The Chemistry of 1,6-Dioxapyrenes Part 3 [1,2]: Scope and Limitations of an Acid Catalyzed Ring-closing Reaction

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One of the few methods for synthesis of 1,6-dioxapyrenes is the acid catalyzed cyclization of 2,6-disubstituted 1,5-bis(2-oxoalkoxy)naphthalenes. The scope and limitations of this reaction has been investigated and 11 new 2,7-disubstituted 1,6-dioxapyrenes have been prepared and characterized. Most of the compounds undergo two reversible oxidations to give the corresponding radical as well as di- cations.

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The 1,6-dioxapyrenes are a family of redox active heterocyclic compounds, which undergo two reversible one-electron oxidations to give first a radical cation (**1**$^{+\bullet}$) and finally the closed shell dication (**1**$^{2+}$), which is isoelectronic with pyrene (Figure 1). For a recent discussion of aromaticity in dioxapyrenes see [3].

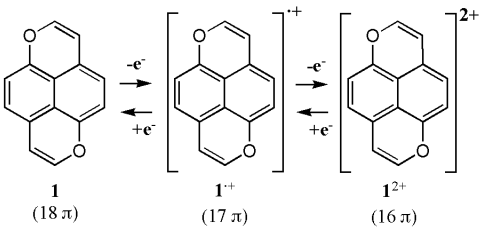
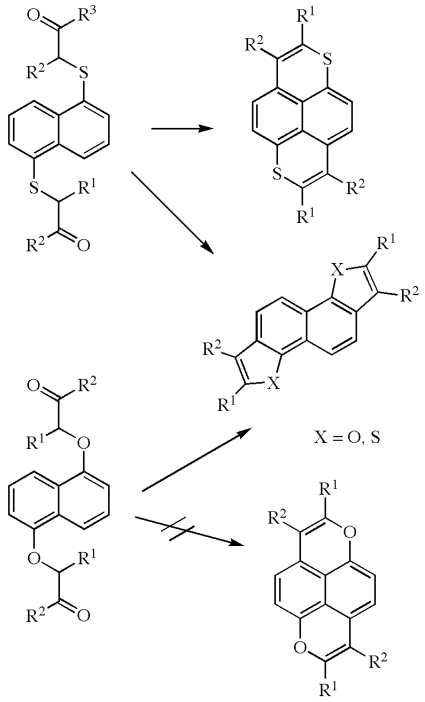


Figure 1

Heterocyclic analogues of pyrene have been used in the study of conducting molecular solids, where materials with properties ranging from semiconductors in the case of 1,6-dioxapyrenes to metals in the case of 1,6-dithiapyrenes have been prepared and studied[4-6]. Although 1,6-dioxa- and 1,6-dithiapyrenes are very similar in structure, there is a substantial difference in the synthetic methodologies for their synthesis. 1,6-Dithiapyrenes and/or thieno[2,3-*f*]-naphthothiophenes are obtained by the acid catalyzed cyclization of bis(2-ketoethylmercapto)naphthalenes [7,8]. The same strategy applied for bis(2-ketoethoxy)naphthalenes gives furo[2,3-*f*]naphthofuranes as the only product regardless of the conditions [9,10]. (Scheme 1).

Two different strategies for solving this problem have been devised. Strategy 1 relies on the intermediacy of 1,4,5,8-tetrasubstituted napthhalenes, which are generally difficult to synthesise due to the peri-strain [2,11], where strategy 2 takes advantage of the use of alkyl substitution in the 2 and 6-positions of the naphthalene ring to prevent ring closure to the furane (Scheme 1) [1]. We wanted to investigate the scope and limitations of this last approach.

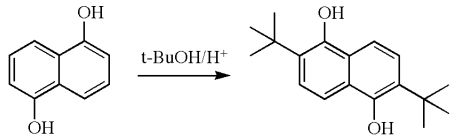
Scheme 1



Results and Discussion.

