

Synthesis and Redox Behavior of Novel 9,10-Diphenylphenanthrenes

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Dedicated to Professor *Bernd Giese* on the occasion of his 70th birthday

The synthesis and electrochemical investigations of 9,10-diphenylphenanthrene **2a** and its derivatives **2b–2e** are reported. The cyclic voltammetry of derivatives **2a–2c** and **2e** in different solvent/ Bu_4NPF_6 electrolyte systems reveals that the redox properties are dependent on solvent, temperature, and sweep rate. The oxidation of 9,10-diphenylphenanthrene **2a** occurred as an irreversible process, while two fully reversible oxidation waves were observed for dimethoxy derivative **2c**. The room-temperature oxidation of brominated compound **2b** is reversible, whereas AcO-substituted phenanthrene **2e** displayed a reversible oxidation peak only at low temperature. Furthermore, the electronic nature of the substituent affects the oxidation potentials. In the CH_2Cl_2 -based electrolyte system, the first oxidation potentials increase in the order **2c** < **2e** < **2b**.

1. Introduction. – Both low- and high-molecular-weight organic compounds which are suitable for electronic and optoelectronic devices have been intensively investigated over the last decade¹⁾. Phenanthrene derivatives are highly attractive building blocks for such purposes, because, due to its high resonance energy and high energy gap, phenanthrene is one of the most stable fused aromatics [2]. In particular, phenanthrenes are less prone to photochemical degradation in the presence of air as compared to other aromatics such as pentacenes, which is important for organic field-effect transistors (OFETs) [3]. As recently shown by *Geng* and co-workers, and *Müllen* and co-workers, phenanthrene oligomers are useful stable p-type semiconductors for OFETs [4] and 9,10-diarylphenanthrenes can be converted into photoluminescent blue-emitting polyphenanthrenes [5]²⁾. Despite these promising features, systematic studies of the redox behavior of diarylphenanthrenes are still lacking, whereas related systems such as dibenzochrysenes and stilbenoprismoids have been investigated by electrochemical methods [7]. Octamethoxydibenzochrysene, for example, which was accessible by an oxidative cyclodehydrogenation of the corresponding tetraphenylethene precursor underwent reversible electrochemical oxidation to a stable cation-radical salt [7a]. A similar behavior was described for electron-rich stilbenoprismoids [7b]. Previously we reported on tetraphenylethene-derived columnar liquid crystals bearing gallic acid derivatives and their oxidative photocyclization to the corresponding 9,10-diphenylphenanthrenes [8]. Although the two compound classes differ only by

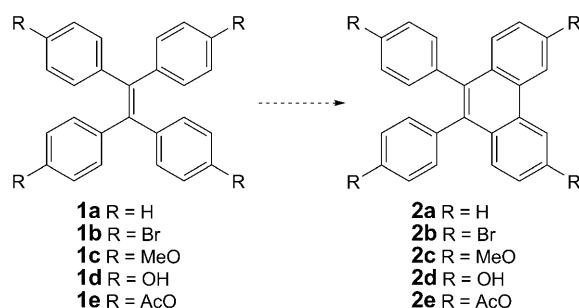
¹⁾ For reviews, see [1].

²⁾ For other work on phenanthrene polymers, see [6].

an additional C–C bond, they behaved very differently with regard to their liquid-crystalline properties³⁾). Moreover, these tetraphenylethenes showed a complex redox behavior. To gain some insight into the electrochemistry, simple tetraphenylethenes **1** were prepared and studied by cyclic voltammetry and IR spectroelectrochemistry [10], which reveal not only solvent effects on the comproportionation constants and the two-electron nature of the composite wave, depending on the substituent, but also two differently charged and thus structurally different aryl groups at each of the central C-atoms were identified.

From the observed differences in mesomorphic properties of tetraphenylethenes and their 9,10-diphenylphenanthrene derivatives, we anticipated that the latter should also differ in their redox behavior. Therefore, the 9,10-diphenylphenanthrenes **2** with different substituents (*Scheme 1*) were prepared and investigated by cyclic voltammetry. The results of this study are reported below.

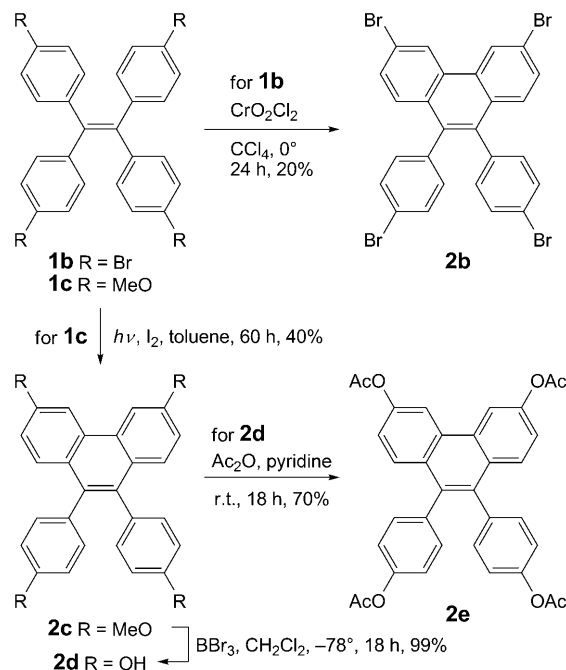
Scheme 1



2. Results and Discussion. – 2.1. *Synthesis of Phenanthrenes 2.* 9,10-Diphenylphenanthrene (**2a**) was available in 75% yield by cyclization of 1,1,2,2-tetraphenylethane-1,2-diol (= benzopinacol) with triflic acid (= trifluoromethanesulfonic acid) in benzene at room temperature according to the method of *Olah et al.* [11]. The synthesis of the differently substituted 9,10-diphenylphenanthrenes **2b–2e** is depicted in *Scheme 2*. According to a procedure of *Gatzke et al.* [12], tetrakis(bromophenyl)ethene **1b** [10] was treated with chromyl chloride (CrO_2Cl_2) at 0° in CCl_4 for 24 h to give the corresponding phenanthrene **2b** in 20% yield⁴⁾. It should be noted that, under these conditions, tetraphenylethene **1a** reacted to **2a** (10%), together with the C=C cleavage product benzophenone. This cleavage is not completely unexpected and was already observed by *Lansbury* and co-workers [13]. All tetraphenylethenes with MeO, AcO, BnO, PhO, NHCOCF_3 substituents, however, yielded only the respective cleavage products.

