Novel Alkylanthracenes
Synthesis, Reductive Alkylation, and Reductive Polymerization

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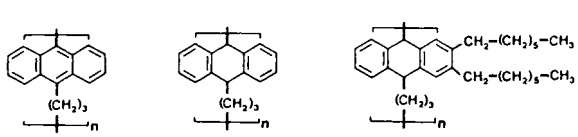
A series of novel substituted anthracenes has been prepared which carry two or four *n*-alkyl groups at C-2 and C-3 (C-6 and C-7). The route taken includes the synthesis of novel 2,3-dialkylbutadienes, their Diels-Alder reaction with 1,4-benzo- or 1,4-naphthoquinone, the dehydrogenation of the adducts, and the reduction of the anthraquinones. The substituted anthracenes are submitted to reduction and reductive alkylation in ethereal solvents and in liquid ammonia to yield 9,10-dialkyl-substituted 9,10-dihydroanthracenes. A modification of the reductive alkylation, i.e. the introduction of 1,*n*-dihaloalkanes as electrophiles, provides polymeric chains, in which dihydroanthracene moieties are linked by alkanediyl bridges. It appears that the behavior of alkyl-substituted anthracenes in reductive alkylation and reductive polymerization reactions is completely different to that of the parent anthracene. This feature, which follows from different solubilities and basicities of carbanionic intermediates in the solvent systems, allows to control the properties of the polymer chains.

Neue Alkylanthracene. – Synthese, reduktive Alkylierung und reduktive Polymerisation

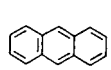
Es wird eine Reihe neuer Anthracene synthetisiert, die in den Positionen C-2 und C-3 (C-6 und C-7) zwei bzw. vier *n*-Alkylgruppen tragen. Das Syntheseverfahren umfaßt die Gewinnung neuer 2,3-Dialkylbutadiene, ihre Diels-Alder-Reaktion mit 1,4-Benzo- oder 1,4-Naphthochinon, die Dehydrierung der Addukte sowie die Reduktion der Anthrachinone. Die substituierten Anthracene liefern bei der Reduktion und reduktiven Alkylierung in etherischen Lösungsmitteln und in flüssigem Ammonik 9,10-Dialkyl-9,10-dihydroanthracene. Eine Modifizierung der reduktiven Alkylierung unter Verwendung von 1,*n*-Dihalogenalkanen als elektrophilen Agenzien führt zu polymeren Ketten, in denen Dihydroanthracen-Einheiten durch Alkandiyl-Brücken verknüpft sind. Das Verhalten der alkylsubstituierten Anthracene bei der reduktiven Alkylierung und reduktiven Polymerisation unterscheidet sich grundlegend von dem der Anthracen-Stammverbindung. Diese Tatsache resultiert aus der unterschiedlichen Löslichkeit und Basizität carbanionischer Zwischenprodukte in den verwendeten Solvenssystemen; sie erlaubt es, die Eigenschaften der Polymerkette gezielt einzustellen.

1. Introduction

Recently we have synthesized the new redox polymer **1** in which separate anthracene moieties are linked by flexible alkanediyl chains[1,2]. The polyanthrylene **1** proved to be an efficient electron storage system[4]. The structures of **1** and its precursor **2** have been fully elucidated by NMR and FD mass spectrometry whereby reference has been made to a series of structurally related oligomers and polymers[3,4]. Thereby alkyl-substituted derivatives of **2** such as **3** appeared as useful model compounds. As we have described elsewhere[1,4] the synthesis of **2** includes a reductive alkylation of anthracene (**4**) with alkali metals and 1,*n*-dihaloalkanes **5** in ethereal solvents or in liquid ammonia. The key step of the process is the S_N-type alkylation reaction between **5** and carbanions formed by reduction of **4**.



1 **2** **3**



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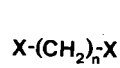

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One major drawback in studying the redox chemistry of **1** is its low solubility in organic solvents. In order to improve the solubility of **1** we decided to replace **4** by suitable alkyl-substituted anthracenes. This approach should preferentially make use of long-chain alkyl groups[5]. Furthermore their positions at the anthracene moiety should be such, e.g. at C-2, C-3 or C-6, C-7, that the subsequent chain formation by regioselective reductive alkylation at carbon C-9/C-10 does not suffer from steric hindrance.

On the other hand, alkyl substitution of **4** is expected to seriously affect the basicity and the nucleophilic properties of the carbanions which are formed upon electron transfer processes; this, in turn, may change the mechanism of the reductive polymerization. While the reduction and reductive alkylation of **4** in liquid ammonia have been extensively studied[6–10] nothing is known about the corresponding alkyl derivatives such as **6** and **7**. In view of the desired reductive polymerization of **6** or **7**, the crucial problem is whether the novel alkylated anthracenes can be transformed into 9,10-dialkyl-9,10-dihydro derivatives.

In the present paper we describe a straightforward synthesis of a series of novel anthracenes **6** and **7** bearing two or four *n*-alkyl substituents with varying chain length at C-2, C-3, and C-6, C-7. It is the advantage of the route taken that it proceeds via the related 9,10-anthraquinones **13** and **14** which, again, are useful starting compounds for reductive alkylation and acylation.

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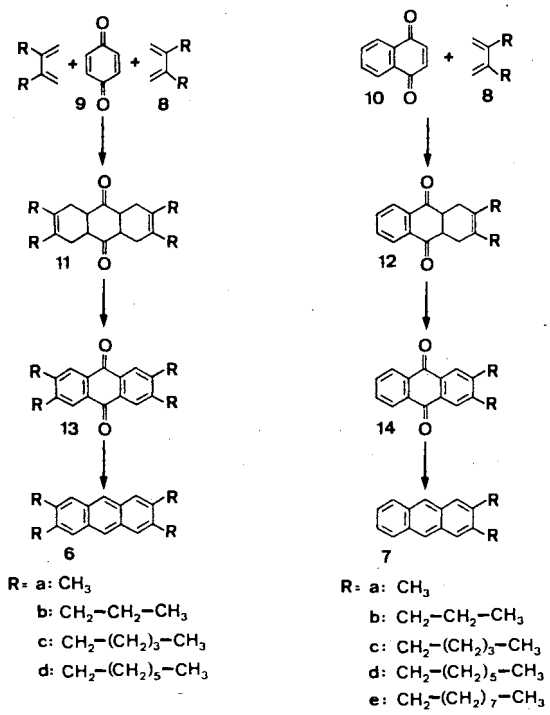
In a subsequent step the title compounds **6** and **7** have been submitted to reduction, reductive alkylation, and reductive polymerization in tetrahydrofuran or mixtures of tetrahydrofuran and liquid ammonia. The experiments lead to the synthesis of the 2,3,6,7,9,10-hexa-*n*-heptylanthracene (**23**) and of a poly(2,3-di-*n*-heptyl-9,10-dihydroanthrylene-trimethylene) (**3**). Furthermore, in order to gain insight into the mechanism of the reduction processes, the ionic intermediates have been characterized by NMR spectroscopy.

2. Synthesis of Alkyl-Substituted Anthraquinones and Anthracenes

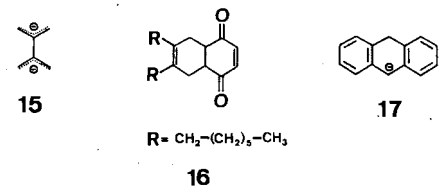
Scheme 1. Synthesis of di- and tetraalkylanthracenes



The method of choice for the synthesis of alkyl-substituted anthraquinones and anthracenes (see Scheme 1) is the Diels-Alder reaction between 1,4-benzoquinone (**9**) (1 eq.) and a 1,3-diene (2 eq.) or between 1,4-naphthoquinone (**10**) (1 eq.) and a 1,3-diene (1 eq.)[11,12]. The primary tricyclic adducts of type **11** and **12** must then be submitted to a dehydrogenation and the resulting quinones **13** and **14** reduced to the corresponding anthracenes **6** and **7**. Crucial questions within such a straightforward synthesis are which of the alkyl derivatives is most easily accessible for the subsequent polymerization and in which case the improvement of the solubility of the hydrocarbons is most pronounced. Therefore, instead of the known 2,3-dimethyl-[13-15] and 2,3,6,7-tetramethylanthracenes[14-17] we need the analogues with long-chain alkyl groups.

The 2,3-dialkyl-1,3-butadienes required for the Diels-Alder reactions are accessible by alkylation of the dianion **15** with 1-haloalkanes[18-21]. Thereby, the dianion **15** is prepared by deprotonation of 2,3-dimethylbutadiene (**8a**) with a mixture of *n*-butyllithium and potassium *tert*-butoxide in pentane following the method of Bates[22]. According to our optimization of the alkylation reaction the yield of **8c-e**, is increased (i) by slower addition of the 2,3-dimethylbutadiene/pentane solution to the base and of the resulting dianion suspension to the alkylating agent, (ii) by the use of an excess of alkylating agent, and (iii) by the use of concentrated solutions of the electrophile (see Experimental). After removal of the inorganic material the reaction mixture was worked up by distillation. Whereas 2,3-dipropyl-1,3-butadiene (**8b**) was obtained in analytically pure form by distillation[23], the other dienes had to be purified by HPLC.

While in the Diels-Alder reaction between **8** and benzoquinone or 1,4-napthoquinone "monodiene-quinone additions" proceed smoothly at temperatures between 20 and 60°C, "bisdiene-quinone additions" require temperatures between 80 and 140°C. These temperatures have been determined from an NMR spectroscopic control of the Diels-Alder reaction between **8b** and **9** (using deuterated chloroform or tetrachloroethane as solvent). The difference in the reaction temperatures, on the other hand, allows the selective preparation of monodiene adducts. The Diels-Alder reactions were performed with the crude 1,3-butadienes obtained upon distillation since the yields of **11** are not improved by using the pure dienes. The Diels-Alder reaction of 2,3-di-*n*-heptyl-1,3-butadiene (**8d**) with **9** provides low yields (< 5%) of the monodiene adduct (**16**) as a side product which, on the other hand, is available by the reaction of **8d** and an excess of **9** in 75% yield.