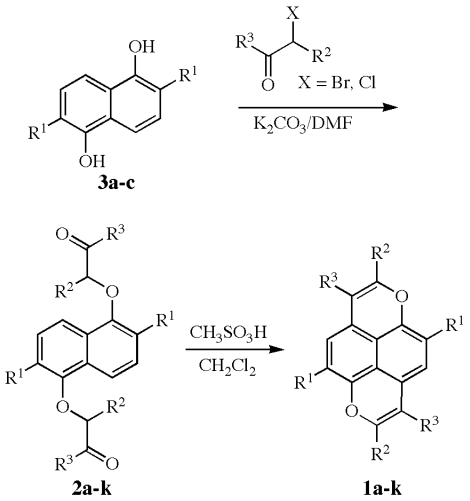
2,6-Dibromo-1,5-dihydroxynaphthalene (**3a**) [12] and 2,6-dimethyl-1,5-dihydroxynaphthalene (**3b**) [1] were prepared according to the literature. 2,6-Di-*t*-butyl-1,5-dihydroxynaphthalene (**3c**) was prepared in 30% yield by Friedel-Crafts alkylation of 1,5-dihydroxynaphthalene with *t*-butyl alcohol in a mixture of phosphoric acid and acetic acid according to the directions given in the patent [13] (Scheme 2). Since no evidence for the structure was given, the structure was proven by comparison with 3,7-di-*t*-butyl-1,5-dihydroxynaphthalene prepared according to Schmand, Kratzin and Boldt [14]. The synthesis of the 1,6-dioxapyrenes is shown in Scheme 3.

Scheme 2



3c

Scheme 3



3a-c **2a-k** **1a-k**

The alkylation with haloketones was carried out under standard conditions (K_2CO_3/DMF) [1] to give the β-ketoethers (**2a-k**) in good yields. The haloketones used were either bromo- or chloroketones, these were either commercially available or prepared according to the literature. Cyclization was performed under standard conditions (10% CH_3SO_3H in CH_2Cl_2) [1]. The 1,6-dioxapyrenes prepared are shown in Table 1.

Of the bromo substituted materials only the tetrasubstituted 2,7-dibromo-1,6-dioxapyrene (**1a**) could be made. Attemps to prepare other 2,7-dibromo-1,6-dioxapyrenes failed even under forcing conditions (CH_3SO_3H/$(CF_3CO)_2O$, 100% CH_3SO_3H with or without heating lead only to decomposition). Another limitation was found in the series of 4,9-diphenyl substituted 1,6-dioxapyrenes. β-Ketoethers with strongly electron withdrawing groups such as 4-nitrophenyl or 4-methylsulfonyl or spacefilling substitution such as 2,4,6-trimethylphenyl did not cyclize. Bulky aliphatic substituents on the naphthalene does not prevent cyclization as seen with the *t*-butyl substituted 1,6-dioxapyrenes (**1c** – **1e**). We also found in general, no difference in yield from cyclization of crude versus pure β-ketoethers (**2a** – **k**), so in most cases purification of the β-ketoethers was omitted before cyclization.

The donor properties of the substituted 1,6-dioxapyrenes were investigated by cyclic voltammetry. The compounds investigated undergo two one-electron oxidations, and the oxidation potentials are collected in Table 2.

All the dioxapyrenes except **1g** and **1k** undergoes two reversible one electron oxidations at relatively low potentials vs SCE confirming the expected good donor properties of the 1,6-dioxapyrenes investigated. Theoretical calculations by Kataoka and Sato [3] have identified the HOMO of the parent 1,6 dioxapyrene as a delocalised pi orbital and thus some substituent effects are to be expected. We find that the first oxidation potentials $E_1^{1/2}$ are slightly sensitive to the substitution pattern on the 1,6-