³⁾ For reviews on columnar liquid crystals, see [9].

⁴⁾ Low yield due to repeated flash chromatography to separate the poorly soluble product **2b** from the product mixture of **1b**, **2b**, and 4,4'-dibromobenzophenone, whose ratio strongly depended on the reaction time.

Scheme 2. Preparation of Substituted Phenanthrene Derivatives **2b–2e**

Irradiation of tetrakis(methoxyphenyl)ethene **1c** [8][10] for 18 h with a 700-W Hg lamp in toluene at room temperature in the presence of I_2 according to a method by Mallory and Mallory [14] afforded 3,6-dimethoxy-9,10-bis(4-methoxyphenyl)phenanthrene (**2c**) in 40% yield. Subsequent demethylation with BBr_3 in CH_2Cl_2 at -78° [15] and workup with MeOH yielded 9,10-bis(4-hydroxyphenyl)phenanthrene-3,6-diol (**2d**), which was acetylated with Ac_2O in pyridine at room temperature for 18 h to give the tetraacetate **2e** in 70% yield.

2.2. Electrochemistry. The redox properties of 9,10-diphenylphenanthrene derivatives **2a–2c** and **2e** were studied by cyclic voltammetry and are summarized in the Table. As first oxidation and reduction potentials differ by more than 3 V, in all cases, monitoring of anodic and cathodic processes required different solvents. The oxidations of 9,10-diphenylphenanthrene (**2a**) in the $\text{CH}_2\text{Cl}_2/0.2\text{M Bu}_4\text{NPF}_6$ electrolyte system at different temperatures are shown in Fig. 1, a.

At room temperature, an irreversible oxidation wave in the range of 0.6–1.6 V was observed, which corresponds to the oxidation of **2a** to **2a^{•+}**⁵⁾. The composite cation is mainly reduced on the return scan, but an additional electrochemically active species at 0.95 V was observed (Fig. 1, a, thin line). Upon decreasing the temperature to 193 K, this cathodic peak disappeared, and only the oxidation of **2a** to **2a^{•+}** with an anodic oxidation at 1.40 V and a return wave at 1.18 V was detected. At both room

⁵⁾ For radical cation generation by using oxidants, see [16].

Table. Electrochemical Data of Diphenylphenanthrenes **2a–2c** and **2e** at 293 K at $\nu = 0.1 \text{ V s}^{-1}$ Employing Bu_4NPF_6 (0.2M) as Supporting Electrolyte

Entry		Solvent	$E_{1/2}^{0/+}$ [V]	$E_{1/2}^{+/2+}$ [V]	$\Delta E_{1/2}$ [V]	$E_{1/2}^{0/-}$ [V]	$E_{1/2}^{-/2-}$ [V]	K_{comp}
1	2a	MeCN	1.19 ^{a)} ^{b)}	–	–	–2.74	–2.92	–
2	2a	DMF	–	–	–	–2.89	–3.24 ^{c)}	–
3	2b	CH_2Cl_2	1.33	–	–	–	–	–
4	2c	CH_2Cl_2	0.68	0.997	0.32	–	–	260000
5	2c	MeCN	0.74	0.93	0.19	–	–	1700
6	1c^{d)}	CH_2Cl_2	0.41	0.53	0.12	–	–	112
7	2e	CH_2Cl_2	1.19 ^{c)}	–	–	–	–	–
8	1e^{d)}	CH_2Cl_2	0.93 ^{c)}	1.05 ^{c)}	0.12	–	–	935

^{a)} At sweep rate 1.2 V s^{-1} . ^{b)} Quasi-reversible. ^{c)} At 233 K. ^{d)} Data from [10]. ^{e)} At 193 K.

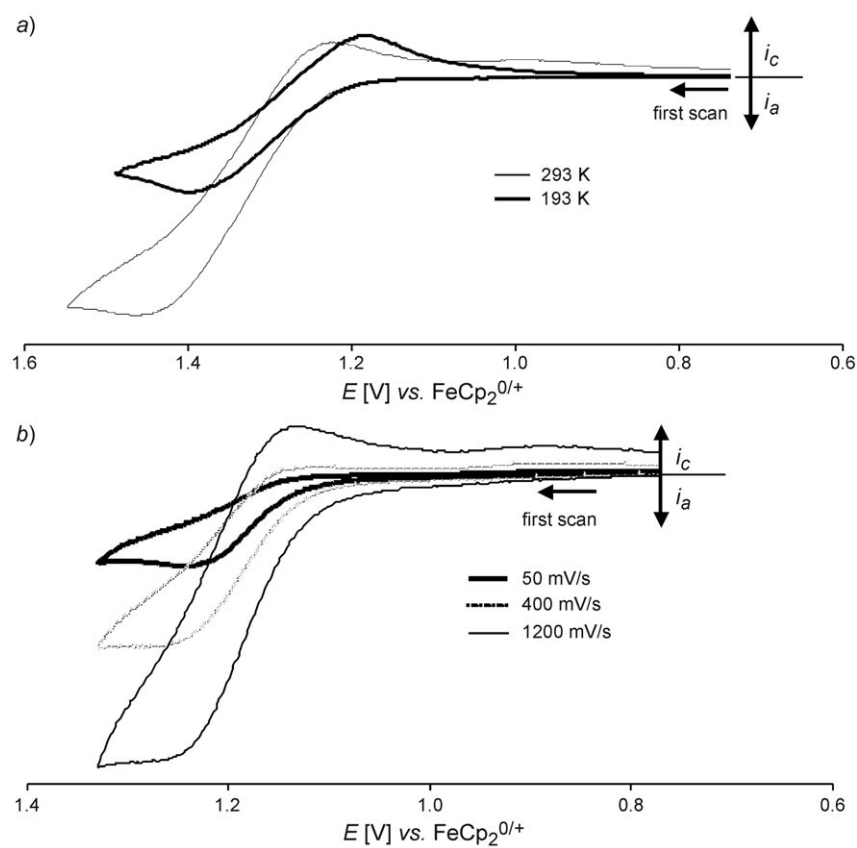


Fig. 1. Cyclic voltammograms of 9,10-diphenylphenanthrene **2a** in a) $\text{CH}_2\text{Cl}_2/0.2\text{M Bu}_4\text{NPF}_6$ at $\nu = 100 \text{ mV s}^{-1}$; b) in $\text{MeCN}/0.2\text{M Bu}_4\text{NPF}_6$ at 293 K

