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Ions Derived from Dianthrylethane Species. How the Mode of Linking Affects the Intramolecular Electron Transfer

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Abstract: Chemical and electrochemical reduction of dianthryl compounds affords mono-, di-, tri-, and tetraanions via successive electron-transfer processes. The diamagnetic or paramagnetic ions are characterized by NMR and ESR spectroscopy, respectively, by cyclic voltammetry, and by quenching reactions. The title dianthryl systems have in common that two anthracene units are linked by ethane bridges in a sterically variable fashion. It appears that the mode of linking drastically affects the rate of intramolecular electron-transfer processes in radical monoanions as well as the charge-storage behavior.

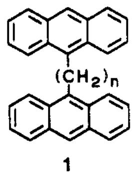
1. Introduction

Electron-transfer reactions of molecules with two or more identical redox centers (electrophors) are of fundamental and practical importance.[1] The relevant charging mechanisms depend sensitively on the energy of interaction between the single electrophors and thus on the nature of the linking groups. Even if saturated spacers are used and a conjugative "coupling" of the electrophors is absent, the latter can still interact electrostatically so that one will not expect independent charging steps. Cyclic voltammetric measurements have been extensively applied to describe the energetics of electron-transfer reactions in bis- and polyelectrophoric redox systems.[2-6] The available information has been used inter alia to evaluate the charge-storage capacity of the substrates and to distinguish between conducting polymers[1,7] and redox polymers.[4,8]

Another important aspect in the redox behavior of bis- and polyelectrophoric systems concerns the possibility of intramolecular electron-hopping processes.[9,10] Investigations of the rate of intramolecular long-distance electron transfer between suitable donor and acceptor functionalities have mostly considered the relation between rate and driving force of the reaction.[10]

In contrast to these processes the intramolecular electron exchange between identical electrophors is a *degenerate* process. The radical anion formed upon injection of an electron into a molecule with two or more separate redox centers may tend to localize the extra charge in one of the subunits or, depending on the rate of the electron-hopping process, establish an effective charge delocalization within the time scale of the ESR experiment. It appears that the actual structure of biselectrophoric radical anions and, in particular, the rate of intramolecular electron transfer are influenced by the length and conformation of the linking groups,[11-13a,15] the nature of the electrophors,[14] and the ion pair structures.[15] Another factor controlling the electron transfer is the number of extra charges since successive reduction to di-, tri-, or even tetraanions affects not only the prevailing ion pair structure, but also the spin multiplicity of the species and the relative spatial arrangement of the subunits.[11,16]

As examples of conformationally mobile bis- and polyelectrophors, anthracene derivatives have been of special significance.[3,12,13,17] We have recently compared the biselectrophoric 1,*n*-di(9-anthryl)alkanes (**1**)[13a] with their structurally related oligomers and polymers (**2**).[11,18] Considering the importance of the linking mode for the redox activity and for the rate of intramolecular electron transfer, we decided to investigate dianthryl species in which the relative spatial arrangement of the subunits can be systematically varied. The title systems **1a**, **3a**, **4a**, and **5**–**7** have in common that anthracene groups are linked by ethane bridges but differ in the centers at which the bridges are attached. The conformational mobility prevailing in the dianthrylethanes



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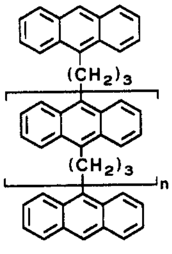
b: n = 3



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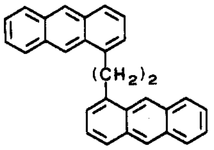
b: n ~10



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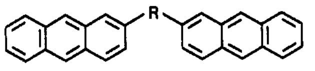

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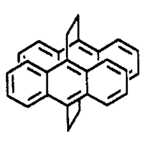
a: R = $-(CH_2)_2$
b: R = $-(CH_2)_3$
c: R = -CH=CH-



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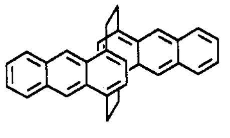

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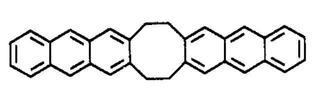

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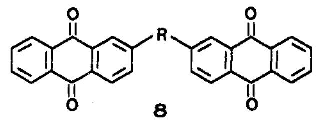
1a, **3a**, and **4a** is reduced in the orthocyclophane **7** or fully removed in the rigid paracyclophanes **5** and **6**.

Herein we report the results of chemically or electrochemically induced electron-transfer processes undergone by the dianthryl species **1** and **3a**–**7** and by the "mono"-anthryl species **12**–**15**. Under appropriate experimental conditions, the dianthrylethanes **1a**, **3a**, and **4a** and the corresponding dianthrylpropanes **1b** and **4b** as well as the orthocyclophane **7**, but not the paracyclophanes **5** and **6**, form stable tetraanion salts which can be characterized by NMR spectroscopy. The degree of electronic interaction between the charged anthracene subunits is experimentally determined by the cyclic voltammetric measurement of the relevant reduction potentials. In spite of the close structural analogy, the radical anions derived from **1a**, **3a**, **4a**, and **5**–**7** differ significantly in the mode of spin density distribution and in the rate of intramolecular electron-hopping processes.

2. Results

2.1 Syntheses. The dianthryl compounds **1a**,^{19} **1b**,^{20} **3a**,^{21} **5**,^{22} and **6**^{23} as well as the methyl-substituted anthracene **12**–**15**^{24} were prepared according to the literature.

The syntheses of **4a**, **4b**, and **7** have not been described previously. Compound **4a** was prepared from the known ethylene compound **8a**^{25} by reduction of the anthraquinone subunits with aluminum tricyclohexanolate to yield **4c** and subsequent hydrogenation of the ethylene bridge.^{26} Compound **4b** was prepared by Friedel–Crafts acylation of 1,3-diphenylpropane with *o*-phthalic anhydride to give **9**, cyclization with concentrated sulfuric acid to **8b**, followed by reduction.