Table 2

Electrochemical Data

Compound	$E_1^{1/2}$ (V) vs SCE	$E_2^{1/2}$ (V) vs SCE	ΔE (V)
1a	0.51	1.07	0.56
1b	0.22	0.92	0.70
1c	0.12	0.72	0.60
1d	0.22	0.88	0.66
1e	0.24	0.91	0.67
1f	0.21	0.84	0.63
1g	0.23	Not well defined	-
1h	0.30	0.91	0.61
1i	0.30	0.69	0.66
1j	0.44	Not reversible	-
1k	0.45	1.40	0.95

Table 1

Compounds Prepared

Compound no.	R^1	R^2	R^3	Yield (%)
1a	Br	CH_3	CH_3	11
1b	Bu^t	H	CH_3	13
1c	Bu^t	CH_3	CH_3	28
1d	Bu^t	H	Bu^t	11
1e	CH_3	H	Bu^t	5
1f	CH_3	H	4-CH_3-Ph	11
1g	CH_3	H	4-CH_3O-Ph	17
1h	CH_3	H	4-$(CH_3)_2N$-Ph	2
1i	CH_3	H	2-F-Ph	12
1j	CH_3	H	4-F-Ph	29
1k	CH_3	H	4-Cl-Ph	26

dioxapyrene system (from +0.12 V to +0.51 V vs SCE) but not in a systematic manner, *i.e*. reflecting the relative electrondonating properties of the substituents. The second oxidation corresponding to the formation of the dication, which occurs at potentials from 0.56 V to 0.95 V more positive than the respective first oxidation. Again no obvious correlation either with molecular size or substitution pattern can be observed.

Conclusion.

We have shown that acid catalyzed cyclization of 2,6-disubstituted 1,5-bis(2-oxoethoxy)naphthalenes is a fairly general method for the preparation of substituted 1,6-dioxapyrenes. However the method is only of limited use in the case of electron withdrawing groups on the naphthalene precursor, and thus alternative synthetic strategies are needed for these types of compounds.

EXPERIMENTAL

2,7-Dibromo-4,5,9,10-tetramethyl-1,6-dioxapyrene (**1a**).

General Procedure for Cyclization Reactions.

A mixture of 3.60 g (**2a**) (7.9 mmol), 40 mL CH_2Cl_2 and 5 mL CH_3SO_3H was stirred at RT overnight. The dark blue mixture was poured into a separation funnel containing 250 mL 2 *M* NaOH, 5 g $Na_2S_2O_4$ and 500 mL CH_2Cl_2, and was shaken until the color didn't change further. An emulsion formed, that was broken by addition of EtOH. The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by column chromatography on Silicagel 60 (0.040 – 0.063 mm) with toluene as eluent to give 0.37 g (11%) of **1a**. An analytical sample crystallized from toluene had mp. > 260 ºC; ^{1}H nmr (carbondisulfide): δ 1.49 (s, 6 H), 1.76 (s, 6 H), 6.21 (s, 2 H).

Anal. Calcd. For $C_{18}H_{14}Br_2O_2$: C, 51.22; H, 3.34. Found: C, 50.72; H, 3.25.

2,7-Di-t-butyl-4,9-dimethyl-1,6-dioxapyrene (**1b**).

Crude 2,6-di-*t*-butyl-1,5-bis(2-oxo-1-propoxy)naphthalene (**2b**) prepared according to the general procedure from **3c** and 1-chloro-2-propanone was cyclized as described for **1a** with the exception, that the reaction mixture was refluxed overnight. The crude compound was crystallized from toluene to give **1b** as yellow crystals in 13 % yield (from **3c**) with mp. 235 – 237 ºC (dec.); ^{1}H nmr (carbondisulfide/deuteriomethylenechloride): δ 0.29 (s, 18 H), 0.76 (s, 6 H), 5.30 (s, 2 H), 5.33 (s, 2 H); ^{13}C nmr (carbondisulfide/deuteriomethylenechloride): δ 12.9, 29.0, 33.5, 112.6, 113.9, 122.3, 127.2, 138.9, 148.1; MS (EI): 348 (M^+), 333, 318, 288, 152, 131.