temperature and 193 K, the electron transport is inhibited, as suggested by a ΔE value of 226 mV, indicating an irreversible oxidation.

In contrast, in MeCN/0.2M Bu₄NPF₆ at room temperature, the oxidation of **2a** occurred as a major irreversible process with an anodic potential at 1.23 V vs. ferrocene (Fig. 1, *b*, bold line). The voltammetric responses strongly depended on the sweep rate. At higher sweep rate, the major wave becomes *quasi*-reversible with a half-wave potential, $E_{1/2}$ of 1.19 V, and a smaller follow-up cathodic peak at 0.88 V appeared. This second process was clearly observed even at a scan rate of 1200 mV s⁻¹ (Fig. 1, *b*, thin line). The ΔE value of 120 mV in MeCN indicated a less inhibited electron transport than in CH₂Cl₂.

The cyclic voltammogram of 3,6-dibromo-9,10-bis(4-bromophenyl)phenanthrene (**2b**) in CH₂Cl₂/0.2M Bu₄NPF₆ at room temperature indicated a reversible oxidation to the radical cation **2b**^{•+} (Fig. 2).

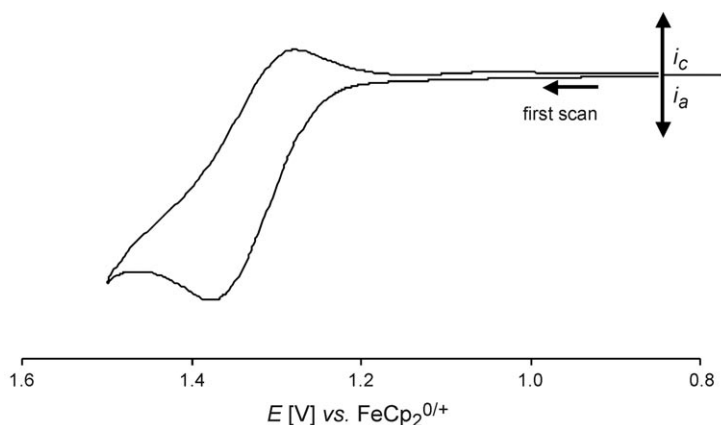


Fig. 2. Cyclic voltammogram of 3,6-dibromo-9,10-bis(4-bromophenyl)phenanthrene (**2b**) in CH₂Cl₂/0.2M Bu₄NPF₆ at 293 K at $\nu = 100 \text{ mV s}^{-1}$

The voltammetric responses of **2b** were found to be influenced by sweep rate and temperature. As the sweep rate was increased ($> 500 \text{ mV s}^{-1}$), the oxidation wave broadens significantly, probably caused by low electron-transfer kinetics. At low temperature (193 K), the oxidation became even more kinetically hindered, leading to irreversible oxidation waves, and chemical follow-up reactions could be monitored. When ferrocene was added to the electrolyte solution to determine the $E_{1/2}$ value of **2b**, an overall change of the CV curve was observed, resulting only in a single very broad irreversible wave, instead of the expected oxidation wave and a reversible wave of the ferrocene/ferrocenium ion pair both at room temperature and 193 K. The replacement of ferrocene by decamethylferrocene or cobaltocene gave similar results. Obviously, the metallocene complex was not as inert as anticipated but interacts with the 3,6-dibromo-9,10-bis(4-bromophenyl)phenanthrene intermediate. However, thianthrene as the internal reference was inert, and the $E_{1/2}$ value of **2b** could be determined as 1.33 V.

3,6-Dimethoxy-9,10-bis(4-methoxyphenyl)phenanthrene (**2c**) was oxidized in the CH₂Cl₂/0.2M Bu₄NPF₆ electrolyte system at room temperature in two well-behaved reversible waves at $E_{1/2} = 0.68 \text{ V}$ and $E_{1/2} = 0.997 \text{ V}$ vs. ferrocene as internal standard (Fig. 3, *a*), which did not change at 193 K. A comproportionation constant $K_{\text{comp}} =$

$2.6 \cdot 10^5$ was calculated⁶⁾. The EPR spectrum (Fig. 3,b) clearly demonstrated the formation of a radical cation $2\mathbf{c}^{+\bullet}$ during the oxidation. The signal is isotropic with a g-factor of 2.003 and 15-G signal width, being typical for an organic radical. The hyperfine signal splitting was not simulated, thus coupling constants could not be determined.