The related syntheses of the 2,3-dialkyl-1,4,4a,9a-tetrahydro-9,10-anthraquinones **12b-e** from **10** and the 2,3-dialkyl-1,3-butadienes **8b-e** proceed in better yields (see Experimental) than those with **9**.

Transformation of the adducts **11b-d** into the corresponding 2,3,6,7-tetraalkyl-9,10-anthraquinones **13b-d** can be performed with oxygen in ethanolic potassium hydroxide (2%) (35°C, 45 min)[24]. This contrasts to the preparation of 2,3,6,7-tetramethyl-9,10-anthraquinone (**13a**) which requires more vigorous conditions (boiling ethanol, 24 h)[17]. The oxidation of the 2,3-dialkyl-1,4,4a,9a-tetrahydro-9,10-anthraquinones **12b-e** was performed in the same fashion between 0 and 20°C. The reduction products **6** and **7** are obtained in good yields by a modification of the Meerwein-Ponndorf-Verley reduction with aluminium cyclohexoxide[15,17,25].

The increased solubility of the anthracene compounds upon substitution is reported in Table 1. Obviously, the readily available disubstituted anthracenes **7c** and **7d** posses the best solubility.

Table 1. Solubility of substituted anthracenes in dichloromethane at 25°C

R	Compound	Solubility [g/l]	$\frac{M_{anthracene}}{M_{compound}}$
H	**4**	20	1
C_3H_7	**6b**	600	0.51
C_5H_{11}	**6c**	80	0.39
C_7H_{15}	**6d**	100	0.31
C_3H_7	**7b**	200	0.68
C_5H_{11}	**7c**	1000	0.56
C_7H_{15}	**7d**	1300	0.48

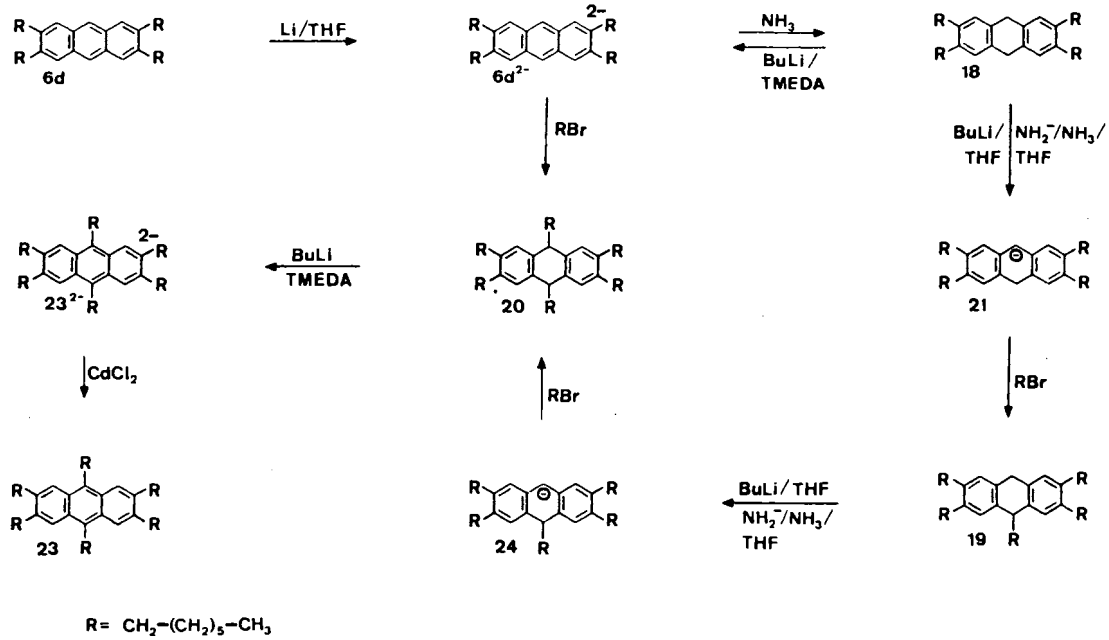
3. Reduction, Reductive Alkylation, and Reductive Polymerization of Dialkyl- and Tetraalkylanthracenes

The questions arise as to whether the solubility-enhancing alkyl substituents affect the reduction and reductive alkylation of the anthracene π systems and whether di- or tetraalkyl-substituted anthracenes are suitable substrates for the reductive polymerization. Reductive alkylations of benzenoid hydrocarbons are mostly performed in mixtures of liquid ammonia and ethereal solvents[6]. In particular we have shown that for anthracene the dianion formed by a two-electron transfer process does not persist in liquid ammonia, but is rapidly protonated to yield the monoanion **17** which is then susceptible to a subsequent alkylation process[26,27]. In order to avoid an eventual protonation we submitted, at first, **6d** and **7d** to a reduction with lithium in THF. The dianion salts $\mathbf{6d}^{2-}/2Li^+$ and $\mathbf{7d}^{2-}/2Li^+$ persist in THF solution and can be fully characterized by ^1H- and ^{13}C-NMR-spectroscopy. In Table 2 the resulting chemical shifts are compared with those of the parent anthracene dianion[28,29].

It appears that the alkyl-substituted dianions are very similar to the anthracene dianion itself: (i) the upfield shifts of the proton signals observed upon dianion formation are much more pronounced than expected from the pure charge effect and point toward a paratropic behavior; (ii) the proportionality constant K_C which is obtained from the charge-induced shift of the average signal and the average π-charge density are much smaller than the usual value of about 160 ppm/e[30–34]; this is characteristic of paratropic ions[35]; (iii) taking, as is generally accepted, the charge-induced shifts of individual carbon signals as a measure of the local π-charge densities, one readily concludes that the quaternary carbons bear a partial positive charge and that the highest excess charge resides on carbons C-9 and C-10; alkyl substitution at C-2 and C-3 tends to decrease the charge density at the neighboring positions C-1 and C-4. As concerns the reactivity of the carbanions one can expect from the high charge density at C-9 and C-10 that a kinetically controlled attack of electrophiles will occur at these particular positions.

The reduction of **6d** with lithium in liquid ammonia/THF differs from that of the parent anthracene. The solution does not adopt a deep color, rather a white precipitate is formed. The only product obtained upon treatment of the reaction mixture with 1-bromoheptane is 2,3,6,7-tetra-*n*-heptyl-9,10-dihydroanthracene (**18**). If the reductive alkylation of **6d** with lithium/1-bromoheptane is performed in the presence of an excess of sodium amide (50 eq.), the mono- and diheptyl adducts **19** and **20** are obtained in addition to **18**. Prolonged treatment of the reaction mixture with $NaNH_2$/1-bromoheptane provides an increased amount of **20** (see Experimental). These results indicate that the basicity of the monohydro monoanion **21** is significantly increased by the alkyl substituents. As a consequence, the equilibrium between the dianion $\mathbf{6d}^{2-}$, the monoanion **21** and the dihydro

Scheme 2. Different routes to 2,3,6,7,9,10-hexa-*n*-heptylanthracene (**23**)

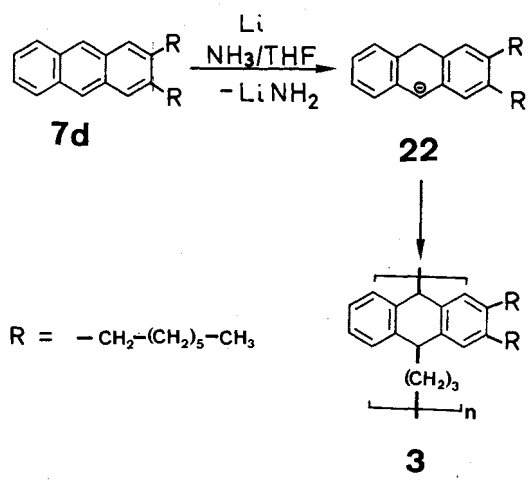


product **18** is shifted toward the latter. It should also be noted that the dihydro product **18** is removed from the equilibrium by precipitation whereby the lower solubility of **18** in liquid ammonia may be due to the lipophilic character of the substituents. Deeper insight into the protonation is obtained from the following experiment.

6d was transformed into a dianion by reduction with lithium in THF at −78 °C. When the reduction was complete (NMR spectroscopic control), dry liquid ammonia was condensed in. The deep blue color of the solution turned to red immediately; upon further standing, the color became orange and finally pale yellow, and a white solid precipitated. The dihydro product **18** was isolated in 95% yield. This result leaves no doubt that in the presence of liquid ammonia the concentration of the anions $\mathbf{6d}^{2-}$ and **21** is extremely low. Consequently, in contrast to anthracene itself, **6d** is not a suitable substrate for reductive polymerization in NH_3/THF, that is for the formation of poly(9,10-dihydroanthrylenetrimethylene) chains by alkylation of the intermediate carbanions with bifunctional electrophiles such as 1,3-dibromopropane.

2,3-Di-*n*-heptylanthracene **7d** should be an intermediate case between anthracene and the tetraheptylanthracene **6d**. Indeed, reduction of **7d** with lithium in a 1:1 mixture of THF and ammonia gave rise to a deep red color of the corresponding monohydro monoanion **22**. 2,3-Di-*n*-heptylanthracene (**7d**) therefore appears as a promising substrate for the polymerization since: (i) the starting compound is readily available, (ii) it possesses a relatively high solubility in organic solvents (which is expected to be the case for the corresponding polymer chains, see below), and (iii) the carbanion **22** persists in liquid and can undergo subsequent alkylation.

The details of the synthesis and structural elucidation of poly(2,3-di-*n*-heptyl-9,10-dihydroanthrylenetrimethylene) are reported elsewhere[36]. Herein we focus on those aspects which are significant for the behavior of the carbanions derived from **7d**.