Anal. Calcd. For $C_{24}H_{28}O_2$: C, 82.72; H, 8.10. Found: C, 82.43; H, 8.21.

2,7-Di-*t*-butyl-4,5,9,10-tetramethyl-1,6-dioxapyrene (**1c**).

Crude 2,6-di-*t*-butyl-1,5-bis(3-oxo-2-butoxy)naphthalene (**2c**) prepared according to the general procedure from **3c** and 3-bromo-2-butanone [15] was cyclized as described for **1b** with the exception, that the CH_2Cl_2 was removed *in vacuo* leaving a suspension of material in water, which was extracted with hot (50 ºC) toluene. The hot toluene-phase was separated, dried over $MgSO_4$ and filtered. The pure **1c** crystallized from toluene upon cooling in 28 % yield (from **3c**) as yellow crystals with mp. 312 ºC (dec.); ^{1}H nmr (carbondisulfide/deuteriomethylenechloride): δ 0.39 (s, 18 H), 0.80 (s, 6 H), 1.04 (s, 6 H), 5.33 (s, 2 H); MS (EI): 376 (M^+), 346, 316, 167, 145.

Anal. Calcd. For $C_{28}H_{32}O_2$: C, 83.06; H, 8.57. Found: C, 82.94; H, 8.57.

2,4,7,9-Tetra-*t*-butyl-1,6-dioxapyrene (**1d**).

Crude 2,6-di-*t*-butyl-1,5-bis(3,3-dimethyl-2-oxo-1-butoxy)-naphthalene (**2d**) prepared according to the general procedure from **2a** and 1-bromo-3,3-dimethyl-2-butanone [16] was cyclized as described for **1b** to give **1d** in 11 % yield (based on **3c**) as yellow crystals with mp. >250 ºC (dec.); ^{1}H nmr (carbondisulfide/deuteriomethylenechloride): δ 1.23 (ds, 36 H), 6.21 (s, 2 H), 6.64 (s, 2 H); MS (EI): 432 (M^+).

Anal. Calcd. For $C_{30}H_{40}O_2$: C, 83.29; H, 9.32. Found: C, 83.49; H, 9.40.

2,7-Dimethyl-3,8-bis(2,2-dimethylethyl)-1,6-dioxapyrene (**1e**).

This compound was prepared from **2e** by the general procedure in 5 % yield as an orange powder; Mp. 223-225 ºC; ^{1}H nmr (carbondisulfide/deuteriomethylenechloride): δ 1.22 (s, 18 H), 1.90 (s, 6 H), 6.14 (s, 2 H), 6.42 (s, 2 H); MS(EI): 348 (M^+), 318, 131.

Anal. Calcd. For $C_{24}H_{28}O_2$: C, 82.72; H, 8.10. Found: C, 82.90; H, 8.13.

2,7-Dimethyl-3,8-bis(4-methylphenyl)-1,6-dioxapyrene (**1f**).

Crude 2,6-di-methyl-1,5-bis(1-(4-methylphenyl)-1-oxo-2-ethoxy)naphthalene (**2f**) prepared according to the general procedure from 2,6-dimethyl-1,5-dihydroxynaphthalene [1] and 2-bromo-1-(4-methylphenyl)ethanone [17] was cyclized as described for **1a** to give **1f** in 17 % yield (based on **3b**) as yellow crystals with mp. 236-238 ºC (dec.); ^{1}H nmr (carbondisulfide): δ 1.80 (s, 6 H), 2.35 (s, 6 H), 5.98 (s, 2 H), 6.06 (s, 2 H), 7.09 (s, 6 H); MS (EI): 416 (M^+), 208.

Anal. Calcd. For $C_{30}H_{24}O_2$: C, 80.34; H, 5.39. Found: C, 80.32; H, 5.46.