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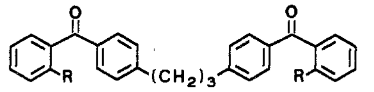
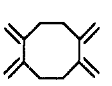
a: R = -CH=CH-
b: R = -(CH$_2$)$_3$



9 (R = COOH)



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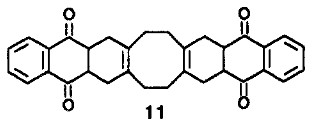

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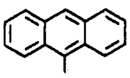

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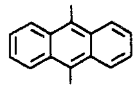

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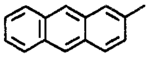

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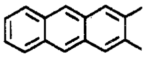

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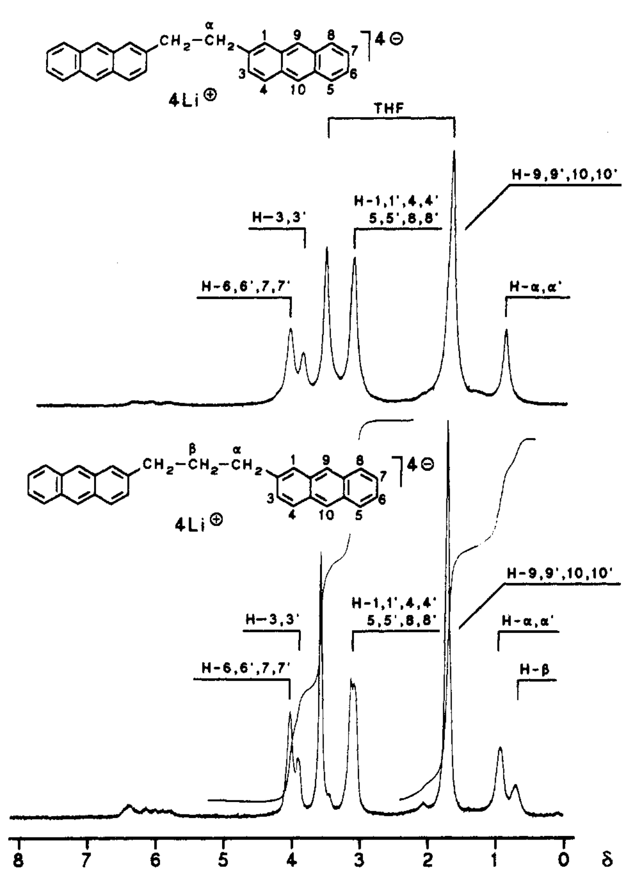

Figure 1. ^{1}H NMR spectra of **4a**$^{4-}$/4Li$^+$ and **4b**$^{4-}$/4Li$^+$ (200 MHz, THF-d_8, −50 °C). The signals of H-9, -9′, -10, and -10′ are covered by those of the solvent.

[2.2](2,3)Anthracenophane (**7**) was synthesized by a twofold Diels–Alder reaction between 1,2,5,6-tetra-*exo*-methylenecyclooctane (**10**) with 1,4-naphthoquinone (2 equiv), which gave a mixture of the syn and anti isomers of 1,4,9,10-tetrahydro-[2.2](2,3)anthracenophane-9,10-dione (**11**) in 70% yield.^{27} Oxidation of **11** with oxygen provided the corresponding compound containing two anthraquinone subunits which was reduced with aluminum tricyclohexanolate (180 °C, 3 days) to **7**.

2.2 NMR Studies. To investigate the electron-acceptor properties of biselectrophors in extended redox sequences, the dianthryl compounds **1** and **3a**–**7** were subjected to reduction with alkali metals in THF-d_8 at low temperatures under ESR and ^{1}H NMR spectroscopic control. The detailed ESR spectroscopic characterization of intermediate paramagnetic products is given below. The final diamagnetic reduction products could be identified as lithium salts of the tetraanions **1a**$^{4-}$,^{13a} **1b**$^{4-}$,^{13a} **3a**$^{4-}$, **4a**$^{4-}$, **4b**$^{4-}$, and **7**$^{4-}$. The structure was proven by high-resolution ^{1}H and ^{13}C NMR spectroscopy and by quenching experiments (Figure 1; Tables I and II). Thus, reaction of the tetraanions with dimethyl sulfate gave rise to tetramethyl derivatives which were identified by MS spectrometry. The ^{1}H signal assignments of the tetraanions shown in Table I follow from relative intensities, splitting patterns, and homonuclear decoupling experiments. To assist the analysis of the ^{1}H NMR spectra, we also prepared the dianions of 9-

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Table I. ^{1}H NMR Chemical Shifts of Di- and Tetraanion Salts

	CH_2	H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-8	H-9	H-10
$\delta_H(\mathbf{1a}^{4-}/4Li^+)^a$	0.36	3.52	4.25	4.14	3.21					–	1.87
$\delta_H(\mathbf{1b}^{4-}/4Li^+)^{a,c}$											
$\delta_H(\mathbf{3a}^{4-}/4Li^+)^d$	0.72	–	4.0–4.4		3.15–3.6		4.0–4.4		3.15–3.6	1.80	1.88
$\delta_H(\mathbf{4a}^{4-}/4Li^+)^b$	0.94	3.20	–	3.96	3.20	3.20	4.14	4.14	3.20	1.72	1.72
$\delta_H(\mathbf{4b}^{4-}/4Li^+)^b$	0.71 0.92	3.12	–	3.90	3.12	3.12	4.03	4.03	3.12	1.72	1.72
$\delta_H(\mathbf{5}^{2-}/2K^+)^a$	1.84	5.11	5.55								
$\delta_H(\mathbf{12}^{2-}/2Li^+)^a$	0.27	3.47	4.30	4.30	3.47						1.97
$\delta_H(\mathbf{14}^{2-}/2Li^+)^b$	0.84	3.18	–	3.92	3.18	3.18	4.10	4.17	3.18	1.74	1.74

[a] 300 MHz, −30 °C, THF-d_8.[13] [b] 200 MHz, −50 °C, THF-d_8.[26] [c] Differences in chemical shifts <0.2 ppm with respect to $\mathbf{1a}^{4-}$. [d] 200 MHz, −30 °C, THF-d_8.

Table II. ^{13}C NMR Chemical Shifts of Di- and Tetraanion Salts

	CH_2	C-1	C-2	C-3	C-4	C-9	C-10	C-4a, -10a	C-8a, -9a
$\delta_C(\mathbf{1a}^{4-}/4Li^+)^a$	20.7	101.2	116.2	113.8	100.7	86.6	76.4	148.6	151.8
$\delta_C(\mathbf{5}^{2-}/2K^+)^a$	23.2	116.2	117.2	117.2	116.2	112.6	112.6	141.9	141.9

	C-9	C-1, -4, -5, -8	C-3, -6, -7	C-2	C-4a, -8a, -9a, -10a
$\delta_C(\mathbf{4a}^{4-}/4Li^+)^a$	74.8 76.4	100.8 101.5 102.7 104.8	113.9 114.2 115.2	129.9	148.8 151.3 151.9
$\delta_C(\mathbf{14}^{2-}/2Li^+)^b$					

[a] 50 MHz, −50 °C, THF-d_8. [b] Data slightly different according to $\mathbf{4a}^{4-}$.[26]

Table III. Cyclic Voltammetric Data for the Reduction of **1a**, **3a**, **4a**, **5–7**, and **12–15**[a]

