1}H signals of the external *vs* the internal acetoxy groups suggests a 9−10 naphthalene unit species representing the "average" oligomer. A molecular weight of 1787 obtained for **5a** by vapor pressure methods ($CHCl_3$ solvent, Galbraith Laboratories) corresponds to an average of 7−8 monomer units for **5a**. This information is in a fair agreement with the data obtained with the spectroscopic method considering that the sample is a mixture. The absence of the terminal naphthalene acetoxy groups suggests that **6a** is a much larger oligomer than **5a**.

The ^{13}C NMR spectra ($CDCl_3$) of acetyl derivative **5a** and **6a** are similar and are characterized by only two

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larger peaks at 123.2 and 128.0 ppm. These peaks are assigned to C3′, C7′ and C4′, C8′, respectively, by correlation with shifts observed in **3a**. Both oligomers lack the signal at 118.8 ppm that in **2a** is attributed to C5. In **5a** and **6a** such carbons are located in the terminal naphthalene rings. A minor peak at 123.7 ppm is identical to that assigned to the C1 carbon in **3a**. Compound **5a** shows a signal at 21.2 ppm, which is also found in **2a** and **3a** and is assigned to the acetoxy group methyl carbons at C6 of the terminal naphthalene units. Similar to those of the acetyl hydrogens in the ^{1}H NMR spectrum, the signals corresponding to the methyl carbons of the terminal rings are also absent in the ^{13}C spectrum of **6a**.

The IR spectra of **5** (KBr pellet) and the free-standing film of **6** were very similar. Both materials present a band at 824 cm^{-1} corresponding to a C−H out-of-plane bending vibration that is characteristic of two adjacent hydrogens in the 3,4- and 7,8-positions of β-substituted naphthalenes.[13] The absence of a characteristic band at 878 cm^{-1} attributed to the C1 and C5 hydrogens of the naphthalene ring confirms that the monomer units are connected through these carbons. The absence of the carbonyl band at 1637 cm^{-1} that is observed in the IR spectrum of polyjuglone[14] indicates that both oligomers exist in their reduced forms. The similarity of the IR spectra of **5** and **6** suggests that the two compounds differ in molecular weight only.

The UV spectra (EtOH) of oligomers **5** and **6** are quite similar to those of **2** and **1**, except that **6** shows a tail absorption between 380 and 450 nm. The 346-nm band in **1** shifts slightly bathochromically with increasing number of the monomer units in the chain (to 356 nm in **2** and to 366 nm in **5**). Similar to the data for β-naphthol and bis-β-naphthol reported by Brandt,[15] the UV data of the compounds under investigation suggests that because of a large dihedral angle, the conjugation of two neighboring naphthalene rings is limited.

Cyclic Voltammetric Studies. A film deposited on a GCE by dipping in a solution of **6** (saturated solution in EtOH or $(Me)_2SO$) was electroactive in an acidic aqueous medium. The cyclic voltammograms showed E_{pa} and E_{pc} at 0.58 and 0.54 V, respectively (i_{pc}/i_{pa} = 0.85). These values are similar to those observed for the first cycle of the CV of a dilute solution of **1** (E_{pa}, E_{pc} at 0.56 and 0.53 V, respectively, i_{pc}/i_{pa} = 0.45).[7] The lower i_{pc}/i_{pa} ratio for the solution experiment results from the high reactivity of the 2,6-NQ, which is quickly consumed in a follow-up polymerization process. Cyclic voltammetry of **1** in a dilute solution shows another redox couple corresponding to 1,2,6-trihydroxynaphthalene/6-hydroxy-1,2-naphthoquinone which appears at less positive potentials. This product forms through a nucleophilic addition of water at the 2,6-naphthoquinone. However, repetitive scanning of the dip-coated poly(2,6-dihydroxynaphthalene) film at potentials extended up to 1.0 V did not produce a new redox couple. Evidently, the small number of the terminal naphthalene units in the oligomer prevents it from showing such a signal.

The film electrochemically deposited on a GCE by repetitive scanning (7.5 × 10^{-5} M solution of **1** in 0.2 M $HClO_4$)[2] presents E_{pa} and E_{pc} at 0.58 and 0.52 V, respectively (i_{pc}/i_{pa} = 0.80). This behavior is quite similar to that of the poly(2,6-dihydroxynaphthalene) film electrode prepared by the dip-coating procedure using the solution of **6**. This similarity suggests that materials of identical electrochemical properties, and probably also composition, can be prepared either by the constant potential electrolysis using a large carbon-cloth electrode or by the potential scanning technique using a small GCE.