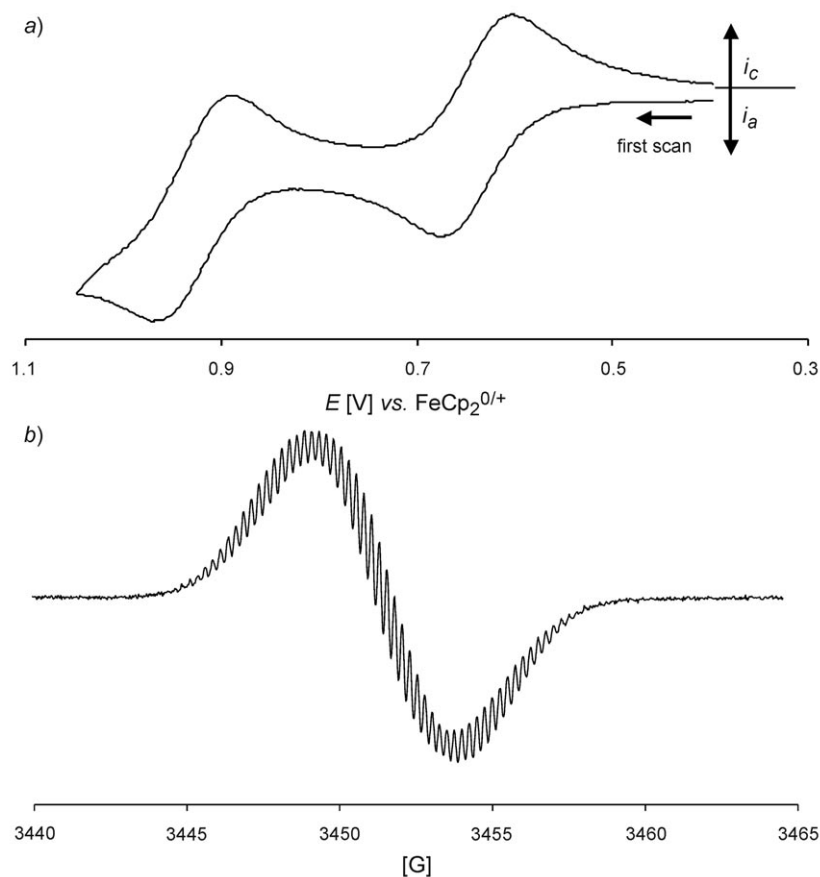


Fig. 3. a) Cyclic voltammogram of 3,6-dimethoxy-9,10-bis(4-methoxyphenyl)phenanthrene ($2\mathbf{c}$) in $\text{CH}_2\text{Cl}_2/0.2\text{M Bu}_4\text{NPF}_6$ at 293 K at $\nu = 100 \text{ mV s}^{-1}$; b) room temperature EPR spectrum for the radical cation $2\mathbf{c}^{+\bullet}$, taken from in situ electrolytic oxidation of $2\mathbf{c}$ in $\text{CH}_2\text{Cl}_2/0.2\text{M Bu}_4\text{NPF}_6$

⁶⁾ $\Delta E_{1/2}$ Values provide a quantitative measure of the comproportionation constant, which relates the thermodynamic stabilities of the monocations to those of the neutrals and the fully oxidized forms according to the equation:

$$K_{\text{comp}} = [\text{A}^+]^2/[\text{A}][\text{A}^{2+}] = \exp\{(nF/RT) \cdot \Delta E_{1/2}\}$$

F denotes the Faraday constant, R the gas constant, and T the temperature.

In the more polar MeCN/0.2M Bu₄NPF₆ system, a temperature dependence was observed. At room temperature, the oxidation waves broadened due to slower electron-transfer kinetics, and only the first wave was fully reversible. Upon cooling to 253 K, however, two completely reversible oxidations at $E_{1/2}^{0/+} = 0.74$ V and $E_{1/2}^{+/2+} = 0.93$ V were detected, and K_{comp} was calculated as $1.7 \cdot 10^3$. Consequently, in the CH₂Cl₂-based electrolyte system, the monocation **2c**⁺ is thermodynamically more stable than in MeCN.

The room-temperature oxidation of the tetraacetate **2e** in CH₂Cl₂/0.2M Bu₄NPF₆ displayed several irreversible peaks together with two corresponding irreversible reduction waves (Fig. 4, a). Upon cooling to 193 K, the cathodic reductions disappeared, and the first oxidation wave A became fully reversible with a peak current ratio $i_{\text{pa}}/i_{\text{pc}} \approx 1$ and $\Delta E = 90$ mV (Fig. 4, b). The $E_{1/2}$ value of this couple was determined as

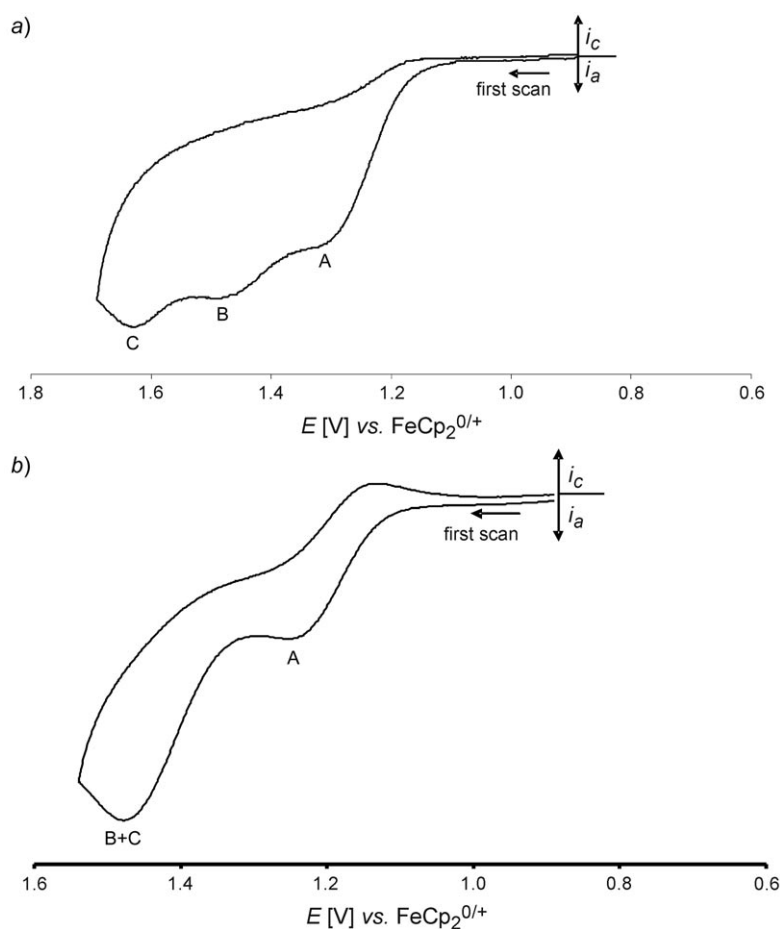


Fig. 4. Cyclic voltammogram of 4-{3,6-bis(acetyloxy)-10-[4'-(acetyloxy)phenyl]phenanthren-9-yl}phenyl acetate (**2e**) in CH₂Cl₂/0.2M Bu₄NPF₆ at $\nu = 100$ mV s⁻¹ at 293 K (a) and 193 K (b)

1.19 V. A second irreversible wave appeared at a peak potential of 1.47 V, where a second and third oxidation ($B + C$) obviously coincide as indicated by the peak height.