	$E^1_{1/2}$, V	$E^2_{1/2}$, V	$E^1_{1/2} - E^2_{1/2}$, mV
1a	−2.215	−2.31	95
3a[b]	−2.205	−2.205	≤80
4a[b]	−2.195	−2.195	≤80
5	−2.05	−2.47	420
6	−2.155	−2.43	275
7[b]	−2.21	−2.21	≤80
12	−2.24		
13	−2.195		
14	−2.205		
15	−2.28		

[a] THF, TBAPF$_6$, T = 0 °C, v = 100 mV/s, calibration with ferrocene (310 mV versus SCE). [b] Two-electron transfer of two independent π-centers.

methylanthracene ($\mathbf{12}^{2-}/2Li^+$), 9,10-dimethylanthracene ($\mathbf{13}^{2-}/2Li^+$), and 2-methylanthracene ($\mathbf{14}^{2-}/2Li^+$). In contrast to **1a**, **3a**, and **4a**, the cyclophanes **5** and **6** do not give rise to tetraanions with intact σ-frame but suffer from reductive cleavage of an ethane bridge upon prolonged metal contact. We have shown that the reduction of **1a** and **2a** gives rise to a tetraanion and a hexaanion, respectively.[11,13a,17]

2.3 Cyclic Voltammetric Studies. In the cyclic voltammetric investigation of the title compounds, special precautions must be taken to record the waves corresponding to the electron transfer at extremely negative potential.[28] The data (Table III) were measured under "superdry" conditions[29] at a temperature of 0 °C. The scan rate was 100 mV/s, and as a standard for calibration ferrocene vs SCE was used. Cyclic voltammograms of the species **1a**, **3a**, **4a**, and **5–7** were obtained and compared to those of the monoanthryl compounds **12–15**. In all cases, reversible dianion formation of the dianthryl compounds with different $\Delta E = E^1_{1/2} - E^2_{1/2}$ values were observed. These differences vary between <80 (**3a**, **4a**, **7**) and 420 mV (**5**). The peak potentials of the first step are slightly different and will be discussed further (Figures 2 and 3).

2.4 ESR/ENDOR Studies. The ESR or ENDOR spectra of the radical monoanions of **1a**,[13a] **1b**,[13a] **5**,[13b] and **6**[30] have already been described in the literature. For the ESR and ENDOR spectroscopic investigation of the paramagnetic anions of **3a**, **4a**, and **7**, the neutral compounds were subjected to a reduction with potassium in ethereal solvents like dimethoxyethane (DME), tetrahydrofuran (THF), and 2-methyltetrahydrofuran (MTHF) and in mixtures of DME and hexamethylphosphoric triamide (HMPA).

The initial ESR spectra observed during reduction were assigned to the radical monoanions (Figure 4). The structure proof for these species rested upon the analysis of the ESR and ENDOR

Table IV. Hyperfine Coupling Constants of the Radical Anions $\mathbf{1a}^{\bullet-}$, $\mathbf{3a}^{\bullet-}$, $\mathbf{4a}^{\bullet-}$, $\mathbf{5}^{\bullet-}$, $\mathbf{6}^{\bullet-}$, and $\mathbf{7}^{\bullet-}$ and of the Radical Trianions $\mathbf{1}^{\bullet 3-}$ and $\mathbf{3}^{\bullet 3-}$

	1, 4, 5, 8[a]	2, 3, 6, 7[a]	9, 10[a]	CH_2[b]
$\mathbf{1a}^{\bullet-}/K^{+c}$	0.148 (4 H)	0.098 (4 H)	0.264 (2 H)	0.096 (4 H)
	0.121 (4 H)	0.059 (4 H)		
$\mathbf{1a}^{\bullet 1}/K^{+d}$	0.282 (2 H)	0.168 (2 H)	0.510 (1 H)	0.250 (2 H)
	0.261 (2 H)	0.136 (2 H)		0.029 (2 H)
$\mathbf{1a}^{\bullet 3-}/3K^{+d}$	0.283 (4 H)	0.146 (4 H)	0.472 (1 H)	0.228 (2 H)
				0.035 (2 H)
$\mathbf{3a}^{\bullet-}/K^{+c}$	0.134 (6 H)	0.070 (8 H)	0.270 (2 H)	0.134 (4 H)
			0.255 (2 H)	
$\mathbf{3a}^{\bullet-}/K^{+d}$	0.280 (1 H)			
	0.260 (1 H)	0.160 (2 H)	0.550 (1 H)	0.143 (2 H)
	0.246 (1 H)	0.143 (2 H)	0.530 (1 H)	
$\mathbf{3a}^{\bullet 3-}/3K^{+c}$	0.295 (2 H)	0.149 (4 H)	0.530 (2 H)	0.125 (2 H)
	0.242 (1 H)			
$\mathbf{4a}^{\bullet-}/K^{+c,d}$	0.279 (2 H)	0.162 (2 H)	0.541 (1 H)	0.096 (2 H)
	0.255 (2 H)	0.141 (1 H)	0.507 (1 H)	
$\mathbf{5}^{\bullet-}/K^{+c,d}$	0.126 (8 H)	0.082 (8 H)		0.163 (8 H)
$\mathbf{6}^{\bullet-}/K^{+c}$	0.111 (4 H)	0.075 (8 H)	0.242 (4 H)	0.164 (4 H)
				0.015 (4 H)
$\mathbf{7}^{\bullet-}/K^{+c,d}$	0.288 (2 H)	0.152 (2 H)	0.528 (2 H)	0.152 (2 H)
	0.244 (2 H)			0.038 (2 H)

[a] Numbers of π-centers. [b] Ethane bridges. [c] DME/HMPA ≈ 5/1 as solvent. [d] MTHF as solvent.

Table V. Zero-Field Parameters Observed for the Triplet Dianions $\mathbf{1}^{\bullet 2-}$, $\mathbf{4a}^{\bullet 2-}$ (A), $\mathbf{4a}^{\bullet 2-}$ (B), $\mathbf{7}^{\bullet 2-}$, and $\mathbf{3a}^{\bullet 2-}$ in Glassy Solutions of MTHF (T = 130 K)

	$\mathbf{1}^{\bullet 2-}$	$\mathbf{4a}^{\bullet 2-}$ (A)	$\mathbf{4a}^{\bullet 2-}$ (B)	$\mathbf{7}^{\bullet 2-}$	$\mathbf{3a}^{\bullet 2-}$
D, mT	8.4	7.1	3.7	8.4	5.9