2,7-Dimethyl-3,8-bis(4-methoxyphenyl)-1,6-dioxapyrene (**1g**).

Crude 2,6-di-methyl-1,5-bis(1-(4-methoxyphenyl)-1-oxo-2-ethoxy)naphthalene (**2g**) prepared according to the general procedure from 2,6-dimethyl-1,5-dihydroxynaphthalene [1] and 2-bromo-1-(4-methoxyphenyl)ethanone [18] was cyclized as described for **1a** to give **1g** in 17 % yield (based on **3b**) as yellow crystals with mp. 241-243 ºC (dec.); ^{1}H nmr (carbondisulfide): δ 1.61 (s, 6 H), 3.56 (s, 6 H), 5.77 (s, 2 H), 5.85 (s, 2 H), 6.59 (d, J = 8.5 Hz, 4 H), 6.90 (d, J = 8.5 Hz, 4 H); MS (EI): 448 (M^+), 433, 390, 224, 203.

Anal. Calcd. For $C_{30}H_{24}O_4$: C, 80.34; H, 5.39. Found: C, 80.32; H, 5.46.

2,7-Dimethyl-3,8-bis(4-(*N*,*N*-dimethylamino)-phenyl)-1,6-dioxapyrene (**1h**).

Crude 2,6-di-methyl-1,5-bis(1-(4-(*N*,*N*-dimethylamino)-phenyl)-1-oxo-2-ethoxy)naphthalene (**2h**) prepared according to the general procedure from 2,6-dimethyl-1,5-dihydroxynaphthalene [1] and 2-bromo-1-(4-(*N*,*N*-dimethylamino)-phenyl)-ethanone [20,21] was cyclized as described for **1a** to give **1h** in 2

% yield (based on **3b**) as yellow crystals with mp. >260 ºC; ^{1}H nmr (carbondisulfide): δ 1.60 (s, 6 H), 2.75 (s, 12 H), 5.80 (s, 2 H), 5.82 (s, 2 H), 6.39 (d, J = 8.8 Hz, 4 H), 6.82 (d, J = 8.8 Hz, 4 H); MS (EI): 474 (M^+), 458, 415, 237, 201, 157.

Anal. Calcd. For $C_{32}H_{30}N_2O_2$: C, 80.98; H, 6.37; N, 5.90. Found: C, 81.35; H, 6.44; N, 5.63.

2,7-Dimethyl-3,8-bis(2-fluorphenyl)-1,6-dioxapyrene (**1i**).

Was prepared from **2i** by the general procedure in 12 % yield as an orange powder; Mp. 281 - 284 ºC (dec.); ^{1}H nmr (carbondisulfide): δ 1.62 (s, 6 H); 5.54 (s, 2 H); 5.93 (s, 2 H), 7.0 (m, 8 H); MS(EI): 424 (M^+), 395, 351, 212, 151.

Anal. Calcd. For $C_{28}H_{18}F_2O_2$: C, 79.23; H, 4.27. Found: C, 79.48; H, 4.44.

2,7-Dimethyl-3,8-bis(4-fluorphenyl)-1,6-dioxapyrene (**1j**).

This compound was prepared from **2j** by the general procedure in 29 % yield as a yellow powder; Mp. 288 - 290ºC; ^{1}H nmr (carbondisulfide): δ 4.69 (s, 6 H), 8.86 (s, 2 H), 9.03 (s, 2 H), 9.91 (m, 4 H), 10.10 (m, 4 H); ^{13}C nmr (CPMAS): δ 20.2, 118.5, 122.3, 124.9, 128.5, 131.9, 136.5, 139.5, 145.6, 151.4; MS (EI): 424 (M^+), 395, 381, 336, 257, 212, 165.

Anal. Calcd. For $C_{28}H_{18}F_2O_2$: C, 79.23; H, 4.27. Found: C, 79.35; H, 4.36.

2,7-Dimethyl-3,8-bis(4-chlorphenyl)-1,6-dioxapyrene (**1k**).