7d was reduced with lithium (2.5 eq.) in a mixture of ammonia and THF. The resulting carbanion solution (**22** and lithium amide) was mixed with 1,3-dibromopropane. Evaporation of solvents and aqueous workup gave a colorless polymer which is completely soluble in chloroform and according to vapor-pressure osmometry possesses a mean molecular weight M_n between 2,500 and 3,100. The molecular weigth M_n does not vary with the experimental conditions such as the rate of mixing of the reagents, the temperature or the concentration. It follows that the reductive polymerization of **7d** differs from that of anthracene **4** itself[4]. In the latter case appreciable amounts of chloroform-insoluble material are formed and the molecular weights vary with the experimental conditions. The ^{1}H-NMR spectra of the crude polymer samples (see Figure 1) indicate that the monomer **7d** has been quantitatively transformed and that the chain possesses the linear structure as depicted in formula **3**. The protons of the benzene units resonate between δ 7.4 and 7.0 while the signals of the benzylic protons 9-H and 10-H appear between δ 4.2 and 3.6. The methyl protons of the *n*-alkyl substituents can be seen at highest field (δ 0.9). Combustion analysis and the ^{13}C-NMR spectra of the polymer samples (see Figure 1) indicate that the linear chains are always terminated by dihydroanthracene units. In accordance with experience obtained for the parent polymer **2**, the axial benzylic protons of terminal methylene groups (10-H) resonate at somewhat lower field (δ 4.2−4.05) than the non-terminal benzylic protons[3,4]. Also characteristic of terminal dihydroanthracene units are the resonances of C-4a (C-10a),

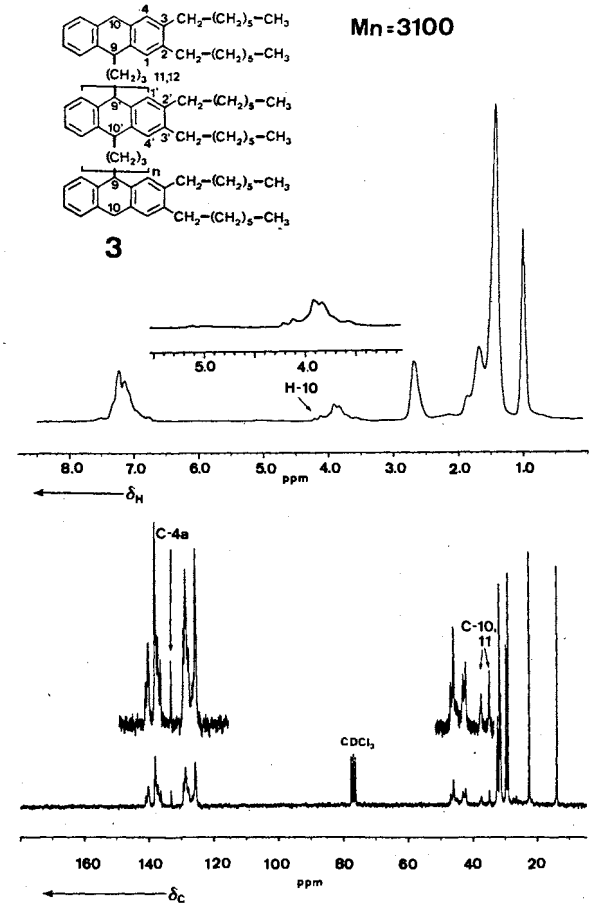


Figure 1. ^{1}H (200 MHz) and ^{13}C (50 MHz) NMR of poly(2,3-di-*n*-heptyl-9,10-dihydroanthrylenetrimethylene (**3**) (M_n = 3100, $CDCl_3$)

C-10 and C-11 at δ 133.5, 37.8 and 35.5, respectively. The mean molecular weights of the polymer products obtained from the relative signal intensities of benzylic protons at the end or within the chain are in reasonable agreement with the values determined from vapor-pressure osmometry.

It should be noted that the polymerization grades P_n of the polymer samples are significantly lower than those obtained for the polymerization of the parent anthracenes. This outcome leaves little doubt that the 2,3-dialkyl substitution of the anthracene unit reduces the reactivity of the latter with respect to reductive chain formation. This conclusion is supported by the results of deprotonation experiments. When solutions of the parent polymer compound **2** (with 9,10-dihydroanthracene units) are treated with lithium amide in NH_3/THF for 10 min, the deep orange color of a metallation product is obtained. We know from subsequent alkylation experiments that this metallation comprises deprotonation at the terminal methylene groups[3]. The same reaction for the dialkyl analogue **3** (with 2,3-di-*n*-heptyl-9,10-dihydroanthracene units) proceeds more slowly: treatment of **3** with excess lithium amide at −33 °C for 30 min gives rise to a solution with a pale orange color which disappears upon the addition of a small amount (less than 0.2 eq. per terminal methylene group) of 1,3-dibromopropane as quenching reagent. The importance of a terminal deprotonation of the polymer chains **4** is that subsequent alkylation with 1,3-dibromopropane should induce a linkage of separate chains and thus give rise to polymer samples with a higher molecular weight. Indeed, when a sample of **3** with M_n = 3100 ($P_n \approx 8$) was treated with a large excess of lithium amide and 1,3-dibromopropane for 5 h, we obtained a sample which was still soluble in chloroform and whose analysis by vapor-pressure osmometry indicated a mean molecular weight of M_n = 9700 ($P_n \approx 23$). Consequently, the polymer chain **3** can be submitted to deprotonation/alkylation reactions.

We conclude from the above results that alkyl substitution of anthracene significantly affects the reductive alkylation under formation of mono- and dialkyl-9,10-dihydroanthracenes and also influences the polymer-forming reductive alkylation: the polymer samples show an improved solubility, but lower polymerization grades.

A novel π system with interesting chemical and physical properties is 2,3,6,7,9,10-hexa-*n*-heptylanthracene (**23**) for which the dihydroanthracene species **20** is a suitable precursor. It has been shown above that the reductive alkylation of **6d** with lithium and 1-bromoheptane in NH_3/THF provides mixtures of **18**, **19**, and **20**. In order to develop an

Table 2. ^1H (δ_H) and ^{13}C (δ_C) NMR chemical shifts of anthracene dianions (lithium salts, [D_8]THF, −40 °C)

Compound	C-1,4	C-2,3	C-5,8	C-6,7	C-9,10	C4a,9a	C-8a,10a	
δ_H (**4**)	7.91	7.39	7.91	7.39	8.31			
δ_H (**4**)$^{2-}$	3.30	4.21	3.30	4.21	1.75			
$\Delta\delta_H$[a]	−4.61	−3.18	−4.61	−3.18	−6.56			
δ_C (**4**)	128.1	125.3	128.1	125.3	126.2	131.8	131.8	$\langle\delta_\pi\rangle$ = 128.1
δ_C (**4**)$^{2-}$	101.1	114.0	101.1	114.0	75.1	150.0	150.0	$\langle\delta_\pi\rangle$ = 115.1
$\Delta\delta_C$[a]	−27.0	−11.3	−27.0	−11.3	−51.1	+18.2	+18.2	$\langle\Delta\delta_\pi\rangle$ = −13.0[a]
Δq_π[b]	−0.300	0.124	−0.300	−0.124	−0.562	+0.200	+0.200	K_C = 91.0[b]
δ_H (**7d**)	7.74		7.95	7.39	8.30			
δ_H (**7d**)$^{2-}$	3.26		3.14	4.05	1.82			
$\Delta\delta_H$	−4.48		−4.81	−3.34	−6.48			
δ_C (**7d**)	126.5	139.6	128.1	124.7	124.9	131.1	131.5	$\langle\delta_\pi\rangle$ = 129.5
δ_C (**7d**)$^{2-}$	106.4	125.0	100.2	114.0	74.6	149.2	151.4	$\langle\delta_\pi\rangle$ = 117.3
$\Delta\delta_C$	−20.1	−14.6	−27.9	−10.7	−50.3	18.1	+19.9	$\langle\Delta\delta_\pi\rangle$ = −12.2
Δq_π	−0.235	−0.171	−0.326	−0.125	−0.588	+0.214	+0.233	K_C = 85.5
δ_H (**6d**)	7.69		7.69		8.17			
δ_H (**6d**)$^{2-}$	3.32		3.32		2.02			
$\Delta\delta_H$	−4.37		−4.37		−6.15			
δ_C (**6d**)	126.5	138.9	126.5	138.9	123.7	130.8	130.8	$\langle\delta_\pi\rangle$ = 130.9
δ_C (**6d**)	104.3	123.9	104.3	123.9	72.0	148.6	148.6	$\langle\delta_\pi\rangle$ = 117.9
$\Delta\delta_C$	−22.2	−15.0	−22.2	−15.0	−51.7	+17.8	+17.8	$\langle\Delta\delta_\pi\rangle$ = −13.0
Δq_π	−0.251	−0.165	−0.251	−0.165	−0.568	+0.196	+0.196	K_C = 91.0
δ_H (**23**)	7.98		7.98					
δ_H (**23**)$^{2-}$	3.85		3.85					
$\Delta\delta_H$	−4.13		−4.13					
(**23**)	123.8	137.9	123.8	137.9	131.3	128.3	128.3	$\langle\delta_\pi\rangle$ = 130.2
(**23**)$^{2-}$/2Li	101.7	124.1	101.7	124.1	78.4	144.6	144.6	$\langle\delta_\pi\rangle$ = 117.0
$\Delta\delta_C$	−22.1	−13.8	−22.1	−13.8	−52.9	+16.3	+16.3	$\langle\Delta\delta_\pi\rangle$ = −13.2
Δq_π	−0.240	−0.150	−0.240	−0.150	−0.570	+0.177	+0.177	K_C = 92.1