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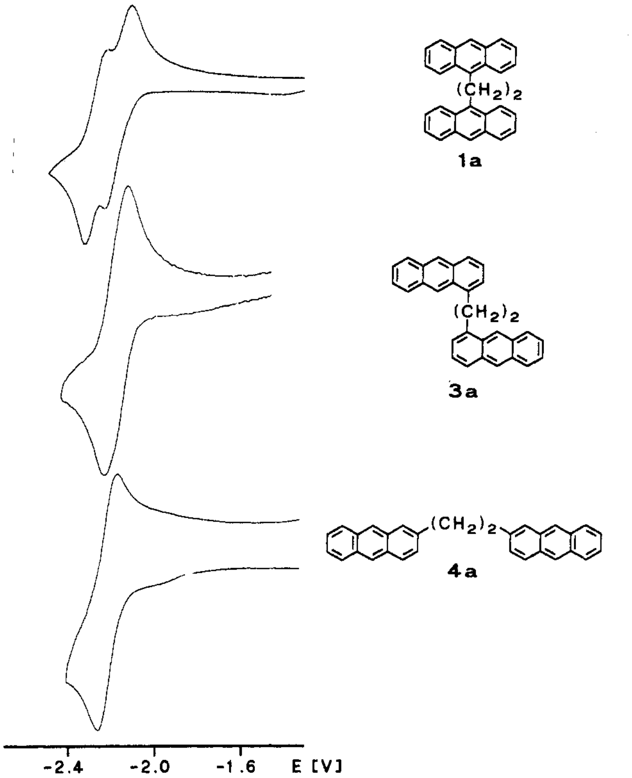

Figure 2. Cyclic voltammograms for the reduction of **1a**, **3a**, and **4a** (v = 100 mV/s) at 0 °C in THF–TBAPF$_6$ versus SCE.

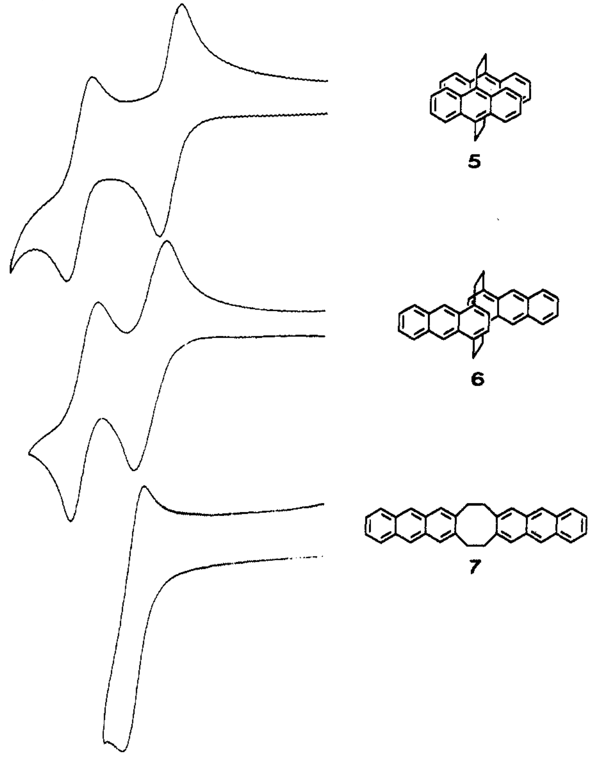

Figure 3. Cyclic voltammograms for the reduction of **5**, **6**, and **7** (v = 100 mV/s) at 0 °C in THF–TBAPF$_6$ versus SCE.

spectra, e.g., on the number and multiplicity of the hyperfine coupling constants.[31] The results of this analysis are summarized in Table IV together with the hyperfine data of the paramagnetic

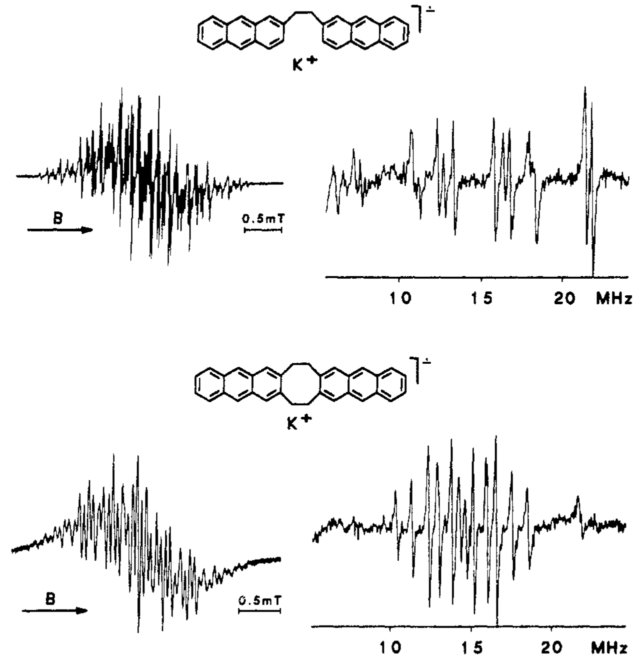

Figure 4. ESR spectra of $\mathbf{4a}^{\bullet-}/K^+$ (DME, −70 °C) and $\mathbf{7}^{\bullet-}/K^+$ (DME/HMPA, −60 °C) as well as ENDOR spectra of $\mathbf{4a}^{\bullet-}/K^+$ (DME, −70 °C) and $\mathbf{7}^{\bullet-}/K^+$ (DME/HMPA, −60 °C).

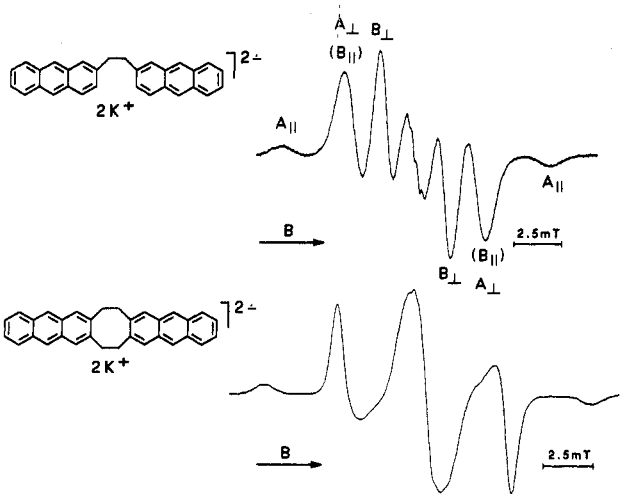

Figure 5. ESR spectra of $\mathbf{4a}^{\bullet 2-}/2K^+$ (DME, −170 °C) and $\mathbf{7}^{\bullet 2-}/2K^+$ (DME/HMPA, −170 °C). The ESR spectrum of $\mathbf{4a}^{\bullet 2-}$ is a superposition of different spectra of the two isomeric forms A and B ($B_{\parallel}$ is covered by $A_{\perp}$).

anions of **1a**, **5**, and **6**. The assignment of the hyperfine coupling constants given in Table IV is based on a comparison with the spin density distribution in the radical anion of anthracene where the sequence of local spin densities is $\rho_{9,10} \gg \rho_{1,4,5,8} > \rho_{2,3,6,7}$. Thus, the assignment is not confirmed by experimental evidence.

