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1,2-DIALKOXYACENAPHTHYLENES AND 2,3,11,12-BIS-(1,2-ACENAPHTHO)-[18]CROWN-6

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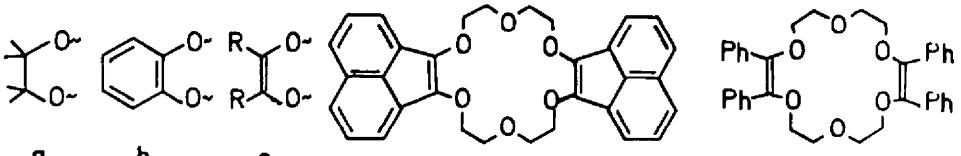
Abstract: A general synthesis of 1,2-dialkoxyacenaphthylenes by dehydrogenation of the corresponding acenaphthene derivatives with high potential quinones is described. The new crown ether, 2,3,11,12-bis(1,2-acenaphtho)-[18]crown-6, **1**, is obtained by this route. The surprisingly poor complexing ability of **1** is ascribed to electronic and geometrical effects of the acenaphthylene rings as shown by spectroscopic and voltammetric data and the crystal structure of the free ligand **1**.



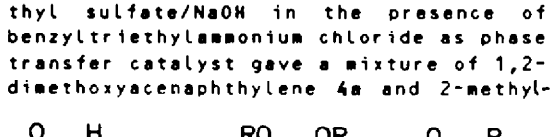
a **b** **c** **1** **2**

Crown ethers in which an ethylene unit (a) is replaced by an unsaturated moiety, e.g. an aromatic ring (b) or a carbon-carbon double bond (c) are of interest for several reasons. The crown ether oxygens are in direct conjugation with a π-system and any substituent at the unsaturated group will influence their electron density or, vice versa, complexation at the crown oxygens will create changes in the electronic properties of the π-system. Furthermore, the unsaturated groups offer the possibility of additional functionalization of the crown ether. Structure (c), in particular, could be used for thermal or photochemical cycloaddition reactions. The first example of type (c), the crown ether **2** containing two cis-stilbene units was synthesized in our laboratories some years ago [1]. The photochemistry of **2** was found to be restricted to cis/trans-isomerizations and the oxidative cyclization to phenanthrene rings, of the stilbene groups [2]. No inter- or intramolecular photocyclizations of **2** itself or with other olefinic reactands could be verified. Since 2+2 photocyclodimerizations of the 1,2 double bond of acenaphthylene and its derivatives have been thoroughly investigated[3], and alternative photoreactions like those of the stilbene system are not possible here, we became interested in the crown ether **1** with two acenaphthylene units.

1,2-dimethoxyacenaphthylene, **4a**, a model compound for the 1,2-acenaphthylenedioxy units in **1** was first obtained by Simonet et al. by the electroreductive alkylation of acenaphthenequinone[4]. From the same laboratory, a [12]crown-4 derivative containing one acenaphthylene ring was reported[5]. No other 1,2-dialkoxyacenaphthylenes appear to have been reported in the literature. In this paper, we report a more general synthesis of 1,2-dialkoxyacenaphthylenes enabling us to prepare the crown ether **1** in three steps from acenaphthenequinone.

Syntheses

In a first approach, we tried to apply our previous method of the phase transfer catalyzed bis-O-alkylation of benzoins[6]. This method is closely related to the electrochemical route since α-hydroxy ketones are in the same oxidation state as enediols. The reaction of 2-hydroxyacenaphthenone, **3** with dimethyl sulfate/NaOH in the presence of benzyltriethylammonium chloride as phase transfer catalyst gave a mixture of 1,2-dimethoxyacenaphthylene **4a** and 2-methyl-



3 **4a,b** **5a,b**

a: R = CH_3; b: R = C_2H_5.