[a] $\Delta\delta_H$,$\Delta\delta_C$: Differences of chemical shifts observed upon going from the neutral compounds to the corresponding dianions; $\langle\delta_H\rangle$, $\langle\delta_C\rangle$: Average chemical shifts. — [b] $K_C = \Delta\langle\delta_\pi\rangle/\Delta\langle q_\pi\rangle$; the changes of local π-charge densities Δq_π are obtained from individual $\Delta\delta_C$ values and K_C.

improved route to **20**, the following methods of ion formation have been investigated (see Scheme 2): (i) the dianion $\mathbf{6d}^{2-}$ was prepared with lithium in THF and quenched with 1-bromoheptane, thereby the yield of **20** is 70%. The ^{1}H-NMR spectrum of the crude reaction product indicates no olefinic resonances which might result from an alkylation at position 1 and 2 of the anthracene. The side products observed are **6d** and **19**. (ii) **20** was obtained in about 80% yield if **18** was treated with excess lithium amide in NH_3/THF or with *n*-butyllithium in THF and subsequently alkylated with 1-bromoheptane. Thereby, *n*-butyllithium converts **18** into the red monoanion **21** which is quenched with 1-bromoheptane. The resulting pentaheptyl-9,10-dihydroanthracene **19** is regioselectively deprotonated with *n*-butyllithium to yield the anion **24** which is again alkylated. The complete transformation of **18** into **20** requires 4–6 repetitive deprotonation/alkylation steps. (iii) A modification of the deprotonation/alkylation sequence is the deprotonation of **18** with *n*-butyllithium/tetramethylethylenediamin (TMEDA)[37] in refluxing hexane and subsequent quenching of the resulting dianion.

The dehydrogenation of the dihydro product **20** to yield the 2,3,6,7,9,10-hexa-*n*-heptylanthracene (**23**) was achieved by deprotonation with *n*-butyllithium/TMEDA and oxidation of the resulting dianion with cadmium chloride[37]. The substitution pattern of **23** is obvious from the singlet signal of the aromatic protons at δ 7.98. The dianion formed upon deprotonation of **20** with *n*-butyllithium/TMEDA can also be prepared by reduction of **23** with lithium in THF. The NMR spectroscopic characterization of $\mathbf{23}^{2-}/2Li^+$ (see Table 2) shows that the properties of the latter are quite similar to those of the anthracene dianions mentioned above.

One could have expected from the substitution pattern of **23** that the π system might give rise to a liquid-crystalline phase. However, compound **23** shows a sharp melting point at 74°C. The failure of hexasubstituted anthracenes to exhibit mesophases is also obvious from an inspection of the optical textures by means of a polarizing microscope equipped with a hot stage. This is in agreement with findings made by Praefke et al.[36] for 1,2,3,4,5,6,7,8-octa(alkylthio)-substituted 9,10-anthraquinones[38].

4. Conclusion

In the present paper we have described a straightforward synthesis of novel anthraquinones and anthracenes with a variety of long-chain *n*-alkyl substituents at positions C-2, C-3 and C-6, C-7. Alkyl substitution greatly enhances the solubility of the π systems in organic solvents which is important for the behavior of the related poly(dihydroanthrylenetrimetylene) chains **3**. It appears, however, that alkyl substitution affects the course of the reductive alkylation of the anthracene π systems. The carbanions obtained upon reduction of the anthracenes are significantly more basic than those of the parent compound. The ease of protonation by the solvent requires special techniques for the reductive alkylation and reductive polymerization of substituted anthracenes.

The reductive polymerization of **6d**[39] includes the linkage of 9,10-dihydroanthracene units by trimethylene chains at positions C-9, C-10 of the subunits. A similar reaction should be possible when the novel anthraquinones which were intermediates for the anthracene synthesis are subjected to reductive alkylation or acylation. Work directed to the synthesis of soluble polyethers and polyesters containing anthrylene groups is in progress.

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Experimental

All reactions of carbanionic intermediates were performed under argon. THF was purified by repeated distillations over potassium and lithium aluminium hydride, respectively, and finally transferred into the reaction flask by distillation under argon. Melting points were measured in open capillaries and are not corrected.

2,3-Dialkyl-1,3-butadienes **8b–e**: 31.5 g (280 mmol) of potassium *tert*-butoxide and 200 ml of a 1.4 N solution of *n*-butyllithium in hexane (280 mmol) were placed in a 500-ml Schlenk tube. To the vigorously stirred mixture was added under argon a solution of 11.5 g (15.8 ml, 140 mmol) of 2,3-dimethyl-1,3-butadiene (**8a**) in 100 ml of pentane over a period of 2 h at room temperature. After 30 min of further stirring the precipitate of the orange dianion salt **15** was separated from the solution by filtration over a fritted glass. The dianion was washed with pentane, and 200 ml of tetrahydrofuran (THF) was added. The resulting suspension was added dropwise to a solution of 0.6 mol of the respective bromide (**8b**: 1-bromoethane, **8c**: 1-bromobutane, **8d**: 1-bromohexane, **8e**: 1-bromooctane) in 50 ml of THF. During the addition the reaction vessel was cooled in a salt–ice bath and then kept at −30°C overnight. The mixture was allowed to warm to room temperature and evaporated under reduced pressure. Hexane and water were added to the residue, the organic layer was washed with water and dried over magnesium sulfate. The solvent and remaining alkylating agent were removed under reduced pressure, and the residue was submitted to fractional distillation over a 10-cm Vigreux column. The boiling points are given below. Only **8b** was obtained pure upon distillation. The higher homologues possess a purity of 85–95% after distillation. Further purification of **8c**, **8d**, and **8e** was achieved by preparative HPLC (Dynamax Macro Si, 8 μm, 250 × 22 mm, hexane).

2,3-Di-n-propyl-1,3-butadienes (**8b**): See ref.[21,39].

2,3-Di-n-pentyl-1,3-butadiene (**8c**): See ref.[21,39] (yield 46%).

2,3-Di-n-heptyl-1,3-butadiene (**8d**): 64%; bp 95–105°C ($2 \cdot 10^{-2}$ mbar). – ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.03 (s, 2 H, 1,4-H), 4.88 (s, 2 H, 1,4-H), 2.21 (t, 4 H, CH_2R), 1.52 (m, 4 H), 1.30–1.20 (m, 16 H), 0.88 (t, 6 H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.2 (C-2,3), 111.2 (C-1,4), 34.3, 31.9, 29.5, 29.2, 28.7, 22.7, 14.0. – MS (70 eV): *m/z* (%) = 250 (14, M^+), 123 (31), 109 (75), 82 (100). – UV: λ_{max} (lg ε) = 229 nm (4.08).

$C_{18}H_{34}$ (250.5) Calcd. C 86.32 H 13.68
Found C 86.20 H 13.99

2,3-Di-n-nonyl-1,3-butadiene (**8e**): 56%; bp 130–155°C ($2 \cdot 10^{-3}$ mbar). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.03 (s, 2 H, 1,4-H), 4.88 (s, 2 H, 1,4-H), 2.21 (t, 4 H, CH_2R), 1.50–1.20 (m, 28 H), 0.88 (t, 6 H, CH_3). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 148.1 (C-2,3), 111.2 (C-1,4), 34.3, 32.0, 29.7, 29.6 (2C), 29.4, 28.7, 22.7, 14.1. – MS

(70 eV): *m/z* (%) = 306 (5, M^+), 109 (36), 95 (33), 82 (100). – UV: λ_{max} (lg ε) 230 nm (4.05).

$C_{22}H_{42}$ (306.6) Calcd. C 86.19 H 13.81
Found C 86.51 H 14.01

2,3,6,7-Tetraalkyl-1,4,5,8.4a,8a,9a,10a-octahydro-9,10-anthraquinones **11b–d**: For the Diels-Alder reaction between benzoquinone (**9**) and the crude 2,3-dialkyl-1,3-butadienes **8b–d**, solutions of **9** (1 mmol) and **8b–d** (2 mmol), respectively, in 2 ml of ethanol were allowed to reflux for 60 h. The reaction mixture was then cooled to –30°C whereupon the white microcrystalline Diels-Alder adduct precipitated. The product was separated by filtration and recrystallized from ethanol (methanol for **8b**).

1,4,5,8,4a,8a,9a,10a-Octahydro-2,3,6,7-tetra-n-propyl-9,10-anthraquinone (**11b**): 37%; mp 125°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.90 (t, 4 H, 4a,8a,9a,10a-H), 2.37 (d, 4 H, 1,4,5,8-H), 2.09 (d, 4 H, 1,4,5,8-H), 1.92 (t, 8 H, CH_2R), 1.33 (m, 8 H), 0.83 (t, 12 H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.8 (C-9,10), 128.3 (C-2,3,6,7), 44.8 (C-4a,8a,9a,10a), 34.8, 28.4 (C-1,4,5,8), 21.4, 14.0. – MS (70 eV): *m/z* (%) = 384 (44, M^+), 341 (10), 43 (100).

$C_{26}H_{40}O_2$ (384.6) Calcd. C 81.20 H 10.48
Found C 81.00 H 10.47

1,4,5,8,4a,8a,9a,10a-Octahydro-2,3,6,7-tetra-n-pentyl-9,10-anthraquinone (**11c**): 41%; mp 99°C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.89 (t, 4 H, 4a,8a,9a,10a-H), 2.37 (d, 4 H, 1,4,5,8-H), 2.10 (d, 4 H, 1,4,5,8-H), 1.92 (t, 8 H, CH_2R), 1.35–1.15 (m, 24 H), 0.83 (t, 12 H, CH_3). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 210.8 (C-9,10), 128.3 (C-2,3,6,7), 44.7 (C-4a,8a,9a,10a), 32.7, 31.9, 28.3 (C-1,4,5,8), 27.9, 22.5, 14.0. – MS (70 eV): *m/z* (%) = 496 (66 M^+), 425 (14).