This compound was prepared from **2k** according to the general procedure. The crude product precipitated during the treatment with $NaOH/Na_2S_2O_4$ and was isolated by filtration. After drying, the product was purified by Soxlet extraction with CH_2Cl_2 to give **1k** in 26 % yield as a yellow powder; Mp. > 300ºC. An analytical sample was prepared by sublimation *in vacuo* (300 ºC/0.01 mm Hg); ^{13}C nmr (CPMAS): δ 25.0, 123.3, 127.0, 129.6, 133.3, 136.6, 141.3, 144.0, 150.2, 156.1; MS(EI): 456 (M^+), 427, 393, 313, 228, 157.

Anal. Calcd. For $C_{28}H_{18}Cl_2O_2$: C, 73.53; H, 3.97; Cl, 15.50. Found: C, 73.43; H, 4.09; Cl, 15.74.

2,6-Dibromo-1,5-bis(2-oxo-3-butoxy)naphthalene (**2a**).

General Procedure for Alkylations.

To a degassed mixture of 10 g K_2CO_3 (72 mmol) in 100 mL DMF was added 10.0 g 2,6-dibromo-1,5-dihydroxynaphthalene [12] (31 mmol) followed by 7 mL 3-bromo-2-butanone [15]. Stirring at RT overnight. The DMF was removed in vacuum, and the dark residue was dissolved in an ether/H_2O-mixture. The organic phase was separated, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was then purified by column chromatography on Silicagel 60 (0.040 – 0.063 mm) with ether:petroleum ether (1:1) as eluent to give 9.7 g (67%) of **2a** as a yellowish-white powder. An analytical sample crystallized from ether/petroleum ether had mp. 115 – 117 ºC; ^{1}H nmr (deuteriochloroform): δ 1.40 (d, 3 H, J = 6.7 Hz), 2.49 (s, 3 H), 4.91 (q, 1 H, J = 6.7 Hz), 7.60 (d, 2 H, J = 8.8 Hz), 7.9 (d, 2 H, J = 8.8 Hz); ^{13}C nmr (deuteriochloroform): δ 17.2, 26.3, 84.3, 113.5, 120.2, 130.8, 131.4, 150.6, 207.8.

Anal. Calcd. For $C_{18}H_{18}Br_2O_4$: C, 47.19; H, 3.96; Br, 34.88. Found: C, 47.29; H, 4.00; Br, 34.55.

2,6-Dimethyl-1,5-bis(3,3-dimethyl-2-oxo-1-butoxy)naphthalene (**2e**).

This compound was prepared from 2,6-dimethyl-1,5-dihydroxynaphthalene [1] and 1-bromo-3,3-dimethyl-2-butanone [16] according to the procedure for **2a**. An analytical sample crystallized from EtOH had mp. 113 – 113 ºC (solidified and melted again: 130 –132 ºC); ^{1}H nmr (deuteriochloroform): δ 1.22 (s, 18 H), 2.41 (s, 6 H), 4.80 (s, 4 H), 7.33 (d, 2 H, J = 8.50 Hz), 7.78 (d, 2 H, J = 8.50 Hz).

Anal. Calcd. For $C_{24}H_{32}O_4$: C, 74.97; H, 8.39. Found: C, 74.93; H, 8.43.

2,6-Dimethyl-1,5-bis(1-(2-fluorphenyl)-1-oxo-2-ethoxy)naphthalene (**2i**).

2,6-Dimethyl-1,5-dihydroxynaphthalene [1] was alkylated with 1-(2-fluorphenyl)-2-bromo-1-ethanone [22] according to the general procedure. The work-up was carried out by pouring the reaction mixture into water, whereby the crude product precipitated; yield: ≈ 100%. An analytical sample crystallized from toluene (treatment with activated carbon) had mp. 193 –195 ºC; ^{1}H nmr (deuteriochloroform): δ 2.50 (s, 6 H), 5.20 (s, 4 H), 7.20 – 8.10 (m, 12 H).