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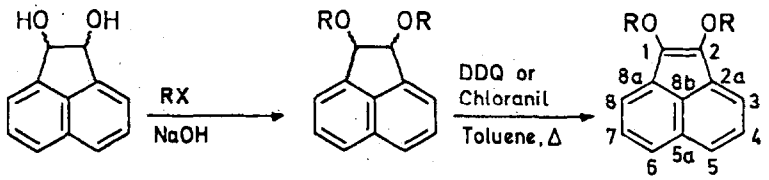
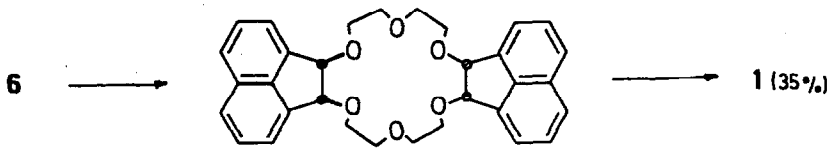
Scheme 1



6 (cis)
7 (trans)

8 (cis, R = CH_3, >95%)
9 (trans, R = CH_3, 95%)
11 (R,R = $-(CH_2)_2-$, 17%)
12 (R,R = $-(CH_2)_3-$, 10%)

4a (R = CH_3, 65%)
4c (R,R = $-(CH_2)_2-$, 58%)
4d (R,R = $-(CH_2)_3-$, 55%)



10 (syn + anti, 12%)

2-methoxyacenaphthenone, 5a. The 4a/5a ratio was 1:9 in benzene/50% aqueous NaOH and 1:6 in DMSO/powdered NaOH, the latter conditions being the optimum ones for the preparation of 4a. Using ethyl tosylate as alkylating agent, 4b was formed in trace amounts only; 5b was obtained in > 95% isolated yield. We have previously demonstrated that the O,O vs. C,O-ratio in the phase-transfer catalyzed bis-alkylation of benzoins is strongly dependent on the reaction conditions and the nature of the alkylating agent[6]. In the present case, we find that the C alkylation is additionally favored by intrinsic electronic factors in the acenaphthylene system. Consequently, this reaction path is not useful for the preparation of 1.

Since it is well known that the acenaphthylene 1,2-double bond can be generated by dehydrogenation of acenaphthene with high potential quinones[7], we attempted the synthesis via the 1.2-dialkoxyacenaphthenes 8-12 (Scheme 1).

Cis- and trans-1,2-acenaphthenediol, 6 and 7, in a 1:4 ratio, are readily available by $LiAlH_4$ reduction of acenaphthoquinone[8]. The diastereomeric ratio is reversed when the reduction is carried out with $NaBH_4$ in methanol at low temperatures. While the alkylation of 6 or 7 with dimethyl sulfate/NaOH in dioxane to the diastereomeric dimethyl ethers 8 and 9 is quantitative within 90 min at 80 °C, the other alkylations given in Scheme 2 proceed slowly with only moderate to poor yields. We propose that this is due to an appreciable concentration of the dianion of 6/7 when the alkylation is slow. The dianion may be in equilibrium with the diradical dianion of naphthalene-1,8-dialdehyde which may subsequently undergo redox and disproportionation reactions. Although we have not investigated these side reactions in detail, an intense blue color during slow alkylations and the presence of 1,8-naphthalenedicarboxylic acid in the products is be indicative of such processes. Similarly, we observed low yields and partial racemization in slow bis-alkylations of optically active hydrobenzoins[9].

In the alkylation with diethyleneglycol ditosylate, only the cis-diol, 6 gives the crown ether 10 (as syn/anti mixture which was not separated). Although the size of the crown ether would also allow for trans connected acenaphthene rings, at least for the syn isomer, the formation of crown ethers starting from 7 was not observed. We suppose that the trans position of the oxygens in 7 prevents the operation of the template effect by sodium ions which appears to be essential in the four component cyclization. In the dehydrogenation of the acenaphthene ethers, DDQ is required for 11 and 12 while the milder chloranil is sufficient and better for 8,9 and 10.