The disappearance of the initial signals of the radical anions $\mathbf{1a}^{\bullet-}$, $\mathbf{3a}^{\bullet-}$, $\mathbf{4a}^{\bullet-}$, and $\mathbf{7}^{\bullet-}$ during further reduction was indicative of the formation of dianions. In glassy solutions of MTHF (T < −130 °C), the dianionic species $\mathbf{1a}^{2-}$,[13a] $\mathbf{3a}^{2-}$, $\mathbf{4a}^{2-}$, and $\mathbf{7}^{2-}$ showed ESR spectra whose fine structure points toward the existence of triplet biradicals (Figure 5). The zero-field splittings taken from these spectra are summarized in Table V. For the dianion $\mathbf{4a}^{2-}/2K^+$ the ESR spectrum is a superposition of two spectra from species labeled A and B. Prolonged metal contact of the solutions of the dianions of $\mathbf{1a}^{2-}$,[13a] $\mathbf{3a}^{2-}$, $\mathbf{4a}^{2-}$, and $\mathbf{7}^{2-}$ leads to the appearance of new ESR spectra. Only for compounds **1a**[13a] and **3a** could the paramagnetic species responsible for these spectra be unambiguously determined via ESR and ENDOR spectroscopy. From the spectroscopic monitoring of the successive reduction processes (i.e., from the appearance and disappearance of ESR spectra) and

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(31) Kurreck, H.; Kirste, B.; Lubitz, W. *Angew. Chem.* **1984**, *96*, 171; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 173.

from the size, number, and multiplicity of the coupling constants (see Table IV), the final spectra can be assigned to the radical trianions.

3. Discussion

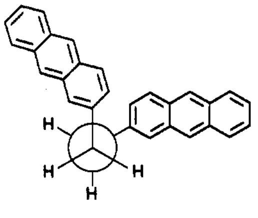
3.1 Redox Activity of Dianthryl Compounds: From Mono- to Tetraanions. When the NMR spectra of the tetraanion salts derived from **1a**, **1b**, **3a**, **4a**, and **4b** are considered, the following features are obvious:

(1) When local π-charge densities are correlated with ^{1}H or ^{13}C NMR chemical shifts,[32] all ionic species exhibit the charge-density order q_π(C-9) > q_π(C-1) > q_π(C-2).

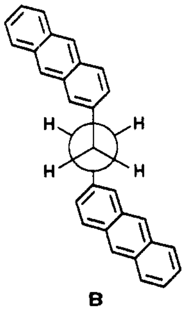
(2) The upfield shift of ^{1}H NMR signals in the charged species is much more pronounced than expected from the sole charge effect alone; this is due to the paratropism of a doubly charged anthracene group.

(3) When the ^{1}H NMR chemical shifts of **1a**$^{4-}$/4Li$^+$ and **4a**$^{4-}$/4Li$^+$ are compared with those of **1b**$^{4-}$/4Li$^+$ and **4b**$^{4-}$/4Li$^+$, respectively, no effect of the bridge length is detectable. Both sets of data are nearly identical and closely correspond to those of the "monomeric" model species **12**$^{2-}$/2Li$^+$ and **14**$^{2-}$/2Li$^+$. Consequently, the tetraanions can be regarded as being made up of two more or less independent anthryl dianion subunits. The conformation of the chain must allow the doubly charged electrophors to move far apart, since the anisotropic shielding effects between the two rings would otherwise be detectable in the observed ^{1}H resonances. In an anti conformation with respect to the ethane bond, e.g., in **1a**$^{4-}$/4Li$^+$ or **4a**$^{4-}$/4Li$^+$, severe Coulomb repulsions between the subunits can be avoided.

The situation in the triplet dianion **4a**$^{2-}$/2K$^+$ appears to be somewhat different. The two species (A and B) observed in the ESR spectra can be explained by assuming two (noninterconverting) isomers. From the experimental zero-field splitting parameters one can roughly estimate the average distance of the unpaired electrons.[33] Accordingly, the two structures can be identified as conformers A and B, which differ in the degree of interaction of the anthracene subunits. Inspection of models favors a gauche conformation for the species A and an anti conformation for component B. A syn conformation should result in a larger zero-field splitting than the measured 7.1 mT and can thus be excluded.



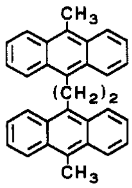
A



B

Although the successful minimization of electrostatic effects is certainly a crucial aspect, it should be noted that the formation of tetraanions is also a matter of carefully controlled reaction conditions. For instance, the reduction of 1,2-diarylethanes has been reported in the literature to induce reductive cleavage of the ethane σ-bond.[34]

Obviously, there is no significant difference for highly charged derivatives of the isomeric dianthrylalkanes **1a**, **3a**, and **4a**. In the cyclophane **5**, however, the Coulomb repulsion in highly charged species is too severe: while a dianion is available,[13b] attempted tetraanion formation induces a reductive σ-bond cleavage with formation of the 10,10′-dimethyl-1,2-di(9-anthryl)ethane (**16**).[13b] The electrostatic repulsion of charged cyclophane species can be lowered by avoiding the face-to-face arrangement of **5** by going to either the 1,4-bridged analogue **6** or the orthocyclophane **7**.



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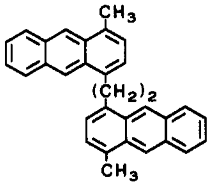

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An analogous cleavage of one ethane bridge is also observed when **6** is reduced to the monoanion in MTHF. In this solvent, which favors the formation of dianions, the primary ESR spectra must be assigned to the radical anion of 4,4′-dimethyl-1,2-di(1-anthryl)ethane (**17**). The coupling constants observed for this radical anion closely resemble those of 1-methylanthracene.[35]

It is not surprising that **7**, in which the anthracene layers are no longer parallel and their mean distance is increased, is again able to form a tetraanion which is evidenced from quenching reactions.

The ease with which an electron is injected into an anthracene ring of the title compounds is measured by the first reduction potential $E^1{}_{1/2}$. The question arises whether the presence of the second electrophoric anthracene group facilitates the reduction of the first one. The first question can be tackled by referring to alkyl-substituted (mono)anthracene compounds with the same substitution pattern as in the biselectrophors. When comparing, e.g., compounds **1a** and **12** or **4a** and **14**, one notes that radical anion formation in the dimers occurs at a slightly less negative potential (see Table III). Such an "assisting effect" in the "dimers", however, is small and can hardly be differentiated from the prevailing solvent and ion-pairing effects.