Conclusions

The reported experiments suggest that the smaller oligomer, **5**, and the larger oligomer, **6**, isolated from preparative electrooxidation of **1** formed through different mechanisms. The former resulted from the polymerization of the primary electrooxidation product, 2,6-NQ, in the bulk solution. Thus, under the hydrodynamic conditions, the quinone was carried away from the electrode surface and reacted in the bulk solution. The growth of the oligomer in the bulk solution was then limited by its solubility in the medium. However, the mechanical stirring was unable to remove all the quinone from the electrode, and polymerization of the quinone retained at the electrode surface and the deposition of the film resulted. This mechanism is analogous to the deposition of a polymeric film using the potential scanning method at a stationary GCE in the CV experiment. The large surface of the anode used in the preparative experiment and the conductivity of the polymer allow deposition of relatively large quantities of the product. The solubility of both **5** and **6** in certain organic solvents suggests that neither oligomer is cross-linked.

CV with a glassy carbon electrode dip coated with **6** showed electroactivity corresponding to the quinole/quinone redox couple. Such electroactivity is preserved only when the naphthalene rings are coupled by C−C rather than C−O bonds. Detailed ^{1}H, and C^{13} NMR, IR, and UV spectroscopic studies of peracetyl derivatives **1a**, **2a**, **3a**, **4a**, **5a**, and **6a** clearly showed that the naphthalene units are linked via carbon atoms in positions 1 and 5. These data indicate that the polymerization of 2,6-NQ under controlled-potential electrolysis conditions proceeded uniformly and without side reactions. In particular, the constant potential electrolysis did not provide conditions suitable for hydroxylation of the terminal 2,6-naphthoquinone units observed at the stationary electrode. Evidently, the polymerization of 2,6-NQ was faster than the nucleophilic addition of water.

That the two new oligomers, **5** and **6**, carry an easily electrochemically tunable extended π-electron system suggests various potential applications for modern electronics and photonics. Their solubility in organic solvents makes these materials easily processible.

Experimental Section

General Methods. Melting points were obtained on a Fisher-Johns melting point apparatus and were uncorrected. The NMR spectra were recorded on a Bruker AM-300 WB NMR spectrometer (operating at 300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C) using Me_4Si as internal standard. For determination of signal area, a 4-s relaxation delay was allowed. 2D experiments were carried out using the software provided by the manufacturer [COSY.AUR (16 scans, 128 × 1 K) and XHCORR.AUR (64 or 128 scans, 128 × 1 K) for ^{1}H ^{1}H COSY and ^{1}H ^{13}C COSY experiments, respectively]. Regular and long-range ^{1}H ^{13}H COSY were tuned for $^1J_{HC}$ (160 Hz) and $^3J_{HC}$

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(8.0 Hz), respectively. IR spectra were recorded on a MIDAC FTIR spectrophotometer. UV/vis spectra were recorded on an HP 8452A diode array UV/vis spectrophotomer. Mass spectra (70 and 30 eV EI) were obtained on a Finnigan-MATCH5-DF mass spectrometer. Electrochemical measurements were carried out with an IBM EC 225 voltammetric analyzer with an IBM 7424MT X-Y-T recorder. Glassy carbon (0.07 cm^2) and Ag/AgCl from Bioanalytical Systems were used as working and reference electrodes, respectively, and a Pt wire was used as the auxiliary electrode. [Experiments with a RDE were performed with a IBM rotating disk electrode controller EC 219 and a glassy carbon electrode.] Preparative-scale anodic oxidations were performed at controlled potential using an ESC 410 potentiostatic controller equipped with an ESC 420 power unit. Current integrations were obtained with a homemade coulometer designed and built by William H. Craig, Chemistry Department, Georgetown University. When not stated otherwise, all the experiments were carried out at room temperature in aqueous solutions.

Reagents and Chromatographic Methods. Compound **1** was purified by crystallization from toluene. All the other reagents were of analytical quality and were used without further purification. Graphite-cloth anode (WCA) was obtained from National Carbon & Graphite. Silica gel IB-F (Baker-flex) plates were used for all the TLC experiments. For all TLC experiments the reported values correspond to R_f, eluent, and stationary phase, unless stated otherwise. Kieselgel 60 F_{254} TLC plates (Merck) were used for the preparative separations. Silica gel 60-100 mesh (Fisher) was used for the column chromatography.