Spectroscopic and Voltammetric Properties

The 1,2-dialkoxyacenaphthylenes 4a-d including crown ether 1 are orange to red crystalline compounds, dilute solutions are orange-yellow. Some spectroscopic and redox potential data are summarized in Table 1 where acenaphthylene is included for comparison. The color arises from a broad absorption band with its maximum near 450 nm with strong tailing to longer wave lenghts. The UV/Vis spectra are independent on solvent polarity thus excluding the possibility of an inter- or intramolecular charge transfer band. The long wave absorption maximum of unsubstituted acenaphthylene has been identified as the HOMO-LUMO transition and it appears as a fine structured shoulder in the UV/Vis spectrum[10]. In 4a-d and 1, this band is well separated from the stronger shorter wave absorptions with a red shift of ca. 100 nm.

Table 1: UV/Vis, ^{13}C-nmr and redox data of 1,2-dialkoxyacenaphthylenes

compound	λ_{max} (nm) (ε)	E_{ox} V.vs.SCE	E_{red}	$^{13}C(\delta$ vs.TMS in $CDCl_3$ at 22.63 MHz)* C1,2	C3,8	C4,7	C5,6	C2a,8a	C5a	C8b
acenaphthylene	322(11000) 434(1700)	+1.55	-1.68	129.7	124.3	127.8	127.3	140.0	128.4	128.7
1	318(17700) 434(1700)	+0.70	-1.75	133.4	120.1	127.4	126.3	140.4	127.0	121.0
4a	318(7800) 430(730)	+0.71	-1.78	133.3	120.0	127.4	126.2	141.2	127.1	121.0
4c	318(6500) 450(600)	+0.81	-1.82	131.3	118.6	127.3	126.2	137.0	127.2	120.0
4d	318(7150) 436(660)	+0.79	-1.80	not determined						

* only the acenaphthylene ring carbons given, numbering see formula 4a, scheme 1; data for acenaphthylene from ref.[11].

Simple HMO calculations show that this is due to charge donation into the acenaphthylene ring from the oxygen atoms resulting in an increased HOMO energy while the LUMO energy is fairly unchanged.

This effect is well documented in the redox properties which were obtained from cyclic voltammograms: the oxidation potentials, corresponding to the removal of an electron from the HOMO, of the dialkoxyacenaphthylenes are some 800 mV more negative than that of the unsubstituted compound whereas the reduction potentials, corresponding to the insertion of an extra electron into the LUMO, are only 50 to 100 mV more negative.

Charge injection into the acenaphthylene π-system is also documented by the upfield shift of the ^{13}C signals of carbons 3,5,6,8 and 8b.

There are distinct differences in the spectroscopic and electrochemical data within 4a-d and 1. The dimethoxy derivative 4a and the crown ether appear very much alike whereas the smaller cyclic ethers 4c and 4d have longer wave Vis-absorptions and higher oxidation potentials. From this we conclude that the smaller rings impose additional strain on the acenaphthylene five membered ring which is not present in 4a as well as in the crown ether. Notably, the electrochemical oxidation of 4a and 1 is chemically irreversible whereas reversible Nernstian cyclic voltammograms are found for 4c and 4d. This finding will be subject to more detailed electrochemical investigations.

Structure and Complexing Behavior of 1

One could expect that the crown ether 1, upon complexing with alkali metal cations would exhibit interesting changes in its spectroscopic and redox properties. In particular, visible color changes might be anticipated[12]. Surprisingly, 1, unlike the related dibenzo-[18]crown-6 (DB18C6)[13], is a very poor complexing ligand towards alkali metal ions: 1 does not extract Na, K or Rb salts from the solid or aqueous phase; solutions of 1 in the presence of alkali metal salts do not show any change in their spectroscopic or electrochemical properties. One reason for this unexpected behavior may be the decreased electron density at the oxygen atoms adjacent to the acenaphthylene rings. In order to examine whether also geometric features were responsible for the failure of complexation by 1, its X-ray crystal structure was determined (Fig. 1). The crown ether shows an elongated structure with two of the aliphatic ethylenedioxy groups having their vicinal oxygens in antiperiplanar position. Hereby, two methylene groups are turned inside with short transannular $CH_2 \cdots O$ contacts. This structure is quite typical for free crown ether ligands manifesting their tendency to "fill their own cavity"[14]. The acenaphthylene rings are planar together with the adjacent oxygen atoms and their geometry is much the same as for unsubstituted acenaphthylene[15], but within one crown ether molecule the normals of two acenaphthylene planes form an angle of 19° and are twisted. The whole molecule is essentially asymmetric but it may be approximately described with a pseudo-C_2 axis perpendicular to and through the center of the ring. The data in Fig. 1 are averaged with respect to this axis. Bond lengths and angles within the 18-membered ring which are relevant for judging the complexing abilities of 1 are given in Table 2 in comparison with corresponding data of DB18C6[16].