$C_{34}H_{56}O_2$ (496.8) Calcd. C 82.20 H 11.36
Found C 82.29 H 11.21

2,3,6,7-Tetra-n-heptyl-1,4,5,8,4a,8a,9a,10a-octahydro-9,10-anthraquinone (**11d**): 45%; mp 95°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.90 (t, 4 H, 4a,8a,9a,10a-H), 2.37 (d, 4 H, 1,4,5,8-H), 2.09 (d, 4 H, 1,4,5,8-H), 1.92 (d, 8 H, CH_2R), 1.35–1.15 (m, 40 H), 0.84 (t, 12 H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.7 (C-9,10), 128.3 (C-2,3,6,7), 44.7 (C-4a,8a,9a,10a), 32.8, 31.8, 29.6, 29.1, 28.4, 28.2, 22.6, 14.0. – MS (70 eV): *m/z* (%) = 608 (38, M^+), 57 (100). – IR (KBr): 2950 cm^{-1}, 2910, 2850 (C–H), 1700 (C=O), 1460.

$C_{42}H_{72}O_2$ (609.0) Calcd. C 82.83 H 11.92
Found C 83.07 H 11.87

2,3-Dialkyl-1,4,4a,9a-tetrahydro-9,10-anthraquinones **12b–e**: The Diels-Alder reaction between 1,4-naphthoquinone (**10**) (1 mmol) and the 2,3-dialkyl-1,3-butadienes **8b–e** (1 mmol) was performed in refluxing ethanol (1 ml/mmol) for 12 h. The reaction mixture was then cooled to –30°C and the precipitating voluminous crystalline mass filtered with suction. Recrystallisation from ethanol (methanol for **12b**) yielded the 2,3-dialkyl-1,4,4a,9a-tetrahydro-9,10-anthraquinones **12** as white microcrystalline materials.

1,4,4a,9a-Tetrahydro-2,3-di-n-propyl-9,10-anthraquinone (**12b**): 62%; mp 93°C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.02 and 7.72 (AA'BB', 4 H, 5,6,7,8-H), 3.32 (t, 2 H, 4a,9a-H), 2.47 (d, 2 H, 1,4-H), 2.14 (d, 2 H, 1,4-H), 1.99 (t, 4 H), 1.37 (m, 4 H), 0.86 (t, 6 H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.2 (C-9,10), 134.1 (C-8a,10a), 134.05 (C-6,7), 128.1 (C-2,3), 126.7 (C-5,8), 47.3 (C-4a,9a), 34.7, 28.6 (C-1,4), 21.4, 14.0. – MS (70 eV): *m/z* (%) = 296 (34, M^+), 253 (100), 210 (21).

$C_{20}H_{24}O_2$ (296.4) Calcd. C 81.04 H 8.16
Found C 80.75 H 8.17

1,4,4a,9a-Tetrahydro-2,3-di-n-pentyl-9,10-anthraquinone (**12c**): 71%; mp 89°C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.02 and 7.72 (AA'BB', 4 H, 5,6,7,8-H), 3.32 (t, 2 H, 4a,9a-H), 2.45 (d, 2 H, 1,4-H), 2.13 (d, 2 H, 1,4-H), 1.95 (t, 4 H, CH_2R), 1.40–1.15 (m, 12 H), 0.84 (t, 6 H, CH_3). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 198.2 (C-9,10), 134.1 (C-6,7,8a,10a), 128.1 (C-2,3), 126.8 (C-5,8), 47.3 (C-4a,9a), 32.7, 31.9, 28.7 (C-1,4), 27.9, 22.5, 14.0. – MS (70 eV): *m/z* (%) = 352 (33, M^+), 281 (100), 210 (15).

$C_{24}H_{32}O_2$ (352.5) Calcd. C 81.77 H 9.15
Found C 81.76 H 9.09

2,3-Di-n-heptyl-1,4,4a,9a-tetrahydro-9,10-anthraquinone (**12d**): 70%; mp 72°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 and 7.72 (AA'BB', 4 H, 5,6,7,8-H), 3.31 (t, 2 H, 4a,9a-H), 2.45 (d, 2 H, 1,4-H), 2.14 (d, 2 H, 1,4-H), 1.98 (t, 4 H, CH_2R), 1.35–1.20 (m, 20 H), 0.85 (t, 6 H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.2 (C-9,10), 134.2 (C-8a,10a), 134.1 (C-6,7), 128.1 (C-2,3), 126.8 (C-5,6), 47.3 (C-4a,9a), 32.8, 31.8, 29.7, 29.2, 28.7 (C-1,4), 28.3, 22.6, 14.0. – MS (70 eV): *m/z* (%) = 408 (58, M^+), 309 (100). – IR (KBr): 3040 cm^{-1}, 2930, 2900, 2830 (C–H), 1670 (C=O), 1580, 1450.

$C_{28}H_{40}O_2$ (408.6) Calcd. C 82.30 H 9.87
Found C 82.38 H 9.77

1,4,4a,9a-Tetrahydro-2,3-di-n-nonyl-9,10-anthraquinone (**12e**): 60%; mp 65°C. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 8.02 and 7.71 (AA'BB', 4 H, 5,6,7,8-H), 3.27 (t, 2 H, 4a,9a-H), 2.30 (m, 4 H, 1,4-H), 1.97 (t, 4 H, CH_2R), 1.35–1.20 (m, 28 H), 0.86 (t, 6 H, CH_3). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 198.3 (C-9,10), 134.1 (C-6,7,8a,10a), 128.1 (C-2,3), 126.8 (C-5,8), 47.3 (C-4a,9a), 32.8, 31.9, 29.7, 29.6, 29.3, (2C), 28.7, (C-1,4), 28.3, 22.7, 14.1. – MS (70 eV): *m/z* (%) = 464 (63, M^+), 337 (100).

$C_{32}H_{48}O_2$ (464.7) Calcd. C 82.70 H 10.41
Found C 82.61 H 10.37

6,7-Di-n-heptyl-5,8,4a,8a,-tetrahydro-1,4-naphthoquinone (**16**): 10 mmol of 2,3-diheptyl-1,3-butadiene (**8d**) and 20 mmol of benzoquinone (**9**) were dissolved in 15 ml of ethanol and refluxed for 3 h. Fractional crystallization from ethanol at –78°C yielded **16** as pale yellow crystals. – **16**: 56%; mp 38°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.61 (s, 2 H, 2,3-H), 3.12 (t, 2 H, 4a,8a-H), 2.38 (d, 2 H, 5,8-H), 2.07 (d, 2 H, 5,8-H), 1.93 (t, 4 H, CH_2R), 1.35–1.20 (m, 20 H), 0.86 (t, 6 H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.0 (C-1,4), 139.3 (C-2,3), 128.0 (C-6,7), 47.0 (C-4a,8a), 32.7, 31.8, 29.6, 29.1, 28.5, 28.2, 22.6, 13.9. – MS (70 eV): *m/z* (%) = 358 (100, M^+), 259 (72).

2,3,6,7-Tetraalkyl-9,10-anthraquinones **13b–d**: A mixture of a $1.5 \cdot 10^{-2}$ M solution of **13c–d** in ethanol (**13b** in methanol) and 2 g of postassium hydroxide (per 100 ml solution) was vigorously stirred at 30°C and a strong stream of oxygen was passed through the solution for 30 min. The solution was then warmed to 65°C in order to complete the oxidation. The reaction mixture was concentrated to a quarter of its original volume and cooled to –30°C. The precipitated pale yellow 2,3,6,7-tetraalkyl-9,10-anthraquinone was separated by filtration, washed with water, and recrystallized from ethanol (**13b** methanol).

2,3,6,7-Tetra-n-propyl-9,10-anthraquinone (**13b**): 72%; mp 130°C. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 8.04 (s, 4 H, 1,4,5,8-H), 2.74 (t, 8 H, CH_2R), 1.72 (m, 8 H), 1.02 (t, 12 H, CH_3). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 183.4 (C-9,10), 147.4 (C-2,3,6,7), 131.5 (C-4a,8a,9a,10a), 127.6 (C-1,4,5,8), 34.9, 23.8, 14.1. – MS (70 eV): *m/z* (%) = 376 (100, M^+).

$C_{26}H_{32}O_2$ (376.5) Calcd. C 82.93 H 8.57
Found C 82.68 H 8.87

2,3,6,7-Tetra-n-pentyl-9,10-anthraquinone (**13c**): 64%; mp 103°C. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 8.04 (s, 4 H, 1,4,5,8-H), 2.75 (t, 8 H, CH_2R), 1.80–1.25 (m, 24 H), 0.91 (t, 12 H, CH_3). –

^{13}C NMR (50 MHz, $CDCl_3$): δ = 183.3 (C-9,10), 147.6 (C-2,3,6,7), 131.5 (C-4a,8a,9a,10a), 127.6 (C-1,4,5,8), 32.9, 31.9, 30.4, 22.5, 14.0 – MS (70 eV): *m/z* (%) = 488 (100, M^+), 417 (99).

$C_{34}H_{48}O_2$ (488.8) Calcd. C 83.55 H 9.90
Found C 83.60 H 9.91

2,3,6,7-Tetra-n-heptyl-9,10-anthraquinone (**13d**): 78%; mp 94°C. – ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (s, 4 H, 1,4,5,8-H), 2.72 (t, 8 H, CH_2R), 1.62 (m, 8 H), 1.40–1.20 (m, 32 H), 0.87 (t, 12 H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.6 (C-9,10), 147.7 (C-2,3,6,7), 131.1 (C-4a,8a,9a,10a), 127.7 (C-1,4,5,8), 33.0, 31.8, 30.8, 29.7, 29.1, 22.6, 14.0. – MS (70 eV): *m/z* (%) = 600 (36, M^+), 501 (40), 57 (100). – UV: λ_{max} (lg ε) = 340 nm (3.82), 274 (5.06). – IR (KBr): 3050 cm^{-1}, 2910, 2850 (C–H), 1665 (C=O), 1590, 1460.