Anal. Calcd. For $C_{28}H_{18}F_2O_4$: C, 73.03; H, 4.82. Found: C, 73.21; H, 4.92.

2,6-Dimethyl-1,5-bis(1-(4-fluorphenyl)-1-oxo-2-ethoxy)naphthalene (**2j**).

2,6-Dimethyl-1,5-dihydroxynaphthalene [1] was alkylated with 1-(4-fluorphenyl)-2-bromo-1-ethanone [22] according to the general procedure. The work-up was carried out by pouring the reaction mixture into water, whereby the crude product precipitated; yield: ≈ 100%. An analytical sample crystallized from toluene (treatment with activated carbon) had mp. 174 –176 ºC; ^{1}H nmr (deuteriochloroform): δ 2.40 (s, 6 H), 5.20 (s, 4 H), 7.20 (m, 6 H), 7.90 (m, 6 H).

Anal. Calcd. For $C_{28}H_{18}F_2O_4$: C, 73.03; H, 4.82. Found: C, 73.38; H, 4.91.

2,6-Dimethyl-1,5-bis(1-(4-chlorphenyl)-1-oxo-2-ethoxy)naphthalene (**2k**).

2,6-Dimethyl-1,5-dihydroxynaphthalene [1] was alkylated with 1-(4-chlorphenyl)-2-bromo-1-ethanone [22] according to the general procedure. The work-up was carried out by pouring the reaction mixture into water, whereby the crude product precipitated; yield: ≈ 100%. An analytical sample crystallized from toluene (treatment with activated carbon) had mp. 199 –201 ºC; ^{1}H nmr (deuteriochloroform): δ 2.40 (s, 6 H), 5.20 (s, 4 H), 7.50 (m, 12 H).

Anal. Calcd. For $C_{28}H_{18}Cl_2O_4$: C, 68.16; H, 4.49; Cl, 14.37. Found: C, 68.30; H, 4.35; Cl, 14.07.

2,6-Di-*t*-butyl-1,5-dihydroxynaphthalene (**3c**).

A mixture of 80.0 g 1,5-dihydroxynaphthalene (0.50 mol), 75.0 g *t*-butanol (1.01 mol), 300 g acetic acid and 750 g 85% phosphoric acid was stirred (mechanical stirring) under N_2 at 85 ºC overnight. The mixture was cooled to RT and filtered. The crude product was washed with water, dried *in vacuo* and crystallized from toluene (treatment with activated carbon) to give 32.6 g (24 %) of pure (**3c**) mp. 155 – 157 ºC. A second crop of material (8.7 g (6 %)) could be isolated by concentration of the mother liquor; ^{1}H nmr (deuteriodimethylsulfoxide): δ 1.67 (s, 18 H), 5.02 (s, 2 H), 7.58 (d, 2 H, J = 8.9 Hz), 7.78 (d, 2 H, J = 8.9 Hz); ^{13}C nmr (deuteriodimethylsulfoxide): δ 28.7, 33.6, 111.8, 123.2, 126.0, 129.9, 149.4.

Anal. Calcd. For $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.33; H, 9.00.

Electrochemistry.

The cyclic voltammetry investigations were performed using a standard three electrode set-up at 25 °C. Potentials were recorded vs SCE at a scan-rate of 100 mV/sec using a platinum button electrode (2 mm^2), a platinum wire counter electrode and 10^{-5} molar solutions of the neutral donors in dry CH_2Cl_2 containing 0.1 *M* nBu_4NPF_6. Electrochemical reversibility of the observed one-electron reaction was ascertained by comparing relative peak heights of oxidative and reductive scans and peak separations (60 mV). We did not perform quantitative oxidation to investigate the long term stability of the cation-radicals and dications formed, but in the time scale of cyclic voltammetry (seconds) the specied formed are stable with the exception of the dications derived from **1h** and **1j**.

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