As expected, however, the presence of a second anthracene layer with strong π-overlap shifts $E^1{}_{1/2}$ to more positive values. This can be deduced from a comparison of **1a**, **5**, and **6** or from a comparison of **5** and **13**. A second question in dealing with the $E^1{}_{1/2}$ values concerns a possible difference of the isomeric systems **1a**, **3a**, and **4a**. The actual effect is small but can be rationalized by referring to the (positive) inductive effects of the bridging group. Within a simple perturbational approach, the substituent-induced destabilization of the LUMO is proportional to the square of the AO coefficient of the relevant π-center. The well-known sequence of AO coefficients $c_9 \gg c_1 > c_2$ for the anthracene LUMO is thus in accord with the data.[36]

Electrochemical formation of a dianion implies the injection of one electron into each of the anthracene subunits. The crucial question concerns the energy of interaction of the charged electrophors. The appropriate criterion is the difference $E^1{}_{1/2} - E^2{}_{1/2}$. Not surprisingly, this difference is largest in **5** and decreases in the series of cyclophanes **5**, **6**, and **7**. Within the dianthrylethane series, the potential difference decreases when going from **1a** to **3a** and **4a**. This outcome can again be explained by the AO coefficients c_9, c_1, and c_2 in the anthracene LUMO since the electrostatic interaction between the charged anthracene rings should mainly depend on the charge (spin) densities at the bridgehead centers.

3.2 Degenerate Electron Transfer in Radical Anions. It appears that an interpretation of the hyperfine data of the radical monoanions is in full agreement with the conclusions drawn from cyclic voltammetry. The first question to deal with is whether the unpaired electron is localized in one electrophoric subunit or undergoes a rapid hopping between both subunits, leading to an "effective" delocalization of the spin density within the time scale

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(35) Ehrenfreund, M.; Huber, W. Unpublished results.

(36) Note, for example, that according to the squared AO coefficients of the anthracene LUMO the compounds **14** and **15** should be reduced with greater ease than **13**, which is at variance with experiment.

of the ESR experiment. The following criteria can be applied:

(1) In radical anions with the unpaired electron localized in one anthracene moiety, the magnitude of related coupling constants resembles that in anthracene or alkyl-substituted anthracene radical anions a(H-9, -10) ≈ 0.5–0.6 mT; a(H-1, -4, -5, -8) ≈ 0.2–0.3 mT; a(H-2, -3, -6, -7) ≈ 0.1–0.2 mT.[37]

(2) Localization of the unpaired electron within one anthracene subunit lowers the symmetry of the system. This symmetry deformation can be investigated by simply counting the number of equivalent protons giving rise to a particular coupling constant.

(3) Radical anions with their unpaired electron symmetrically delocalized over the two subunits possess coupling constants half as large as those in anthracene or alkyl-substituted anthracene radical anions.

Relying on these experimental criteria, the radical monoanions of compounds **1a**, **3a**, **4a**, and **5**–**7** can be classified into three groups. Class I comprises the radical anions **5**$^{\bullet-}$ and **6**$^{\bullet-}$. Independent of the solvent and the temperature, the unpaired electron of these radicals appears to be *delocalized* over both anthracene subunits. Class III comprises radical anions **4a**$^{\bullet-}$ and **7**$^{\bullet-}$, which behave in a completely different fashion. For all solvents studied, the unpaired electron is *localized* in one anthracene subunit. Class II comprises the radical anions **1a**$^{\bullet-}$ and **3a**$^{\bullet-}$ for which the distribution of the unpaired electron is highly affected by the solvent. In solvents such as MTHF, which favor the formation of contact ion pairs, these radical anions possess a spin-*localized* structure. Turning to solvents with a high cation-solvating power like mixtures of DME and HMPA, the observed hyperfine data become indicative of a system in which the unpaired electron is *delocalized* over both anthracene subunits. For solvents with intermediate cation solvation such as THF or THF/DME, one observes mixtures of radical anions with either localization or delocalization of the unpaired electron. Remarkably enough, the spin-localized and spin-delocalized radical anions, although representing different modes of ion pairing, do not interconvert in solution.

The strong influence of the ion-pairing situation in biselectrophoric systems upon the rate of intramolecular electron hopping follows from the fact that the electron transfer must be accompanied by a migration of the counterion and thus by a reorganization of the ion pair structure. The energy involved contributes to the total reorganization energy. Accordingly, in contact ion pairs with a tight interaction of organic anion and counterion the intramolecular electron exchange becomes slow; i.e., the rate constant is lower than about 10^6 s^{-1}. It should be pointed out that even with an appropriate choice of the bridging units and of the ion pairing the rate constant may still correspond to the time scale of the ESR experiment and give rise to temperature-dependent line broadening effects.[11]

Why do the radical anions of differently linked, but closely related, dianthrylethane species fall into three categories? The intramolecular electron transfer between separate electrophors requires some mixing of electronic wave functions of starting system and product and will thus depend on the through-space and/or through-bond electronic interaction of the redox subunits. Thereby, the interactions of the nearest π-centers (the "bridgehead" centers) are particularly important. One can thus refer to the sum of the spin densities (or equally well to the sum of the squared AO coefficients of the SOMO) at the π-centers linked by ethane bridges. From such values [ρ(**5**) > ρ(**6**) > ρ(**1a**) > ρ(**3a**) ≫ ρ(**7**) > ρ(**4a**)] one obtains qualitatively a similar classification as by the interpretation of the spectroscopic and cyclic voltammetric data. From this estimation, **5** and **6** are expected to have high electronic interaction, whereas this interaction is of minor importance for compounds **4a** and **7**. Compounds **1a** and **3a** lie between these two extremes. In these compounds, the gain in stabilization energy via π–π interaction seems to be in the same order of magnitude as the stabilization energy resulting from ion pairing.

4. Conclusion

In the present empirical approach NMR spectroscopic, ESR spectroscopic, and cyclic voltammetric experiments have been combined to describe the redox activity and the rate of intramolecular electron exchange for biselectrophoric π-systems. Both features appear to depend sensitively upon even slight structural changes. It is, thus, possible to control the energy profile of degenerate electron-hopping processes by choosing an appropriate mode of linking of the single electrophors. This finding demands particular attention since intramolecular electron transfer has recently been considered as a background process of intramolecular electronics, that is, the use of single molecules to process electrical signals.[38]

5. Experimental Section

NMR Experiments. To prepare lithium–organic compounds, special NMR tubes were used, which could be connected to a vacuum line. Dried (stirred over Na/K alloy) and degassed solvent (THF-d_8) was condensed on the compound, and lithium was transferred with a press as a thin wire into the reduction cell, which in turn was connected to the NMR tube. The tube was sealed off and the solution carefully degassed under vacuum. When the tube was turned upside down, the solution was brought into contact with the metal at low temperature. By means of NMR and ESR spectrometry, one was able to control the reduction process.