The reductions of the phenanthrene derivatives **2** were outside the potential window of the $\text{CH}_2\text{Cl}_2/\text{Bu}_4\text{NPF}_6$ electrolyte but were monitored in DMF and THF owing to their cathodic discharge limits.

The room-temperature reduction of 9,10-diphenylphenanthrene (**2a**) in DMF/0.2M Bu_4NPF_6 is represented by a reversible two-electron wave at $E_{1/2} = -2.89$ V vs. ferrocene $^{+/0}$ and by a second irreversible one-electron wave at -3.08 V vs. ferrocene. Both reductions were accompanied by two anodic follow-up waves at -1.51 and 0.39 V (Fig. 5, thin line). If the scanning is terminated prior to the start of the second reduction event, the anodic wave at 0.39 V is not visible, thus being clearly attributed to the second reduction. Upon cooling to 233 K, the second reduction process is observed as a partially reversible couple and is cathodically shifted to $E_{1/2} = -3.24$ V (Fig. 5, bold line). The second reduction product was completely oxidized on the return scan, and the anodic follow-up peak at 0.39 V, which is coupled to the second reduction peak, could not be detected anymore. The distance between the two reduction peaks increased from 191 mV at room temperature to 406 mV at 233 K, indicating an inhibited electron transfer, which is caused by rearrangement in the structure during the absorption of electrons. This observation may also be taken as evidence for the enhanced stability of the anion **2a $^-$ at lower temperatures.**

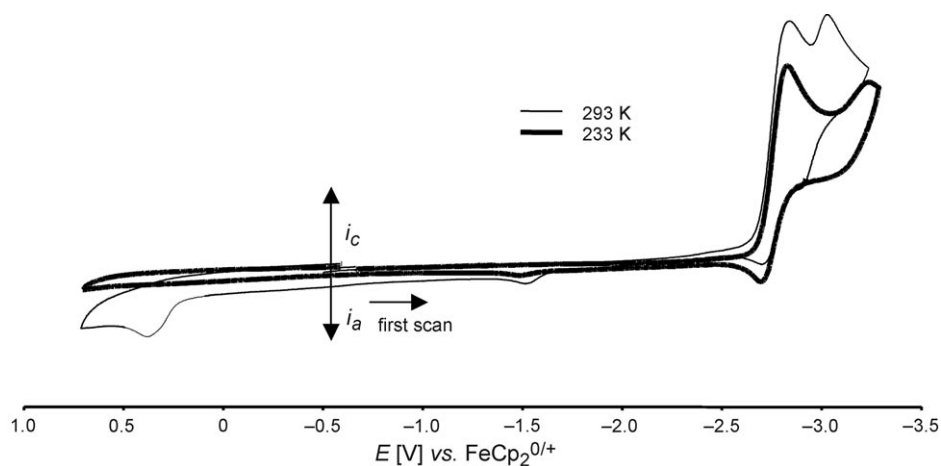


Fig. 5. Cyclic voltammogram of 9,10-diphenylphenanthrene (**2a**) in DMF/0.2M Bu_4NPF_6 at $v = 100 \text{ mV s}^{-1}$

The reduction of **2a** in MeCN at room temperature vs. ferrocene as internal standard gave qualitatively similar results with the first reversible wave at $E_{1/2} = -2.74$ V along with its anodic follow-up wave at -1.1 V and the second quasireversible reduction wave at $E_{1/2} = -2.92$ V. At 253 K, the behavior of **2a** resembled that at room temperature (data not shown).

The CV of the reduction of Br-substituted diphenylphenanthrene **2b** at room temperature in DMF/0.2M Bu_4NPF_6 displayed two irreversible reduction peaks close to

the solvent-discharge limit. Again, the addition of an equimolar amount of ferrocene caused a complete change of the CV curve, which was found to depend on the sweep direction. The two reduction peaks at -2.82 and -3.10 V, respectively, and the broad oxidation wave of ferrocene were observed upon cathodic-to-anodic scan direction. Upon reversal of the initial sweep direction, however, only the broad ferrocene wave was visible (*Fig. 6*), being typical for electrolyte solutions of metal complexes with high molecular mass such as polyvinyl ferrocene [17] or poly-Fe-complexes with tetra-(ethynylphenyl)ethene subunits, as was recently recorded by *Akita* and co-workers [18]. A chemical reaction with the cyclopentadienyl ring seems to be rather unlikely because, upon new reversal of the sweep direction, both irreversible reduction waves reappeared.

