Synthesis of Oligomeric Chains with 9,10-Dihydroanthracene Units by Carbanion Alkylation

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Deprotonation of 9,10-dihydroanthracene (2) affords the monoanion 6 which is subjected to alkylation reactions with mono *and* bifunctional electrophiles. Crucial intermediates in syntheses using 6 are 9-(3-bromopropyl)-9,10-dihydroanthracene (7) and 1,3-bis(9,10-dihydro-9-anthryl)propane (9) since they provide access to linear oligomers in which 9,10-dihydroanthracene units are linked by trimethylene groups. The alkylation processes of these species can be extended to the structurally related polymer 4. The regio- and stereoselectivity of the alkylation reactions are investigated by ^{1}H- and ^{13}C-NMR spectroscopy.

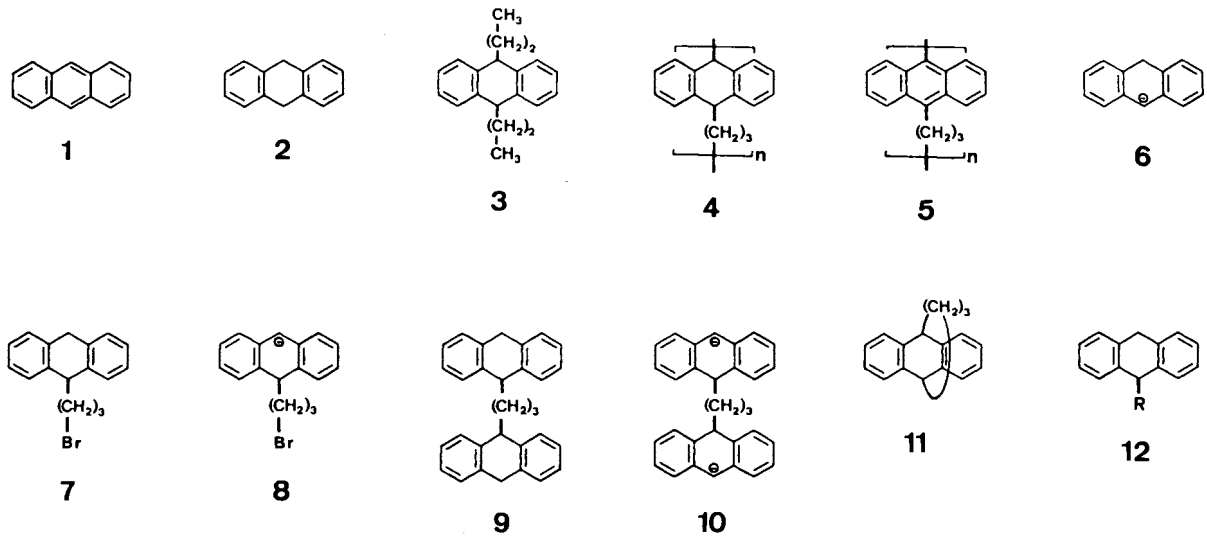
Oligomere Ketten mit 9,10-Dihydroanthracen-Einheiten durch Carbanionalkylierung

Die Deprotonierung des 9,10-Dihydroanthracens (2) liefert das Monoanion 6, welches der Alkylierung mit mono- und bifunktionellen Elektrophilen unterworfen wird. Zentrale Zwischenprodukte der von 6 ausgehenden Synthesen sind das 1,3-Di(9-anthryl)propan 9 und 9-(3-Brompropyl)-9,10-dihydroanthracen (7). Sie eröffnen den Zugang zu linearen Oligomeren, in denen 9,10-Dihydroanthracen-Einheiten durch Trimethylengruppen verknüpft sind. Die Alkylierungsreaktionen dieser Verbindungen können auf das strukturverwandte Polymer 4 übertragen werden. Regio- und Stereoselektivität der Alkylierungsreaktionen werden ^{1}H- und ^{13}C-NMR-spektroskopisch untersucht.

1. Introduction

The reductive alkylation of anthracene (1) and the successive deprotonation and alkylation of 9,10-dihydroanthracene (2) to provide alkyl-substituted derivatives such as 3 have been the topic of numerous synthetic, mechanistic, and spectroscopic studies[1–15], the results of which are significant for the understanding of regio- and stereoselective carbanion alkylations. A fascinating extension of this chemistry is the alkylation of 1 or 2 with bifunctional alkylating agents such as 1,*n*-dihaloalkanes[16–20]. Under appropriate experimental conditions the latter can react with *two* ionic anthracene units and thus initiate the formation of oligomeric or polymeric chains[16–21]. Indeed, this technique enabled us to create polymers with the novel structure of type 4 in which dihydroanthracene moieties are linked regioselectively by flexible spacer groups of various length[16,20,21]. Compounds 4 can be dehydrogenated to the corresponding polyanthrylene species 5 in which the π system may undergo successive electron-transfer processes. Indeed, 5 proves to be an efficient electron-storage system upon electrochemical or chemical redox reactions[22,23].