The data show that significant differences occur only at the bonds to the

Fig. 1: Molecular structure of 1 showing dimensions obtained by averaging across a pseudo-twofold axis per pendicular to the plane of paper, and the disorder for one oxygen atom (bond lenghths in Å).

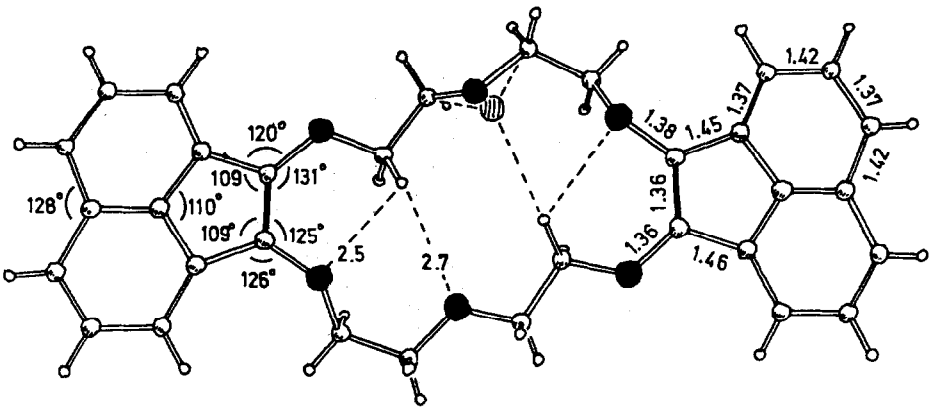


Table 2: Comparison of selected structural data of 1 and DB18C6[a]

	1	DB18C6
mean bond length sp^3 C-O	1.41	1.41
mean bond length sp^3 C-sp^3 C	1.49	1.49
mean bond angle -O-C-$C_{aliph.}$	108	109
mean bond length sp^2 C-O	1.37	1.36
mean bond length sp^2 C-sp^2 C	1.36	1.41
mean bond angle -O-C-$C_{arom.}$	128	113

bond lengths in Å, angles in degrees

aromatic ring, in particular, the C-C-O angles at the acenaphthylene ring are much greater than at the benzene ring. Thus, although the C-C bond length is shorter in 1, the distance of the two vicinal oxygen atoms (3.04 Å) is substancially longer than in DB18C6 (2.6 Å). On the other hand, metal complexation in a hexagonal array requires vicinal O-O distances of 2.6-2.8 Å[16,17]. As pointed out in the previous section, we assume that the crown ether ring does not impose strain on the acenaphthylene system as contrasted by the smaller cyclic ethers 4c and 4d. Thus the energy gain by metal complexation is not sufficient to overcome the strain energy reqired to compress the two ether bonds by an appreciable amount. Despite these observations we were able to isolate a KSCN complex of 1 by slow evaporation of an 1:1 crown ether/salt solution in dichloromethane/methanol (4:1). The complex forms red needles, m.p. 245-49 °C. It is insoluble in dichloromethane and disintegrates into its components in pure methanol. Unfortunately we were not able to obtain crystals suitable for X-ray analysis, so far.

Acknowledgement

Support of this work by the Fonds der Chemischen Industrie is gratefully acknowledged.