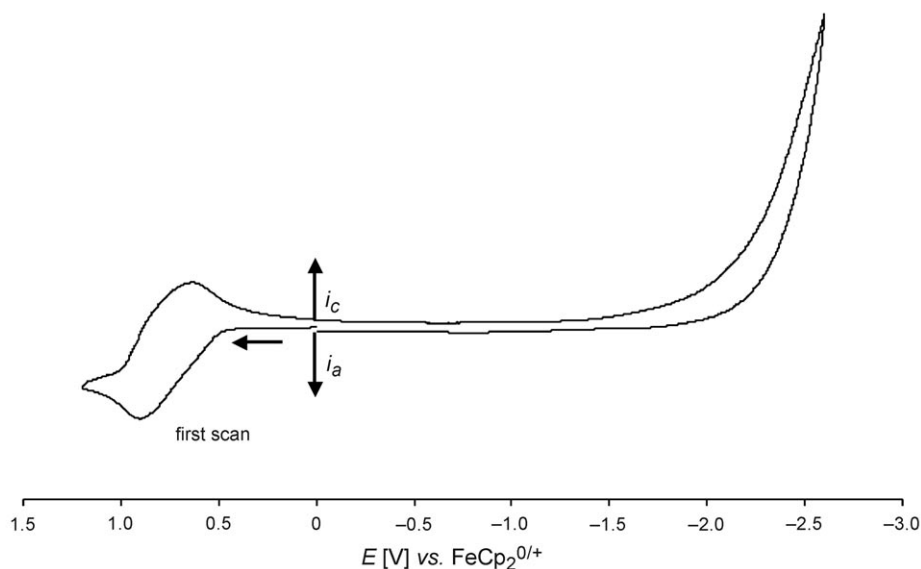


Fig. 6. Cyclic voltammogram of 3,6-dibromo-9,10-bis(4-bromophenyl)phenanthrene (**2b**) with an equimolar amount of ferrocene in DMF/0.2M Bu₄NPF₆ at 293 K, $\nu = 100 \text{ mV s}^{-1}$

In contrast, in the DMF/0.2M Bu₄NPF₆ electrolyte system any redox processes of bis(methoxyphenyl)phenanthrene **2c** were not detected. Acetoxy derivative **2e** displayed irreversible reductions in MeCN/0.2M Bu₄NPF₆ at -2.99 V and in DMF/0.2M Bu₄NPF₆ at -2.87 V.

The data listed in the *Table* reveal the influence of the substituent on oxidation potentials. In the system CH₂Cl₂/Bu₄NPF₆, compound **2e** with electron-withdrawing AcO group showed an oxidation potential at 1.19 V (*Entry 7*), while the Br substituent has an even larger effect (*Entry 3*). The electron-donating MeO groups, however, shifted the oxidation potential to a value by 0.65 V lower as compared to the Br substituent (*Entry 4*). These data reflect an oxidation tendency of the studied phenanthrene derivatives in the order **2c** > **2e** > **2b**.

Whereas tetraphenylethenes **1** generally displayed two consecutive one-electron oxidations, which are combined with a structure change [10], the appearance of a one-

electron oxidation wave is typical of phenanthrene derivatives **2** in our study. The cyclization of tetraphenylethenes **1** to phenanthrenes **2** caused an extension and flattening of the aromatic system, and the second oxidation is inhibited with the MeO compound **2c** as exception. The increased electron density in the aromatic system by the MeO groups apparently enabled a second oxidation. The direct comparison of electrochemical data of tetraphenylethene **1c** listed in the *Table* with its phenanthrene counterpart **2c** shows that, in the $\text{CH}_2\text{Cl}_2/0.2\text{ M Bu}_4\text{NPF}_6$ electrolyte system, the $E_{1/2}$ values of **2c** are shifted to values by 0.27 and 0.46 V higher as compared to **1c** (*Entries 4 and 6*). The values of $\Delta E_{1/2}$ [10]⁶ vary between 120 mV for **1c** and 320 mV for **2c**, and thus reflect the relative stabilities of the mono-oxidized forms (**2c** > **1c**). As $\Delta E_{1/2}$ values provide a measure of the comproportionation constant K_{comp} , the values **1c** vs. **2c** clearly differ (112 and 260,000, *Entries 4 and 6*). Consequently, **2c** requires more energy to be oxidized than the corresponding tetraphenylethene **1c**.

A similar trend was observed for the low-temperature oxidation of derivatives **1e** and **2e** bearing AcO groups in the CH_2Cl_2 -based electrolyte system, where the higher $E_{1/2}$ value of **2e** indicates a higher relative stability as compared to **1e** (*Entries 7 and 8*). In contrast to tetraphenylethene derivative **1e**, however, the second oxidation wave of phenanthrene **2e** is irreversible.

The need of different solvents in electrochemical experiments does not allow a direct comparison of the data determined for tetraphenylethenes **1a** and **1b**, and phenanthrenes **2a** and **2b**. The electrochemistry of both 9,10-diphenylphenanthrene (**2a**) and tetraphenylethene (**1a**) was influenced by the solvent, leading, in the case of **2a**, to an irreversible oxidation in the CH_2Cl_2 -based electrolyte system and a partly reversible oxidation wave in MeCN. In contrast, **1a** showed a reversible first oxidation in CH_2Cl_2 but irreversible processes in MeCN [19]. The Br derivatives **1b** and **2b** differ in their behavior towards ferrocene. Under the experimental conditions, analyte **2b** interacted with ferrocene resulting in a complete change of the CV curves. This behavior was not observed for **1b**.

3. Conclusions. – Some novel 9,10-diphenylphenanthrene derivatives **2** were prepared, and their electrochemical behavior has been investigated by cyclic voltammetry. The first oxidation potentials of phenanthrenes **2** in the range of 0.68–1.33 V are higher than those of the corresponding tetraphenylethenes **1** (0.41–1.08 V). This result indicates not only a more difficult oxidation of the conjugated diphenylphenanthrenes but also an increased relative stability of the mono-oxidized forms as compared to the electron-rich tetraphenylethene analogues, which have a decreased conjugation.

The generous financial support by the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie*, and the *Ministerium für Wissenschaft, Forschung und Kunst des Landes Baden-Württemberg* is gratefully acknowledged. We would like to thank *Lisa Steudle* for the EPR spectroscopy.

Experimental Part

General. Solvents CH_2Cl_2 (*Fluka*) and MeCN (*Roth*) for electrochemical work were distilled over CaH_2 prior to use. DMF (*Fluka*) was stored over molecular sieves (4 Å) and purged with Ar prior to use. Flash chromatography (CC): silica gel 60 (mesh 40–63 µm; *Fluka*) with hexanes (b.p. 30–75°). IR Spectra: *Bruker Vector 22* FT-IR spectrometer with ATR technique; in cm^{-1} . ^1H - and ^{13}C -NMR spectra: *Bruker ARX 500* instrument; at 500 and 125 MHz, resp., δ in ppm, J in Hz, Me_4Si as internal standard; ^{13}C

multiplicities assigned by DEPT experiments. MS and ESI-MS: *Varian MAT 711*, *Finnigan MAT 95*, and *Bruker micrOTOF-Q*; in m/z (rel. %). EPR Spectra in the X band: *Bruker System ESP 300*; a two-electrode capillary served to generate intermediates for X band EPR studies [20].