$C_{42}H_{64}O_2$ (601.0) Calcd. C 83.94 H 10.74
Found C 83.64 H 10.64

2,3-Dialkyl-9,10-anthraquinones **14b–e**: The oxidation of the 2,3-dialkyl-1,4,4a,9a-tetrahydro-9,10-anthraquinones **14b–e** was performed in a similar fashion as that of **13b–d** at 15°C. Upon addition of the potassium hydroxide (2 g per 100 ml) to a $4 \cdot 10^{-2}$ M ethanolic solution (**14b** methanolic solution) of the starting compound, the color turned red immediately. The reaction was complete after 15 min. The workup procedure was as described for **13b–d**.

2,3-Di-n-propyl-9,10-anthraquinone (**14b**): 86%; mp 115°C. – ^1H NMR (90 MHz, $CDCl_3$): δ = 8.27 and 7.75 (AA′, BB′, 4 H, 5,6,7,8-H), 8.05 (s, 2 H, 1,4-H), 2.74 (t, 4 H, CH_2R). 1.70 (m, 4 H), 1.02 (t, 6 H, CH_3). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 183.0 (C-9,10), 147.7, (C-2,3), 133.7 (C-6,7,8a,10a), 131.2 (C-4a,9a), 127.6 (C-1,4), 126.9 (C-5,8), 34.8, 23.7, 14.1. – MS (70 eV): *m/z* (%) = 292 (100 M^+), 235 (84).

$C_{20}H_{20}O_2$ (292.4) Calcd. C 82.16 H 6.90
Found C 81.99 H 6.88

2,3-Di-n-pentyl-9,10-anthraquinone (**14c**): 83%; mp 90°C. – ^1H NMR (90 MHz, $CDCl_3$): δ = 8.27 and 7.75 (AA′BB′, 4 H, 5,6,7,8-H), 8.05 (s, 2 H, 1,4-H), 2.75 (t, 4 H, CH_2R), 1.80–1.20 (m, 12 H), 0.91 (t, 6 H, CH_3). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 183.1 (C-9,10), 147.9 (C-2,3), 133.7 (C-6,7,8a,10a), 131.3 (C-4a,9a), 127.6 (C-1,4), 126.9 (C-5,8), 32.9, 31.9, 30.3, 22.5, 14.0. – MS (70 eV): *m/z* (%) = 348 (77, M^+), 277 (100), 235 (99).

$C_{24}H_{28}O_2$ (348.5) Calcd. C 82.72 H 8.10
Found C 82.48 H 8.34

2,3-Di-n-heptyl-9,10-anthraquinone (**14d**): 87%; mp 72°C. – ^1H NMR (400 MHz, $CDCl_3$): δ = 8.27 and 7.75 (AA′BB′, 4 H, 5,6,7,8-H), 8.05 (s, 2 H, 1,4-H), 2.74 (t, 4 H, CH_2R), 1.64 (m, 4 H), 1.42–1.20 (m, 16 H), 0.90 (t, 6 H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.3 (C-9,10), 148.1 (C-2,3), 133.85 (C-8a,10a), 133.8 (C-6,7), 131.4 (C-4a,9a), 127.8 (C-1,4), 127.1 (C-5,8), 33.0, 31.8, 30.8, 29.7, 29.1, 22.6, 14.0. – MS (70 eV): *m/z* (%) = 404 (52, M^+), 305 (100), 235 (40). – IR (KBr): 3060 cm^{-1}, 2900, 2840 (C–H), 1660 (C=O), 1570.

$C_{28}H_{36}O_2$ (404.6) Calcd. C 83.12 H 8.97
Found C 82.95 H 8.81

2,3-Di-n-nonyl-9,10-anthraquinone (**14e**): 88%; mp 80°C. – ^1H NMR (90 MHz, $CDCl_3$): δ = 8.25 and 7.73 (AA′BB′, 4 H, 5,6,7,8-H), 8.01 (s, 2 H, 1,4-H), 2.72 (t, 4 H, CH_2R), 1.90–1.20 (m, 28 H), 0.86 (t, 6 H, CH_3). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 183.1 (C-9,10), 148.0 (C-2,3), 133.7 (C-6,7,8a,10a), 131.3 (C-4a,9a), 127.7 (C-1,4), 127.0 (C-5,8), 32.9, 31.9, 30.7, 29.7, 29.51, 29.48, 29.3, 22.7, 14.1. – MS (70 eV): *m/z* (%) = 460 (100, M^+), 333 (83), 235 (33).

$C_{32}H_{44}O_2$ (460.7) Calcd. C 83.42 H 9.63
Found C 83.17 H 9.61

2,3,6,7-Tetraalkylanthracenes and 2,3-Dialkylanthracenes: The reduction of the 2,3-di- and 2,3,6,7-tetraalkyl-9,10-anthraquinones **13b–d** and **14b–e** was performed in a mixture with a 1.5 M solution of aluminium tri(cyclohexyloxide) (15 mol per starting compound) which was heated to reflux for 48 h under argon. After cooling, the excess aluminium tri(cyclohexyloxide) was hydrolyzed. The resulting solid material was filtered, washed with ethanol, and dried. The filtrate, which contained an appreciable amount of the product, was evaporated to dryness and the solid residue subjected to Soxhlet extraction (argon atmosphere) with toluene for 3 h. The solvent was removed under reduced pressure and the solid residue was crystallized from methanol/CH_2Cl_2 to afford the anthracenes **6b–d** and **7b–e** as pale yellow crystals. Filtration over silica gel with *n*-hexane gave the products as white crystalls.

2,3,6,7-Tetra-n-propylanthracene (**6b**): 73%; mp 88°C. – ^1H NMR (90 MHz, $CDCl_3$): δ = 8.20 (s, 2H, 9,10-H), 7.72 (s, 4H, 1,4,5,8-H), 2.80 (t, 8H, CH_2R), 1.78 (m, 8H), 1.08 (t, 12H, CH_3). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.7 (C-2,3,6,7), 130.7 (C-4a,8a,9a,10a), 126.5 (C-1,4,5,8), 123.7 (C-9,10), 35.1, 23.9, 14.3. – MS (70 eV): *m/z* (%) = 346 (100, M^+).

$C_{26}H_{34}$ (346.6) Calcd. C 90.11 H 9.89
Found C 90.01 H 10.05

2,3,6,7-Tetra-n-pentylanthracene (**6c**): 81%; mp 97°C. – ^1H NMR (90 MHz, $CDCl_3$): δ = 8.21 (s, 2H, 9,10-H), 7.73 (s, 4H, 1,4,5,8-H), 2.82 (t, 8H, CH_2R), 2.0–1.3 (m, 24H), 0.97 (t, 12H, CH_3). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.9 (C-2,3,6,7), 130.8 (C-4a,8a,9a,10a), 126.4 (C-1,4,5,8), 123.7 (C-9,10), 33.0, 32.1, 30.6, 22.7, 14.1. – MS (70 eV): *m/z* (%) = 458 (100, M^+).

$C_{34}H_{50}$ (458.8) Calcd. C 89.01 H 10.99
Found C 88.84 H 11.18

2,3,6,7-Tetra-n-heptylanthracene (**6d**): 71%; mp 84°C. – ^1H NMR (400 MHz, $CDCl_3$): δ = 8.17 (s, 2H, 9,10-H), 7.69 (s, 4H, 1,4,5,8-H), 2.78 (t, 8H, CH_2R), 1.72 (m, 8H), 1.50–1.30 (m, 32H), 0.91 (t, 12H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.9 (C-2,3,6,7), 130.8 (C-4a,8a,9a,10a), 126.5 (C-1,4,5,8), 123.7 (C-9,10), 33.1, 31.9, 31.0, 29.8, 29.3, 22.7, 14.1. – MS (70 eV): *m/z* (%) = 570 (100, M^+). – UV: λ_{max} (lg ε) 387 nm (3.55), 369 (3.74), 350 (3.65), 268 (5.29). – IR (KBr): 3010 cm^{-1}, 2910, 2840 (C–H), 1455, 900, 730 (C–H).

$C_{42}H_{66}$ (571.0) Calcd. C 88.35 H 11.65
Found C 88.40 H 11.47

2,3-Di-n-propylanthracene (**7b**): 70%; mp 127°C. – ^1H NMR (90 MHz, $CDCl_3$): δ = 8.35 (s, 2 H, 9,10-H), 8.04 and 7.48 (AA′BB′, 4 H, 5,6,7,8-H), 7.81 (s, 2 H, 1,4-H), 2.83 (t, 4 H, CH_2R), 1.83 (m, 4 H), 1.10 (t, 6 H, CH_3). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.4 (C-2,3), 131.5 and 131.1 (C-4a,8a,9a,10a), 128.2 (C-5,8), 126.6 (C-1,4), 125.1 (C-9,10), 124.8 (C-6,7), 35.2, 24.0, 14.4. – MS (70 eV): *m/z* (%) = 262 (100, M^+).

$C_{20}H_{22}$ (262.4) Calcd. C 91.55 H 8.45
Found C 91.47 H 8.49

2,3-Di-n-pentylanthracene (**7c**): 65%; mp 99°C. – ^1H NMR (90 MHz, $CDCl_3$): δ = 8.34 (s, 2H, 1,4-H), 8.00 and 7.45 (AA′BB′, 4H, 5,6,7,8-H), 7.79 (s, 2H, 1,4-H), 2.84 (t, 4H, CH_2R), 1.90–1.40 (m, 12 H), 0.99 (t, 6H, CH_3). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.7 (C-2,3), 131.5 and 131.1 (C-4a,8a,9a,10a), 128.2 (C-5,8), 126.6 (C-1,4), 125.1 (C-9,10), 124.8 (C-6,7), 33.1, 32.2, 30.7, 22.8, 14.2. – MS (70 eV): *m/z* (%) = 318 (100, M^+), 205 (76).