Experimental Section

General

Analytical instrumentation:
IR: Beckman acculab; UV/Vis: Beckman Acta M5; ^{1}H and ^{13}C-nmr: Bruker XL90; MS: Varian-MAT 311A.
IR data are given in cm^{-1}; nmr chemical shifts in δ vs. TMS, coupling constants in Hz, all in $CDCl_3$ solvent.
All preparations were carried in a dry nitrogen atmosphere. Dioxane was distilled from solid KOH prior to use. Acenaphthenequinone was recrystallized from o-dichlorobenzene. Melting points were taken on a Kofler hot stage microscope and are corrected.

Preparations

2-Hydroxyacenaphthenone, 3
The following procedure was developed following a German patent[18]:
Acenaphthenequinone (10 g, 55 mmol), ethylene glycol (3.41 g, 55 mmol), toluenesulfonic acid (0.5 g) were heated to reflux in toluene (200 ml) for 14 h, until no more water was collected in a Dean-Stark apparatus. After filtration from unchanged acenaphthenequinone and washing with aqueous NaOH, a crude mixture of acenaphthenequinone mono- and bis ethylene ketals was obtained which was separated by fractional crystalliza-

tion from methanol. Monoketal **3a**: 6.0 g (48%), m.p. 96-97 °C. Ir: $\nu_{C=O}$ 1725; ^{1}H-nmr: AA'BB'-spectrum,4H,centered at 4.50,4H; 7.0-8.4,m,6H. Bis-ketal **3b**: 1.8 g (12%),m.p.209-210 °C; ^{1}H-nmr: AA' BB'-spectrum centered at 3.95,8H; 7.3-8.0,m,6.

The monoketal **3a** (2.26 g, 10 mmol) and sodium borohydride (0.19 g, 5 mmol) were stirred overnight at room temperature in ethanol (50 ml). Upon dilution with 2N HCl (200 ml), 2-hydroxyacenaphthenone, **3** precipitated. Crystallization from toluene yielded 1.5 g (82%) pure **3**, m.p. 114-115 °C. Ir ν_{O-H} 3420, $\nu_{C=O}$ 1715; ^{1}H-nmr 4.43,d,1H, J=5 (O-H, signal disappears on shaking with D_2O); 5.33,d,1H,J=5 (aliph.CH, coupling disappears on shaking with D_2O);7.0-8.0, 6H.

Alkylations of **3** (Preparations of **4a**,**5a**,**5b**)

a. dimethyl sulfate

A mixture of **3** (0.55g, 3.0 mmol), dimethyl sulfate (0.95 g, 7.5 mmol), benzyltriethylammonium chloride (10 mg) and dimethyl sulfoxide (20 ml) was stirred for 30 min at 80 °C. Upon addition of water and extraction with dichloromethane a semicrystalline mixture was obtained from which 480 mg (77%) 2-methoxy-2-methyl-acenaphthenone, **5a**, were separated by washing with cyclohexane. The washings were filtered over a short SiO_2 column to give 90 mg (13%) red crystals of 1,2-dimethoxyacenaphthylene, **4a**, m.p. 41-42°C. These compounds had spectroscopic as given in ref. [4].

b.ethyl mesylate

Under the same conditions as under a.,using ethyl mesylate (0.93 g, 7.5 mmol) instead of dimethyl sulfate, 684 mg (95%) 2-ethoxy-2-ethyl-acenaphthenone, **5b**, m.p. 101-102 °C were obtained after crystallization of the crude product with cyclohexane. The red mother liquor contained traces of **4b** which were not isolated.

5b:Ir $\nu_{C=O}$ 1720; ^{1}H-nmr 0.71,t,3H,J=7; 1.02,t,3H,J=7; 2.12,q,2H,J=7; 3.15 and 3.17,2q,2H,J=7, for the diastereotopic -O-CH_2- groups); 7.5-8.2,m,6H.