Electrochemical Experiments. All electrochemical experiments were performed in a home-built cylindrical vacuum-tight one-compartment cell. Typical three-electrodes arrangement was used. A spiral-shaped Pt wire and a Ag wire as the counter and reference electrodes, resp., were sealed directly into opposite sides of the glass wall, while the respective working electrode (Pt, 1.1 mm, polished with 0.25- μm diamond paste (*Buehler–Wirtz*) before each experiment) was introduced via a *Teflon* screw cap with a suitable fitting. The cell was attached to a conventional *Schlenk* line via two side arms equipped with *Teflon* screw valves and allowed experiments to be performed under Ar with ca. 2.5 ml of analyte soln. In all experiments, Bu_4NPF_6 (0.2M in the respective solvent) was used as the supporting electrolyte. In all experiments, ferrocene or thianthrene were used as the internal standard, whereas the $E_{1/2}$ value of thianthrene was also calibrated vs. ferrocene. For each compound, cyclic voltammograms were run at sweep rates from 0.05 to 1.0 V s^{-1} at r.t. and low temp. (193 K in CH_2Cl_2 , 233 K in MeCN or DMF). Scans recorded at high sweep rates suffer, however, from distortions owing to *Ohmic* drop and somewhat slow electron-transfer kinetics, especially at low temp.

9,10-Diphenylphenanthrene (2a). Trifluoromethanesulfonic acid (=triflic acid; 1.72 ml, 8.60 g, 57.0 mmol) was added to a soln. of *1,1,2,2-tetraphenylethane-1,2-diol* (=benzopinacol; **1a**; 0.73 g, 2.00 mmol) in benzene (4 ml) at 10°, and the mixture was stirred at r.t. for 20 h. The mixture was poured onto ice, and the aq. layer was extracted with CH_2Cl_2 (3×10 ml). The combined org. layers were washed with H_2O (3×20 ml) and dried (MgSO_4). After removal of the solvent, the solid residue was recrystallized from CH_2Cl_2 to give **2a** (490 mg, 1.50 mmol, 75%). Colorless crystals. $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.13–7.18 (*m*, 4 arom. H, Ph); 7.19–7.23 (*m*, 2 arom. H, Ph); 7.24–7.27 (*m*, 4 arom. H, Ph); 7.49 (*ddd*, $J = 8.5, 6.8, 1.2$, 2 arom. H); 7.56 (*ddd*, $J = 8.3, 1.4, 0.5$, 2 arom. H); 7.67 (*ddd*, $J = 8.3, 6.8, 1.4$, 2 arom. H); 8.82 (*ddd*, $J = 8.5, 1.2, 0.5$, 2 arom. H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 122.5, 126.4, 126.6, 127.8 (C(1), C(2), C(3), C(4), C(5), C(6), C(7), C(8)); 126.5 (C(4')); 127.6, 131.0 (C(2'), C(3'), C(5'), C(6')); 129.9, 131.9, 137.2, 139.6 (C(1a), C(4a), C(5a), C(8a), C(9), C(10), C(1')). EI-MS: 330 (100, M^+), 313 (10), 289 (5), 252 (20), 156 (10).

3,6-Dibromo-9,10-bis(4-bromophenyl)phenanthrene (2b). At 0°, a soln. of CrO_2Cl_2 (0.60 ml, 0.11 g, 0.70 mmol) in CCl_4 (4 ml) was added dropwise to a soln. of *tetrakis(4-bromophenyl)ethene* (**1b**; 0.20 g, 0.31 mmol) in CCl_4 (20 ml). The mixture was stirred at 0° for 1 h and at r.t. for 24 h. The precipitate was filtered off, and the filtrate was washed with a $\text{Na}_2\text{S}_2\text{O}_5$ soln. (3×20 ml), dried (MgSO_4), and concentrated *i.v.* The solid residue was purified twice by CC (SiO_2 ; hexanes/ CH_2Cl_2 20:1) to give **2b** (38.0 mg, 0.06 mmol, 20%). Yellow crystals. ATR-FT-IR: 3301, 3078, 3026w, 2923m, 2854m, 1839m, 1738m, 1592vs, 1504vs, 1390vs, 1212m, 1070vs, 1010vs, 919, 794vs. $^1\text{H-NMR}$ (500 MHz, CDCl_3): 6.97 (*d*, $J = 8.6$, 2 H–C(2'), 2 H–C(6')); 7.35 (*d*, $J = 8.6$, 2 H–C(3'), 2 H–C(5')); 7.42 (*d*, $J = 8.4$, H–C(1), H–C(8)); 7.60 (*dd*, $J = 8.4, 1.9$, H–C(2), H–C(7)); 8.82 (*d*, $J = 1.9$, H–C(4), H–C(5)). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 121.4, 121.7 (C(3), C(6), C(4')); 125.5 (C(1), C(8)); 129.3 (C(4), C(5)); 130.4, 130.5 (C(1a), C(4a), C(5a), C(8a)), 130.7 (C(2), C(7)); 131.3, 132.3 (C(2'), C(3'), C(5'), C(6')); 136.1 (C(1')); 137.3 (C(9), C(10)). EI-MS: 645 (100, M^+), 565 (5), 485 (10), 406 (10), 326 (30), 202 (10), 163 (75), 80 (10). HR-EI-MS: 641.7830 ($\text{C}_{26}\text{H}_{14}\text{Br}_4^+$; calc. 641.7829).