Quenching of the Anions. To quench the highly charged anions, the NMR tube was opened in a silicon skin filled with argon. The necessary reagent (dimethyl sulfate) was injected. After the disappearance of the color, the solution was stirred for half an hour, and 10 mL of concentrated aqueous NH_3 solution was added. The organic layer was washed with water, dried, and concentrated. The product was filtered with $CHCl_3$ through a pipet filled with silica gel and evaporated. To characterize the product, NMR spectrometry and mass spectrometry were used.

Cyclic Voltammetric Experiments. The cyclic voltammetry was carried out under strictly inert conditions. The 5×10^{-2} M solution of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in THF was degassed in the cell and dried at a temperature of 0 °C under N_2 overpressure with an integrated alumina column. Ca. 5 mg of the compound (10^{-3}–10^{-4} mol/l) was added in a N_2 counterflow, and a series of cyclic voltammograms was recorded potentiostatically at different temperatures and scan rates. The data from Table III were obtained at 0 °C and 100 mV/s. As a working electrode, a platinum disk (o.d. = 1 mm), and as a counter electrode, a platinum wire, were used, whereby the latter was wound concentrically around the electrode. A silver wire was employed as a quasi-reference, and ferrocene was used as an internal standard (310 mV versus SCE) for calibration.

1,3-Diphenylpropane. A mixture of 1,3-diphenylacetone (88 g, 0.42 mol), hydrazine hydrate solution (62.8 g, 1.26 mol, 85 wt % in water), and powdered KOH (79.2 g, 1.41 mol) in triethylene glycol (500 mL) was heated to reflux. After 2 h, the hydrazine and the water were removed by distillation, and after 5 h, the nitrogen generation was finished. The solution was cooled to room temperature and poured into HCl (500 mL, 2 N). The mixture was extracted with methylene chloride, and the combined organic layers were washed with Na_2CO_3/H_2O solution and with water. After being dried, the crude product was purified by fractional distillation (150 °C, 9 Torr) to give 65.5 g (80%) of 1,3-diphenylpropane: ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.90 (m, 2 H), 2.53 (t, 4 H), 7.05 (m, 10 H).

1,3-Bis[4-(2-carboxybenzoyl)phenyl]propane (9). 1,3-Diphenylpropane (15 g, 76.5 mmol) and *o*-phthalic anhydride (22.3 g, 150 mmol) were dissolved in chlorobenzene (200 mL), and $AlCl_3$ (40 g) was added under vigorous stirring at room temperature. After stirring for 5 h at 80–90 °C, H_2SO_4 (200 mL, 2 N) was poured into the solution and the aqueous layer was extracted with methylene chloride. The combined organic layers were dried over sodium sulfate, and the solvent was evaporated. The residue was treated with a saturated $NaHCO_3/H_2O$ solution and submitted to a water vapor distillation. After acidifying with HCl, one obtained a mixture (46.4 g) of mono- and diacetylated product, which contained **9** as main component (70%). The crude product could not be separated and was used for the next reaction without further purification.

1,3-Di(2′-anthraquinoyl)propane (8b). A suspension of **9** (4 g, 8.1 mmol) in concentrated H_2SO_4 (70 mL) was heated for 5 h to 150 °C. After being cooled to room temperature, the mixture was poured onto ice and extracted with methylene chloride. The combined organic layers were washed with a $NaHCO_3/H_2O$ solution as well as water and dried

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over sodium sulfate. After evaporation of the solvent, the residue was chromatographed over silica gel. Methylene chloride eluted the cyclization product, which was recrystallized from benzene to give **8b** (450 mg, 10%): mp 306 °C (colorless needles); ^{1}H NMR (200 MHz, $C_2D_2Cl_4$) δ 8.18 (m, 4 H), 8.12 (d, 2 H), 8.00 (d, 2 H), 7.72 (m, 4 H), 7.54 (dd, 2 H), 2.79 (t, 4 H), 2.04 (q, 2 H); MS (70 eV), *m/e* (rel intensity) 456 (M^+, 72), 235 ($M^+ - C_{15}H_9O_2$, 40), 221 ($M^+ - C_{16}H_{11}O_2$, 100), 193 ($M^+ - C_{16}H_{11}O_2 - CO$). Anal. Calcd for $C_{31}H_{20}O_4$: C, 81.56; H, 4.42. Found: C, 81.53; H, 4.51.

1,3-Di(2′-anthryl)propane (4b). The anthraquinone derivative **8b** (0.52 g, 1.4 mmol) was boiled under an argon atmosphere with a aluminum tricyclohexanolate/cyclohexanol solution (50 mL, 2 M) for 72 h. The mixture was cooled to room temperature and hydrolyzed with HCl (250 mL, 2 N). After extraction with methylene chloride, the combined organic layers were washed with a $NaHCO_3/H_2O$ solution as well as water and dried over sodium sulfate. The residue that remained after removal of the solvent was chromatographed over silica gel. Hexane/chloroform (3:1) eluted the anthracene compound, which was recrystallized from tetrachloroethane to give pure **4b** (210 mg, 47%): mp 250 °C (colorless microcrystals); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ 8.32 (s, 2 H), 8.28 (s, 2 H), 7.92 (m, 2 H), 7.89 (d, 2 H), 7.72 (s, 2 H), 7.38 (m, 4 H), 7.31 (d, 2 H), 2.84 (t, 4 H), 2.14 (q, 2 H); ^{13}C NMR (100 MHz, $C_2D_2Cl_4$) δ 139.6 (C-9, -9′, -10, -10′), 132.2/132.1/131.5/130.9 (C-4a, -4a′, -8a, -8a′, -9a, -9a′, -10a, -10a′), 128.4/128.3/127.8/126.2/125.7/125.6 [C-1(1′)–C-8(8′)], 36.1 (α-CH_2), 32.1 (β-CH_2); MS (70 eV), *m/e* (rel intensity) 396 (M^+, 44), 204 ($C_{16}H_{12}$, 100), 198 (M^{2+}, 11). Exact mass calcd for $C_{31}H_{24}$: 396.18780. Found: 396.18786.

1,3-Di(9′,10′-dimethyl-2′-anthryl)propane: MS (70 eV), *m/e* (rel intensity) 452 (M^+, 100), 437 ($M^+ - CH_3$, 99.5), 422 ($M^+ - 2CH_3$, 11).

1,2-Di(2′-anthraquinoyl)ethylene (8a). A suspension of potassium–*tert*-butoxide (21.25 g, 0.2 mol) in dry DME (200 mL) was prepared, water (0.6 mL) and 2-methylanthraquinone (2.5 g, 0.11 mol) were added, and the mixture was boiled under an argon atmosphere. After 4 h, the solution was cooled to room temperature, a saturated $NaCl/H_2O$ solution was added, and the aqueous mixture was stirred in the presence of air until a yellow compound precipitated. The crude material was washed three times with hot methanol/water, three times with hot toluene, and two times with hot chloroform. After filtration and drying under vacuum at 150 °C, one obtained 2.1 g (85%) of **8a**: mp > 370 °C; MS (70 eV), *m/e* (rel intensity) 440 (M^+, 44), 220 ($M^+ - C_{15}H_8O_2$, 100), 192 ($M^+ - C_{16}H_8O_3$, 25).