$C_{24}H_{30}$ (318.5) Calcd. C 90.51 H 9.49
Found C 90.40 H 9.45

2,3-Di-n-heptylanthracene (**7d**): 80%; mp 73°C. – ^1H NMR (400 MHz, $CDCl_3$): δ = 8.30 (s, 2H, 9,10-H), 7.95 and 7.39 (AA′BB′,

4H, 5,6,7,8-H), 7.74 (s, 2 H, 1,4-H), 2.82 (t, 4H, CH_2R), 1.73 (m, 4H), 1.50–1.25 (m, 16H), 0.91 (t, 6 H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.6 (C-2,3), 131.5 and 131.1 (C-4a,8a,9a,10a), 128.1 (C-5,8), 126.5 (C-1,4), 124.9 (C-9,10), 124.7 (C-6,7), 33.0, 31.9, 30.9, 29.8, 29.3, 22.7, 14.1. – MS (70 eV): *m/z* (%) = 374 (100, M^+), 205 (50). – UV ($CHCl_3$): λ_{max} (lgε) = 384 nm (3.67), 362 (3.78), 348 (3.68), 331 (3.46), 261 (5.24). – IR (KBr): 3050 cm^{-1}, 2910, 2850 (C–H), 1455, 900, 745, 725.

$C_{28}H_{38}$ (374.6) Calcd. C 89.78 H 10.22
Found C 89.72 H 10.06

2,3-Di-n-nonylanthracene (**7e**): 45%; mp 65°C. – ^1H NMR (90 MHz, $CDCl_3$): δ = 8.32 (s, 2 H, 9,10-H), 7.98 and 7.42 (AA'BB', 4 H, 5,6,7,8-H), 7.77 (s, 2 H, 1,4-H), 2.81 (t, 4 H, CH_2R), 2.0–1.2 (m, 28 H), 0.93 (t, 6 H, CH_3). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.6 (C-2,3), 131.5 and 131.1 (C-4a,8a,9a,10a), 128.1 (C-5,8), 126.5 (C-1,4), 125.0 (C-9,10), 124.7 (C-6,7) 33.1, 32.0, 30.9, 29.9, 29.7 (2C), 29.5, 22.8, 14.2. – MS (70 eV): *m/z* (%) = 430 (100, M^+), 205 (44).

2,3,6,7-Tetra-n-heptyl-9,10-dihydroanthracene (**18**): A solution of 1 g (1.75 mmol) of **6d** in 30 ml of dry degassed THF was contacted with lithium wires in a sealed glass ampoule at –78°C. The ampoule contained two separate compartments. This allowed to separate the dianion solution from the metal and to perform a subsequent quenching reaction. When the color of the dianion solution had turned deep blue (reaction time 3–4 weeks) the ampoule was opened at a side arm under argon and 30 ml of dry ammonia was condensed in. The color of the solution turned from blue to red, orange, yellow and then pale yellow. The reaction mixture was stirred for 30 min, 5 ml of water was added. Thr ammonia was allowed to evaporate and the THF removed under vacuum. 50 ml of chloroform and 50 ml of water were added to the residue, the organic layer was washed with water, and dried. Evaporation of the solvent and crystallization of the residue from dichloromethane/methanol afforded 0.95 g (95%) of **18** as a colorless crystalline product. – **18**: 95%; mp 39°C. – ^1H NMR (400 MHz, $CDCl_3$): δ = 7.02 (s, 4 H, 1,4,5,8-H), 3.82 (s, 4 H, 9,10-H), 2.55 (t, 8 H, CH_2R), 1.54 (m, 8 H), 1.40–1.20 (m, 32 H), 0.87 (t, 12 H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.2, (C-2,3,6,7), 134.2 (C-4a,8a,9a,10a), 128.2 (C-1,4,5,8), 35.3 (C-9,10), 32.5, 31.9, 31.6, 29.8, 29.3, 22.7, 14.1. – MS (70 eV): *m/z* (%) = 572 (100, M^+).

Alkylation of $\mathbf{6d}^{2-}/2Li^+$ *with 1-Bromoheptane:* 10 mg ($1.75 \cdot 10^{-2}$ mmol) of **6d** was placed at the bottom of a 5-mm NMR tube and 0.5 ml of dry [D_8]THF was distilled in under vacuum. The solution was degassed by repeated freeze-pump cycles. Lithium wires were inserted into the evacuated tube by means of a press. The highly active metal was kept in the upper part of the tube by a constriction in the glass. The tube was sealed and the solution was brought into contact with the metal at –78°C. The dianion formation was complete after 3 weeks. The color of the solution was deep blue and a highly resolved ^1H-NMR spectrum of the resulting dianion could be recorded. The tube was opened under argon, and 100 mg (0.56 mmol) of 1-bromoheptane (in 0.3 ml of THF) was added with a syringe which caused immediate decolorization of the dianion solution. The solvent and the reagent were removed by evaporation under reduced pressure. The residue was solved in chloroform, washed with water, and dried over sodium sulfate. The analysis of the reaction product by ^1H-NMR spectroscopy showed that 2,3,6,7,9,10-hexa-*n*-heptyl-9,10-dihydroanthracene (**20**) had been formed in approximately 70% yield.

Alkylation of **18** *with n-Butyllithium/1-Bromoheptane:* To 400 mg (0.70 mmol) of **18** in 25 ml of THF at –20°C was added dropwise under argon 0.84 mmol (0.7 ml) of *n*-butyllithium in hexane. The resulting red solution was allowed to stir at –20°C for 1 h and then quenched with 1 ml of a 0.84 M (0.84 mmol) solution of 1-bromoheptane in THF. The deprotonation/alkylation reaction was repeated five times. Finally, 2 ml of water was added, the solvent was removed under vacuum, and the residue dissolved in chloroform. The organic layer was washed with water, dried over sodium sulfate, and the solvent removed by evaporation. Filtration of the crude product over silica gel (*L* = 20 cm, ∅ = 3 cm, hexane) yielded 450 mg (85%) of a colorless oil which, according to a ^1H-NMR spectroscopic analysis, contained 90% of *2,3,6,7,9,10-hexa-n-heptyl-9,10-dihydroanthracene* (**20**). This material was used as starting compound for the preparation of **23** (see below).

Reductive Alkylation of **6d** *with Lithium and 1-Bromoheptane in* NH_3/THF: To a solution of 18 mg (2.6 mmol) of lithium in 25 ml of liquid ammonia at –33°C was added dropwise under argon a solution of 500 mg (0.875 mmol) of **6d** in 50 ml of dry THF over a period of 10 min. Upon the addition of **6d**, the original blue color of the ammonia solution disappeared. The solution was stirred at –33°C for 1 h, and a solution of 315 mg (1.75 mmol) of 1-bromoheptane in 10 ml of THF was added. The reaction mixture was stirred for another 30 min, and 1.95 g (50 mmol) of sodium amide and 8.95 g (50 mmol) of 1-bromoheptane were added. After 1 h at –33°C the reaction mixture was quenched with 5 ml of water. The ammonia was evaporated, and the solvent and the alkylating agent were removed under reduced pressure. Column chromatography of the residue yielded 460 mg of a colorless oil which, according to ^1H-NMR spectroscopy, was a mixture of *2,3,6,7-tetra-n-heptyl-9,10-dihydroanthracene* (10%), *2,3,5,6,7-penta-n-heptyl-9,10-dihydroanthracene* (20%), *2,3,6,7-tetra-n-heptylanthracene* (30%), and *2,3,6,7,9,10-hexa-n-heptyl-9,10-dihydroanthracene* (40%).

Alkylation of **18** *with* $LiNH_2$/*1-Bromoheptane in* NH_3/THF: A suspension of 50 mmol of lithium amide in ammonia was prepared by addition of a few crystalls of iron(III) chloride to a solution of 345 mg (50 mmol) of lithium in 50 ml of liquid ammonia under argon. After the blue color of the dissolved metall had disappeared, a solution of 572 mg (1 mmol) of **18** in 25 ml of dry THF was added dropwise over a period of 5 min. The reaction mixture was allowed to stir for 12 h at –33°C, during which period a solution of 8.95 g (50 mmol) of 1-bromoheptane in 20 ml of dry THF was added dropwise to the suspension. The further workup is described above. Column chromatography yielded 650 mg of a colorless oil which, according to ^1H-NMR spectroscopy, contained 80% of **20** and 20% of **18**. The pure compound **20** was isolated by semipreparative HPLC (Dynamax Macro Si, 8 µm, 250 × 22 mm, hexane) (290 mg, 38%) as a colorless oil. – **18**: ^1H NMR (400 MHz, $CDCl_3$): δ = 7.00 (s, 4H, 1,4,5,8-H), 3.74 (t, 2H, 9,10-H), 2.60 (t, 8H, CH_2R), 1.73 (m, 4H, CH_2R), 1.65–1.25 (m, 60H), 0.90 (m, 18H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.7 and 137.6 (C-2,3,6,7 and C-4a,8a,9a,10a), 129.4 (C-1,4,5,8), 46.0 (C-9,10), 42.6, 32.5, 32.0, 31.9, 31.5, 29.8, 29.75, 29.3, 28.7, 22.7, 14.1. – MS (70 eV): *m/z* (%) = 766 (M^+ – 2 H, 7), 670 (48), 57 (100).