Cyclic Voltammetry. A 25-mL cell was used for all the experiments. In a typical run, the appropriate quantity of a 3.75×10^{-2} M stock solution of the substrate in CH_3CN was added to 10 mL of 0.2 M $HClO_4$. The solution was magnetically stirred for 5 min; then Ar was bubbled in for 5 min, and the Ar atmosphere was maintained throughout the experiment. The working electrode was abraded with a slurry of 0.05-μm γ-alumina (Buehler Ltd.) in water deposited on a MICROCLOTH (Buehler Ltd.) polishing cloth and rinsed thoroughly with water. Unless stated otherwise, all the reported voltammograms correspond to the first cycle recorded immediately after the working electrode was polished. Films on the glassy carbon electrode were made by (a) repeated potential scanning between 0 and 0.8 V at 100 mV s^{-1} of **1** (7.5×10^{-5} M in 0.2 M $HClO_4$ solution degassed with N_2) (such film was stable after washing with H_2O and EtOH, but was removed with Me_2CO); and (b) dip coating of the glassy carbon electrode in a solution of **6** (8 mg/10 mL) in DMSO or saturated solution of **6** in EtOH.

Synthesis of 2,2′,6,6′-Tetraacetoxy-1,1′-binaphthalene (2a). By means of the reported procedure,[4] **2a** was synthesized by oxidation of **1** with $FeCl_3$ or I_2 (1 equiv). The reaction mixture was acetylated using the acetic anhydride–sodium acetate method, and the target product was separated by column chromatography (Silica gel, benzene–chloroform mixture as eluent); mp 187–187.5 °C. IR (KBr): 1763, 1610, 1514, 1373, 1198, 893, 825 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.88 (6H, s, 2 and 2′ COMe), 2.34 (6H, s, 6 and 6′ CO*Me*), 7.04 (2H, dd, J = 8.95 Hz, J' = 2.26 Hz, H7 and H7′), 7.17 (2H, d, J = 9.1 Hz , H8, H8′), 7.43 (2H, d, J = 9.06 Hz, H3, H3′), 7.68 (2H, d, 2.2 Hz, H5, H5′), 7.94 (2H, d, J = 9.0 Hz, H4,H4′). ^{13}C NMR ($CDCl_3$): δ 20.6 (2 and 2′ CO*Me*), 21.2 (6 and 6′ CO*Me*), 118.8 (C5, C5′), 122.0 (C7, C7′), 122.8 (C3, C3′), 123.0 (C1), 127.8 (C8, C8′), 129.3 (C4, C4′), 131.2 (C9, C9′), 132.0 (C10, C10′), 146.7 (C2, C2′), 148.4 (C6, C6′), 169.3, 169.4 (*C*OMe at 2, 2′, 6, 6′). MS (20 eV): *m/z* 486 (0.1%, M^+), 444 (1.5%, $M^+ - CH_2{=}C{=}O$, 443 (7%, M^+ – MeCO), 402 (11%, $M^+ - 2CH_2{=}C{=}O$), 360 (9%, $M^+ - 3CH_2{=}C{=}O$), 318 (12%, $M^+ - 4CH_2{=}C{=}O$).