Cis- and trans-1,2-acenaphthenediol, **6** and **7**

6 and **7** were prepared according to ref. [8], or, when a higher proportion of **6** was desired, by the following procedure:

To a suspension of acenaphthenequinone (20.0 g, 0.11 mol) in methanol (350 ml) containing KOH (0.2 g), solid $NaBH_4$ (8.30g, 0.22 mol) was added with vigorous stirring at -10 °C within 5 min. Stirring was continued for 10 min at -5 °C and for further 10 min without external cooling, and the mixture was poured into 600 ml of 2N HCl. The precipitated **6** was collected, dried and recrystallized from toluene with the aid of active charcoal. Yield: 7-9 g (34-43%) pure **6**, m.p. 215-217 °C. The trans isomer **7** was is obtained by dichloromethane extraction of the aqueous mother liquor: 2-3 g (9-15%), m.p. 159-60 °C, recrystallized from ethyl acetate/hexane.

Cis- and trans-1,2-dimethoxyacenaphthenes, **8** and **9**

6 or **7** (3.0 g, 16 mmol), dimethyl sulfate (4.6 g, 3.62 mmol), benzyltriethylammonium chloride (200 mg) and powdered NaOH (3.0 g) in dioxane (50 ml) were stirred at 80 °C for 1.5 h. Dilution with water and extraction with dichloromethane gave **8** or **9**, respectively in quantitative yield.

8 (cis-isomer): m.p. 41-43 °C; ^{1}H-nmr 3.55,s,6H; 5.22,s,2H; 7.4-7.9,m,6H.

9 (trans-isomer): colorless oil; ^{1}H-nmr 3.61,s,6H; 5.23,s,2H; 7.5-7.9,m,6H.

8 and **9** have been recently prepared in a similar way and also by anodic methoxylation of acenaphthylene[19].

1,2-(Dimethylene-1,2-dioxy-)-acenaphthene, **11**
and
1,2-(Trimethylene-1,3-dioxy-)-acenaphthene, **12**

were prepared by a similar procedure using the ditosylates of ethylene glycol or 1,3-dihydroxypropane, respectively.

11 (25 mmol run, reaction time 20 h, the product was isolated from the crude product mixture by elution with CH_2Cl_2/pentane, 9:1 from an SiO_2 column): 890 mg (17%), m.p. 92-93 °C; ^{1}H-nmr 3.73,s,4H; 5.26,s,2H; 7.4-7.9,m,6H.

12 (5 mmol run, reaction time 72 h, product isolated from crude product mixture by crystallization with ethanol): 120 mg (10%), m.p. 144-45 °C; ^{1}H-nmr 1.5-2.5,m,2H; 3.7-4.8,m,4H; 5.45,s, 2H; 7.5-7.8,m,6H.

Preparation of
1,2-dimethoxyacenaphthylene, **4a**,
2,3-(1,2-acenaphtho)-1,4-dioxane, **4c**,
and
2,3-(1,2-acenaphtho)-1,4-dioxacycloheptane, **4d**

by dehydrogenation of **8** or **9**, **11** and **12**. The acenaphthene ethers were treated with 10% excess tetrachloro-p-benzoquinone (chloranil), for **8** and **9**, or 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ), for **11** and **12**, in boiling toluene for 12 h. The deep red reaction mixtures were purified by filtration over SiO_2 and elution of the red zone with pentane.

4a: 65% yield, properties as in ref.[4].

4c: 58% yield, red needles, m.p.91-93 °C from methanol; ^{1}H-nmr 4.40,s,4H; 7.2-7.6,m,6H; ^{13}C-nmr, aliphatic carbons 65.971,other chemical shifts see Table 1

4d: 55% yield, orange needles, m.p. 124-25 °C from methanol, ^{1}H-nmr 2.1-2.4,m,2H; 4.2-4.4,m,4H; 7.2-7.6,m,6H.