2,3,6,7,9,10-Hexa-n-heptylanthracene (**23**): 300 mg of crude **20** (obtained by alkylation of **18** with *n*-butyllithium/1-bromoheptane) was dissolved under argon in 5 ml of cyclohexane and 1.5 ml (2.25 mmol) of *n*-butyllithium in hexane. Then 3 ml of TMEDA was added. The solution was heated to refluxe for 4 h under argon. After cooling, 500 mg of freshly sublimed $CdCl_2$ was added, and the mixture was stirred for 30 min at room temperature. The black suspension was concentrated under reduced pressure, and 20 ml of aqueous hydrochloric acid (2N) and 20 ml of chloroform was added. The organic layer was washed several times with acid and dried over sodium sulfate. The residue remaining after evaporation of the solvent was chromatographed over silica gel (*L* = 40 cm, ∅ 3 cm,

hexane) to give 110 mg (40%) of **23** as lemon yellow crystals which were recrystallized from dichloromethane/ethanol).

23 *by One-Pot Reaction from* **18**: A solution of 286 mg (0.5 mmol) of **18** in 5 ml of cyclohexane was added to 3 ml of TMEDA and 1.2 ml (1.8 mmol) of *n*-butyllithium in hexane. The reaction mixture was heated to reflux under argon for 2 h. After cooling, a solution of 322 mg (1.8 mmol) of 1-bromoheptane in 1 ml of cyclohexane was added dropwise. The mixture was allowed to stir for 30 min at room temperature and a solution of 2 ml (3 mmol) of *n*-butyllithium in hexane was added by a syringe. After heating to reflux for 4 h, the reaction mixture was allowed to cool, and 550 mg (3 mmol) of sublimed $CdCl_2$ was added. The resulting supension was stirred at room temperature for 30 min. 2 ml of water was added, and the solvents were evaporated. 25 ml of chloroform and 25 ml 2NHCl were added to the residue. The organic layer was carefully washed several times with 2NHCl and dried over sodium sulfate. Chromatography over silica gel (L = 40 cm, $\varnothing$ = 3 cm, hexane) yielded 116 mg (30%) of **23** which was recrystallized from dichloromethane/methanol. – **23**: mp 74°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (s, 4H, 1,4,5,8-H), 3.52 (t, 4H, CH_2R, 9,10-H), 2.81 (t, 8H, CH_2R), 1.85–1.25 (m, 60H), 0.90 (t, 18H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.9 (C-2,3,6,7), 131.3 (C-9,10), 128.3 (C-4a,8a,9a,10a), 123.8 (C-1,4,5,8), 33.3, 31.9, 31.3, 31.0, 30.3, 29.7, 29.3, 28.0, 22.7, 14.1. – MS (70 eV): m/z (%) = 766 (100, M^+), 682 (15). – UV ($CHCl_3$): λ_{max} (lg ε) = 411 nm (3.66), 389 (3.74), 370 (3.61), 347 (3.54), 329 (3.52), 276 (5.51)

$C_{56}H_{94}$ (767.4) Calcd. C 87.65 H 12.35
Found C 87.81 H 12.23

Poly(2,3-di-n-heptyl-9,10-dihydroanthrylenetrimethylene) (**3**): The synthesis of **3** was performed in a mixture of liquid ammonia and THF whereby the amount of the organic cosolvent was varied between 30 and 60%. In a typical experiment 347 mg (50 mmol) of lithium was dissolved under argon in 200 ml of dry liquid ammonia at –33°C. A solution of 7.5 g (20 mmol) of 2,3-di-*n*-heptylanthracene (**7d**) in 250 ml of THF was added dropwise. After stirring the deep red mixture for 1 h, a solution of 4.04 g (20 mmol) of 1,3-dibromopropane in 25 ml of THF was added over a period of 90 min. Stirring was continued for 1 h, and 5 ml of water was added to the suspension. The ammonia was evaporated and the THF removed under reduced pressure. 200 ml of chloroform and 200 ml of water were added, the organic layer was washed with water and dried over sodium sulfate. Removal of the solvent under reduced pressure gave a colorless glassy polymer which was dried for 24 h at $1 \cdot 10^{-2}$ mbar. The yield was 8.2 g (98%). ^{1}H-NMR spectroscopic analysis of the raw material indicated that the reductive transformation was quantitative. The characteristic aromatic resonances of **7d** had disappeared. Traces of 2,3-di-*n*-heptyl-9,10-dihydroanthracene could be removed by preparative GPC (200 mg of compound, sephadex LH-20 gel, THF, L = 70 cm, $\varnothing$ = 3.5 cm) or column chromatography over silica gel (1 g of compound, L = 30 cm, $\varnothing$ = 3.5 cm, hexane/$CHCl_3$, gradient 0–100%). The mean molecular weight M_n of the material (determined after removal of 2,3-di-*n*-heptyl-9,10-dihydroanthracene) was 3100 according to vapor-pressure osmometry. Variation of the solvent mixture or of the rate of the addition of the alkylating reagent did not affect the molecular weight of **3**. – **3**: ^{1}H NMR (200 MHz, $CDCl_3$; M_n = 3100): δ = 7.40–6.70 (1–8-H, 1′–8′-H), 4.20–4.00 (10-H), 4.00–3.50 (9, 10-H, 9′,10′-H), 2.70–2.40 (CH_2R), 1.90–1.20 ($[CH_2]_3$, $[CH_2]_5$), 0.90 (CH_3). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 141.2, 140.4, 138.3, 137.5, 136.7, 133.5, 129.6, 129.0, 128.6, 128.0, 126.0, 47.3, 46.4, 43.5, 42.6, 37.8, 35.3, 32.8, 32.1, 31.8, 30.2, 29.5, 27.9, 27.0, 23.0, 14.4: ^{13}C-NMR end group signals. – ^{13}C-NMR signals of the end groups: δ 133.5 (C-4a,10a), 47.3 (C-9), 37.8, (C-11), 35.3 (C-10), 27.0 (C-12). – ^{13}C-NMR signals of the inner groups: δ 140.4 (C-8′a,10′a), 138.3 and 137.5 (C-2′,3′,4′a,9′a), 129.6 and 129.0 (C-1′,4′,5′,8′), 126.0 (C-6′,7′), 46.4 (C-9′,10′), 42.6 (C-11′), 27.9 (C-12′). – ^{13}C NMR, heptyl group: 32.9, 32.2, 31.8, 30.2, 29.5, 23.0, 14.4.

$(C_{31}H_{44})_\infty$ (416.7) Calcd. C 89.36 H 10.64
Found C 88.88 H 11.01

Increasing the Molecular Mass of **3** *by Metallation with Lithium Amide and Alkylation with 1,3-Dibromopropane:* 347 mg (50 mmol) of lithium was dissolved under argon in 200 ml of liquid ammonia at –33°C, and a few crystals of iron(III) chloride were added in order to catalyze the formation of lithium amide. After the blue color of the solvated electrons had disappeared the solution of 2.1 g of polymer **3** (M_n = 3100) in 200 ml of THF was added dropwise over a period of 15 min. The reaction mixture was stirred at –33°C for 30 min whereby the color of the suspension turned orange. A 0.2 M solution of 1,3-dibromopropane in THF was added dropwise until the color of the polymer suspension disappeared. The deprotonation/alkylation sequence was repeated three times. After the fourth alkylation the ammonia was allowed to evaporate. 180 ml (90% of the ammonia) was evaporated over a period of 3 h. A few drops of a 1,3-dibromopropane solution were added every 30 min. After 5 h the colorless reaction mixture was quenched with water and worked up as described above. This treatment increased the molecular weight M_n from 3100 to 9700 as determined from vapor-pressure osmometry. The ^{1}H- and ^{13}C-NMR spectra of the product (see below) failed to indicate separate signals of end groups. – **3**: ^{1}H NMR (200 MHz, $CDCl_3$; M_n = 9700): δ = 7.40–6.70 (1′,4′,5′–8′-H), 4.00–3.50 (9′,10′-H), 2.70–2.40 (CH_2R), 1.90–1.20 ($[CH_2]_3$, $[CH_2]_5$), 0.90 (CH_3). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.5, 138.2, 137.5, 129.5, 128.9, 125.8, 46.2, 42.5, 32.7, 32.1, 31.7, 30.1, 29.5, 22.9, 14.3; δ = 140.5 (C-8′a, 10′a), 138.2 and 137.5 (C-2′,3′,4′a,9′a), 129.5 and 128.9 (C-1′,4′,5′,8′), 125.8 (C-5′,6′), 46.2 (C-9′,10′), 42.5 (C-11′); heptyl group: δ = 32.7, 32.1 31.7, 30.1, 29.5, 22.9, 14.3.

$(C_{31}H_{44})_\infty$ (416.7) Calcd. C 89.36 H 10.64
Found C 88.84 H 10.93

CAS Registry Numbers

3: 113568-88-0 / **6b**: 113568-60-8 / **6c**: 113568-61-9 / **6d**: 113568-62-0 / **7b**: 113568-63-1 / **7c**: 113568-64-2 / **7d**: 113568-65-3 / **7e**: 113568-66-4 / **8a**: 513-81-5 / **8b**: 16356-06-2 / **8c**: 84652-75-5 / **8d**: 113568-67-5 / **8e**: 113568-69-7 / **9**: 106-51-4 / **10**: 130-15-4 / **11b**: 113568-71-1 / **11c**: 113568-74-4 / **11d**: 113568-75-5 / **12b**: 113568-76-6 / **12c**: 113568-77-7 / **12d**: 113568-78-8 / **12e**: 113568-79-9 / **13b**: 113568-80-2 / **13c**: 113568-81-3 / **13d**: 113568-82-4 / **14b**: 113568-83-5 / **14c**: 113568-84-6 / **14d**: 113568-85-7 / **14e**: 113568-86-8 / **15**: 102637-43-4 / **16**: 113568-68-6 / **18**: 113568-20-0 / **20**: 113568-72-2 / **23**: 113568-73-3 / 2,3,5,6,7-pentaheptyl-9,10-dihydroanthracene: 113568-87-9 / 1-bromoethane: 74-96-4 / 1-bromobutane: 109-65-9 / 1-bromohexane: 111-25-1 / 1-bromooctane: 111-83-1 / 1-bromoheptane: 629-04-9 / 1,3-dibromopropane: 109-64-8

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