1,2-Di(2′-anthryl)ethylene (4c). The anthraquinone derivative **8a** (1.7 g, 3.9 mmol) was boiled under an argon atmosphere with a aluminum tricyclohexanolate/cyclohexanol solution (130 mL, 2.5 M) for 48 h. The mixture was cooled to room temperature, poured into HCl (500 mL, 2 N), and diluted with methanol (500 mL). After filtration, the solid material was washed with hot methanol and extracted with toluene and chloroform, respectively. After recrystallization from tetrachloroethane, one obtained 1.41 g (96%) of **4c**: mp >360 °C (yellow powder); ^{1}H NMR (90 MHz, $C_2D_2Cl_4$, 150 °C) δ 8.35 (s, 1 H), 8.32 (s, 1 H), 8.04–7.87 (m, 8 H), 7.76 (d, 1 H), 7.67 (d, 1 H), 7.48–7.33 (m, 2 H); IR, ν (cm^{-1}) 3060, 1630–1460, 957, 894, 732; MS (70 eV), *m/e* (rel intensity) 380 (M^+, 34), 202 ($M^+ - C_{14}H_{10}$, 24), 191 ($C_{15}H_{11}$, 100), 178 ($C_{14}H_{10}$). Anal. Calcd for $C_{30}H_{20}$: C, 94.70; H, 5.30. Found: C, 94.66; H, 5.29.

1,2-Di(2′-anthryl)ethane (4a). A suspension of **4c** (250 mg, 0.66 mmol) and Pd/C (90 mg, 5% metal) in dry dioxane (300 mL) was placed in a hydrogenation apparatus. After evacuation and flushing with H_2 three times, the mixture was heated to 60 °C under vigorous stirring. When 50 mL of H_2 was absorbed, the suspension was cooled to room temperature and the catalyst was separated by filtration. After evaporation of the solvent, one obtained a colorless solid, which was identified as being overhydrogenated product by mass spectroscopy. For dehydrogenation, the crude material was heated with Pd/C (500 mg, 5% metal), in diglyme (30 mL) under a stream of nitrogen to 150 °C. The suspension was allowed to stir for 65 h, the catalyst was separated by filtration, and the residue, obtained after evaporation of the solvent, was washed with methanol. The extraction with toluene for 12 h gave 107 mg (43%) of the anthracene compound **4a**, which was recrystallized from tetrachloroethane: mp 443 °C (green needles); ^{1}H NMR (200 MHz, $C_2D_2Cl_4$, 100 °C) δ 8.32 (s, 2 H), 8.29 (s, 2 H), 7.92 (m, 6 H), 7.78 (s, 2 H), 7.39 (m, 4 H), 7.31 (d, 2 H), 3.62 (s, 4 H); MS (70 eV), *m/e* (rel intensity) 382 (M^+, 12), 191 ($M^+ - C_{15}H_{11}$, 100). Anal. Calcd for $C_{30}H_{22}$: C, 92.20; H, 5.80. Found: C, 94.19; H, 5.96.

1,2-Di(9′,10′-dimethyl-2′-anthryl)ethane: MS (70 eV), *m/e* (rel intensity) 438 (M^+, 33), 423 ($M^+ - CH_3$, 18.5), 175 ($C_{14}H_7$, 100).

1,4,9,10-Tetrahydro[2.2](2,3)anthracenophane-9,10-dione (11). A solution of the tetraene **10** (906 mg, 5.7 mmol) and sublimed 1,4-naphthoquinone (2.24 g, 14.2 mmol) in toluene (30 mL) was boiled under an argon atmosphere for 24 h. After the mixture had been cooled to room temperature, the precipitated crude material of *syn*- and *anti*-**11** was separated by filtration and washed with cold methanol. The product was recrystallized from methylene chloride/methanol (2:1) and dried under vacuum. One obtained 1.9 g (70%) of the isomer mixture, which was used in the next reaction without further purification. *syn*-, *anti*-**11**: MS (70 eV), *m/e* (rel intensity) 476 (M^+, 100), 458 ($M^+ - H_2O$, 71), 238 ($M^+ - C_{16}H_{14}O_2$, 17).

[2.2](2,3)Anthraquinophane. The isomer mixture of *syn*- and *anti*-**11**, suspended in a KOH/ethanol solution (600 mL, 5 wt %), was heated to 50 °C. A stream of O_2 was bubbled through the hot suspension, whereby the color changed from green to yellow. The reaction mixture was poured into 600 mL of ice–water, and the yellow precipitate was separated by filtration. The solid residue was washed with water as well as methanol and digested with hot toluene. After drying under vacuum, one obtained 1.06 g (70%) of the insoluble [2.2](2,3)anthraquinophane: mp >360 °C (light yellow powder); MS (70 eV), *m/e* (rel intensity) 468 (M^+, 29), 454 ($M^+ - CH_2$, 6), 440 ($M^+ - CO$, 3), 234 ($M^+ - C_{16}H_{10}O_2$, 6).

[2.2](2,3)Anthracenophane (7). Aluminum chips (1.19 g, 44.1 mmol) were activated with a trace of $HgCl_2$ over a flame, 45 mL of cyclohexanol was added, and the mixture was boiled until all metal had dissolved and H_2 formation had ceased (1.5–2 h). After the alcoholate solution had cooled to room temperature, [2.2]-(2,3)-anthraquinophane (2.04 g, 4.4 mmol) was added, and the suspension was evacuated and flushed with argon and boiled under an argon atmosphere for 3 days. The reaction mixture was cooled to room temperature, HCl (100 mL, 5 N) was added, and the resulting suspension was boiled under vigorous stirring for 10 min. The crude solid material was separated by filtration, washed with hot water as well as ethanol, and dried under vacuum. After repeated crystallizations from *o*-dichlorobenzene, one obtained 1.33 g (75%) of the sparingly soluble anthracene compound **7**: mp >360 °C (light yellow microcrystals); UV (CH_2Cl_2) 384 (1400), 364 (1700), 347 (150), 330 (900), 315 (600), 269 (25 500), 262 (14 100), 250 (14 900) nm; MS (70 eV), *m/e* (rel intensity) 408 (M^+, 100), 204 ($M^+ - C_{16}H_{12}$, 37). Anal. Calcd for $C_{32}H_{24}$: C, 94.08; H, 5.92. Found: C, 93.64; H, 5.97.

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