Isolation of Isomeric 2,2′,2″,6,6′,6″-Hexahydroxy-1,1′:5′,1″-Ternaphthalenes (3a and 4a). Two hundred milligrams of the acetylated mixture produced by the $FeCl_3$ oxidation of **1** were spotted on two preparative TLC plates. After four successive elutions with $CHCl_3$ the zone of R_f 0.59–0.66 was scraped off and stripped with ethanol. The extract was concentrated under vacuum, and the residue was applied to a new preparative TLC plate. After repetitive elutions with a benzene–chloroform (1:1) mixture, two close zones and that residing on the application line were separated and stripped with ethanol. Further concentration of the material extracted from the higher R_f zone produced a quantity of **3a** that was sufficient for NMR characterization. Subtraction of ^1H NMR spectrum of this product from that of the mixture obtained from the first chromatographic separation allowed us to obtain the spectrum of **4a**. The relative areas of the acetoxy hydrogens of this mixture indicated a 1:1 mixture of **3a** and **4a**. **3a**: ^1H NMR ($CDCl_3$) δ 1.85, 1.83 (12H, s, 2 and 2′-,6′-, and 6″-CO*Me*), 2.37 (6H, s, 6- and 6″-CO*Me*), 7.15 (2H, dd, J = 9.2 Hz, J' = 2.5 Hz, H7 and H7″), 7.23 (2H, d, J = 9.2 Hz, H3′, H7′), 7.34 (2H, d, J = 9.0 Hz, H4, H8′), 7.36 (2H, d, J = 9.2 Hz, H8, H8″), 7.48 (2H, d, J = 8.8 Hz, H3, H3″), 7.71 (2H, d, J = 2.3 Hz, H5, H5″), 7.99 (2H, d, J = 8.9 Hz, H4, H4″). **4a**: ^1H NMR ($CDCl_3$) δ 1.84, 1.94 (12H, s, 2 and 2′-, 6′-, and 6″-CO*Me*), 2.36 (6H, s, 6- and 6″-CO*Me*), 7.09 (2H, dd, J = 9.2 Hz, J' = 2.4 Hz, H7 and H7″), 7.23 (2H, d, J = 8.9 Hz, H3′, H7′), 7.23 (2H, d, J = 9.0 Hz, H8, H8″), 7.33 (2H, d, J = 10.0 Hz, H4′, H8′), 7.49 (2H, d, J = 9.0 Hz, H3, H3″), 7.70 (2H, d, J = 2.8 Hz, H5, H5″), 7.98 (2H, d, J = 9.0 Hz, H4, H4″). ^{13}C NMR spectra data for both products are reported in Table 2.

Anodic Oxidation of 1. The two-compartment electrolytic cell, an amber beaker (150 mL) with a porous cup (8- × 2.5-cm diameter) fixed in the center, was placed on a magnetic stirrer. A 3- × 10-cm graphite-cloth anode supported with a polystyrene net was placed outside the cup, and the cathode (Pt wire) was placed inside the cup. A saturated calomel reference electrode was placed near the anode. The electrolyte was a 7:3 0.2 M $HClO_4$–*tert*-butyl alcohol mixture that in the working compartment contained 1 mmol of **1** in a 100-mL volume. All the experiments were carried out at 0.6 V. After consuming ca. 190 C, the anolyte was filtered and diluted with 1 L of water. The white fine precipitate was centrifuged off, and the solid was washed with water and dried under vacuum to give **5** (48 mg, 30%). Compound **5** was soluble in acetone and ethanol and became black after prolonged storage in the air; mp > 270 °C. IR (KBr): 3500–3000, 1592, 1505, 1375, 1332, 1202,1144, 968, 816 cm^{-1}. UV: λ_{max} (EtOH) 228, 286 (sh), 366 nm. A peracetylated derivative, **5a**, was prepared by refluxing **5** (100 mg) with an large excess of $(Ac)_2O$ and NaOAc for 2 h. After the usual workup, a white solid was obtained, mp > 270 °C. IR (KBr): 3033, 2936, 1769, 1609, 1513, 1367, 1198, 887, 820, 759 cm^{-1}. ^1H NMR data ($CDCl_3$) is presented in Table 1, and ^{13}C NMR data ($CDCl_3$, 14501 scans) in Table 2. The anode was washed with water and extracted continuously with acetone or ethanol. A dark green transparent film, **6** (73 mg, 46%), was obtained after the solvent was stripped in vacuum. Compound **6** is slightly soluble in Me_2SO, EtOH, and Me_2CO and forms a dark green solution when dissolved in 1 M NaOH; mp > 270 °C. IR (free standing film): ν 3500–3000, 1601, 1512, 1387, 1343, 1213, 1150, 970, 824 cm^{-1}. UV: λ (EtOH) 230, 288 (sh), 368, and a tail absorption at 400–480 nm. ^1H NMR (Me_2SO) δ (ppm): 7.9 (wide), 6.8–7.5 (aromatic hydrogens), also present bands corresponding to Me_2CO, EtOH, and *tert*-butyl alcohol. The acetyl derivative **6a** was prepared by the procedure described for **5a**; mp > 270 °C. IR (KBr): ν 4000–3000 (weak), 1767, 1651, 1556, 1512, 1371, 1190, 1018, 881, 817 cm^{-1}. ^1H NMR data are presented in Table 1, ^{13}C NMR ($CDCl_3$, 65111 scans) in Table 2.

Supplementary Material Available: Copies of ^1H NMR spectra of **2a**, **3a**, (**3a** and **4a**), **5a**, and **6a**; copies of ^{13}C NMR spectra of **3a**, **5a**, and **6a**; copies of 2D NMR spectra of **2a** and **3a** (13 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.