2,3,11,12-Tetrahydro-2,3,11,12-bis-(1,2-acenaphtho)-[18]crown-6, **10**

6 (9.4 g, 50 mmol), diethyleneglycol ditosylate (20.8 g, 50 mmol) and powdered NaOH (8.6 g), in dioxane (200 ml) were heated at 80 °C for 12 h. The reaction mixture was diluted with 500 ml of water and extracted with dichloromethane to give 10 g of a yellowish viscous oil which was dissolved in 30 ml of boiling 2-methoxyethanol. On cooling a mixture of syn and anti isomers of **10** was obtained as colorless crystals, m.p. 212-220 °C. Yield 3.07 g (12%), syn/anti(28:72); ^{1}H-nmr: 3.4-3.9,m,16H; 5.35 (syn),5.41(anti),2s,4H; 7.5-8.0,m,12H.

2,3,11,12-Bis-(1,2-acenaphtho)-[18]-crown-6, **1**

10 (1.14 g, 2.23 mmol) and chloranil (1.13 g, 4.59 mmol), in toluene (15 ml), were heated to reflux for 8 h. The crude crown ether crystallized on cooling. Recrystallization from 2-methoxyethanol gave 0.40 g (35%) **1**, orange platelets, m.p. 235 °C; ^{1}H-nmr 3.87-3.98 and 4.87-4.68,symm. AA'BB'-spectrum,16H; 7.25-7.68,m,12H; ^{13}C-nmr, aliphatic carbons: 70.222 and 71.804; other carbons see Table 1.

Elementary analyses or high-resolution molecular masses of all new compounds are given in Table 3.

X-ray crystal structure of **1**

Crystal data of **1**: $C_{32}H_{28}O_4$, Pbca orthorhombic; a=9.113(3),b=14.706(4), c=38.282(11) Å, D_x=1.317 Mgm^{-3} for Z=8; The structure was solved by multisolution direct methods (SHELXTL, written by G.M.S.) and refined anisotropically using 2439 unique observed [$F > 3\sigma(F)$] profile-fitted diffractometer data (Mo-K_α -radiation, $2\theta_{max}$ = 47°); H atoms were included in calculated positions [CH = 0.96 Å, $U_{iso}(H_i) = 1.2\ U_{eq}(C_i)$], the disorder of one O atom was resolved into two positions with occupancy factors f = 0.591(5) for O(13) and f' = 1-f for O(13'); final R = 0.078, R_w = 0.067.

Cyclic voltammetry

The voltammograms of **1** and **4a-d** were taken at ambient temperature in a conventional H-cell with a three electrode configuration in 0.1 M tetra-n-butylammonium perchlorate in dry acetonitrile as solvent/supporting electrolyte. The working electrode was a platinum disk, the saturated calomel reference electrode was separated from the working electrode chamber by a salt bridge containing the supporting electrolyte. The instrumentation was a Princeton Applied Research Mod. 170 Electrochemical System together with an X-Y recorder.

Table 3: Analytical Data of New Compounds[a]

Formula No.	Molecular Formula	Molecular Weight	Calculated %C	%H	Found %C	%H
1	$C_{32}H_{28}O_4$	508.57	75.59	5.51	74.99	5.57
			508.18859		508.18837[b]	
3	$C_{12}H_8O_2$	184.20	78.25	4.38	78.21	4.32
3a	$C_{14}H_{10}O_3$	226.24	74.33	4.46	74.27	4.48
3b	$C_{16}H_{14}O_4$	270.28	71.10	5.52	71.21	5.45
4a	$C_{14}H_{12}O_2$	212.25	79.23	5.70	79.25	5.63
4c	$C_{14}H_{10}O_2$	210.23	79.98	4.79	79.83	4.86
4d	$C_{15}H_{12}O_2$	224.26	224.08385		224.08373[b]	
5a	$C_{14}H_{12}O_2$	212.25	79.23	5.70	79.48	6.02
5b	$C_{16}H_{16}O_2$	240.31	79.97	6.71	79.87	6.52
10	$C_{32}H_{32}O_4$	512.60	512.21989		512.21904[b]	
11	$C_{14}H_{12}O_2$	212.25	79.23	5.70	79.18	5.74
12	$C_{15}H_{14}O_2$	226.28	79.62	6.24	79.78	6.08

[a] Elementary analyses carried out in the Microanalytical Lab, Universitat Regensburg; [b] molecular mass by high resolution mass spectrometry.

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