3,6-Dimethoxy-9,10-bis(4-methoxyphenyl)phenanthrene (2c). A soln. of *tetrakis(4-methoxyphenyl)ethene* (**1c**; 0.52 g, 1.20 mmol) and I_2 (0.30 g, 1.20 mmol) in freshly distilled toluene (750 ml) was irradiated for 18 h with vigorous stirring in a reactor equipped with 700-W Hg lamp at r.t. The solvent was removed *i.v.*, and the residue was washed with a dil. $\text{Na}_2\text{S}_2\text{O}_3$ soln. and dried (MgSO_4). After removal of the solvent, the residue was purified by CC (SiO_2 ; hexanes/ AcOEt 10:1) and recrystallized from AcOEt to give **2c** (0.12 g, 0.30 mmol, 40%). Colorless crystals. $^1\text{H-NMR}$ (500 MHz, CDCl_3): 3.79 (*s*, 2 MeO); 4.03 (*s*, 2 MeO); 6.78 (*d*, $J = 8.7$, 2 H–C(3'), 2 H–C(5')); 7.04 (*d*, $J = 8.7$, 2 H–C(2'), 2 H–C(6')); 7.12 (*dd*, $J = 9.1, 2.6$, H–C(2), H–C(7)); 7.50 (*d*, $J = 9.1$, H–C(1), H–C(8)); 8.06 (*d*, $J = 2.6$, H–C(4), H–C(5)). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 55.1, 55.6 (MeO); 104.4 (C(4), C(5)); 113.0 (C(3'), C(5')); 116.1 (C(2), C(7)); 127.4 (C(1a), C(8a)); 129.5 (C(1')); 130.7 (C(1), C(8), C(9), C(10)); 132.2 (C(2'), C(6')); 132.3 (C(4a), C(5a)); 134.7 (C(3), C(6)); 157.9 (C(4')). ESI-MS: 473.18 ($[M + \text{Na}]^+$).

9,10-Bis(4-hydroxyphenyl)phenanthrene-3,6-diol (2d). In a *Schlenk* flask under inert gas atmosphere, a soln. of BBr_3 (1M in CH_2Cl_2 , 0.60 ml) was added slowly to a soln. of **2c** (0.06 g, 0.14 mmol) in abs. CH_2Cl_2 (10 ml) at -60° , and the mixture was stirred at -60° for 1 h and at r.t. for 20 h. After cooling to 0° , H_2O was added dropwise, and the precipitate was filtered off and recrystallized from $\text{EtOH}/\text{H}_2\text{O}$ 1 : 1 to give **2d** (55.0 mg, 0.14 mmol, 99%). Fine light-red crystals. $^1\text{H-NMR}$ (500 MHz, (D_6) acetone): 5.50 (br. s, 4 OH); 6.61 (*d*, $J = 8.2$, 2 H–C(3'), 2 H–C(5')); 6.83 (*d*, $J = 8.2$, 2 H–C(2'), 2 H–C(6')); 6.94 (*dd*, $J = 8.8$, 2.5, H–C(2), H–C(7)); 7.26 (*d*, $J = 8.8$, H–C(1), H–C(8)); 7.93 (*d*, $J = 2.5$, H–C(4), H–C(5)). $^{13}\text{C-NMR}$ (125 MHz, (D_6) acetone): 107.1 (C(2), C(7)); 115.3 (C(3'), C(5')); 117.7 (C(4), C(5)); 127.7, 130.1, 131.8 (C(1a), C(4a), C(5a), C(8a), C(1')); 132.3 (C(1), C(8)); 133.0 (C(2'), C(6')); 135.2 (C(9), C(10)); 156.46, 156.51 (C(3), C(6), C(4')).

[3,6-Bis(acetyloxy)phenanthrene-9,10-diyl]dibenzene-4,1-diyl Diacetate (2e). Ac_2O (0.50 ml, 180 mg, 1.73 mmol) was added to a soln. of **2d** (55.0 mg, 0.14 mmol) in pyridine (10 ml), and the mixture was stirred at r.t. for 15 h. The solvent was removed *i.v.*, the residue was dissolved in CH_2Cl_2 (10 ml), successively washed with dil. HCl (3×10 ml) and a sat. soln. of NaHCO_3 (3×10 ml), and dried (MgSO_4). The solvent was removed *i.v.*, and the residue was purified by CC (SiO_2 ; hexanes/ AcOEt 3 : 2) to give **2e** (55.0 mg, 0.10 mmol, 70%). Colorless crystals. ATR-FT-IR: 3063, 3031 w , 2937 s , 2323 w , 1753 vs , 1609 m , 1526, 1499, 1428, 1366 vs , 1180 vs , 1010 s , 908 s . $^1\text{H-NMR}$ (500 MHz, CDCl_3): 2.29 (*s*, 2 Me–C(4')); 2.40 (*s*, Me–C(3), Me–C(6)); 7.00 (*d*, $J = 8.8$, 2 H–C(3'), 2 H–C(5')); 7.12 (*d*, $J = 8.8$, 2 H–C(2'), 2 H–C(6')); 7.25 (*dd*, $J = 8.9$, 2.6, H–C(2), H–C(7)); 7.61 (*d*, $J = 8.9$, H–C(1), H–C(8)); 8.36 (*d*, $J = 2.6$, H–C(4), H–C(5)). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 21.2, 21.3 (Me); 114.9 (C(4), C(5)); 120.9 (C(3'), C(5')); 121.6 (C(2), C(7)); 129.5 (C(1), C(8)); 129.9 (C(1a), C(8a)); 130.7 (C(4a), C(5a)); 131.9 (C(2'), C(6')); 136.1, 136.5 (C(1'), C(10), C(9)); 149.3, 149.4 (C(3), C(6), C(4')); 169.3, 169.7 (C=O). EI-MS: 562 (100, M^+), 520 (50), 478 (60), 436 (40), 394 (50), 365 (5), 321 (5), 254 (1), 197 (1), 127 (1), 99 (1), 43 (10). HR-ESI-MS: 585.1518 ($[M + \text{Na}]^+$, $\text{C}_{34}\text{H}_{26}\text{NaO}_8^+$; calc. 585.1525).

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Received June 21, 2010