The method of choice to synthesize 4 is the reductive alkylation of anthracene (1) with lithium and 1,*n*-dihaloalkanes in liquid ammonia[24]. The molecular weight of the resulting polymer depends on the experimental conditions such as the concentration and the ion pair situation of the intermediate carbanions[16,21]. The control of the properties of the polymer thus requires insight into the formation and subsequent alkylation of the relevant carbanionic intermediates. Our preliminary studies of the polymer forming re-



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ductive alkylation reveal that anthracene (**1**), after having been transformed into its dianion, is rapidly protonated by the solvent to yield the monoanion **6** and the amide anion[24]. Alkylation of **6** with 1,3-dibromopropane then affords the dihydroanthracene compound **7**[25]. The latter is still an electrophile and is susceptible to undergo an S_N-type alkylation with the monoanion **6** which, under the prevailing reaction conditions, is present as the major component. The resulting 1,3-di(9-anthryl)propane **9** should therefore constitute the key intermediate of the polymerization reaction since its deprotonation and subsequent alkylation at C-10 are expected to allow chain propagation.

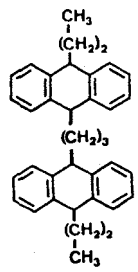
This mechanistic view, although straightforward and in accordance with various pieces of experimental evidence, still raises a number of questions. Instead of reacting as an electrophilic bromoalkane, the primary product **7** may be deprotonated by the base present in the solution to yield **8** which is both a nucleophile and an electrophile. The *intra*molecular alkylation of **8** would afford the trimethylene-bridged dihydroanthracene **11**[16,25,26]; on the other hand, *inter*molecular alkylation could occur between **8** and 1,3-dibromopropane or between two equivalents of **8**, thus initiating, again, the formation of an oligo(dihydroanthrylene-trimethylene) chain.

Another complication within this mechanistic scheme arises from the fact that deprotonation of **7** or **9** might, in principle, not only occur at the bisbenzylic methylene, but also at the methine positions (C-9) of the dihydroanthracene units[11]. In the case of **4**, deprotonation at inner benzyl positions of the dihydroanthracene moieties and subsequent alkylation with 1,*n*-dihaloalkanes could initiate cross linking of the polymer chains and could thus severely influence their chemical and physical behavior. In this context the deprotonation and alkylation of 9-alkyl-9,10-dihydroanthracenes **12** and of tetrahydrodianthrylalkanes such as **9** can serve as model reactions.

The present paper describes the synthesis of novel monomeric and oligomeric hydrocarbons containing 9,10-dihydroanthracene moieties by carbanion alkylation. The structures of products such as **3**, **7**, **9**, **13**, and **14**–**17**, are elucidated by ^{1}H- and ^{13}C-NMR spectroscopy. Special emphasis is paid to the existence of regio- and stereoisomerism. The alkylation of 9,10-dihydroanthracene (**2**) and of its mono- and disubstituted derivatives provides products constituting potential intermediates in the reductive polymerization of anthracene to yield **4**. Therefore, our approach provides insight into the mechanism of the polymer forming reductive alkylation and into the structure of the polymer.

A major advantage of the reductive alkylation with bifunctional electrophiles to yield polymers of the general structure **4** lies in the fact that the reaction can easily be modified to incorporate linkages other than polymethylene.

Particularly interesting is the introduction of unsaturated moieties such as the xylylidene group[27]. This should not only affect the conformation of the resulting polymer chains **20** and **21**, respectively, but also the electronic interaction between the anthracene units of **21**[23]. In this context, we have prepared the dianthryl compounds **24** and **25** by replacement of 1,*n*-dihaloalkanes with bifunctional electrophiles such as **22** and **23**. The latter serve as suitable models for the related polymer **20**.



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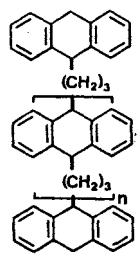
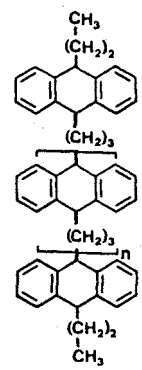


n=1 **14**
n=2 **15**
n=3 **16**
n=4 **17**



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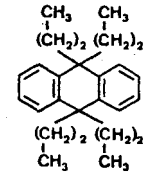

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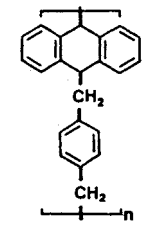

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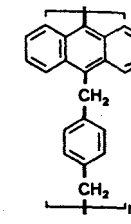

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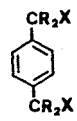
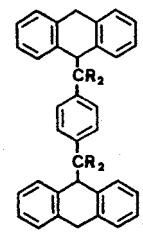
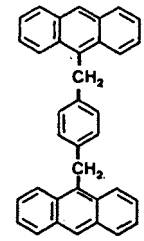


X=Cl
R=H **22**
R=CH$_3$ **23**



R=H **24**
R=CH$_3$ **25**



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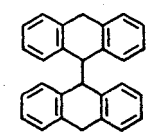

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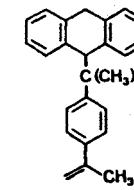

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2. Results

9,10-Dihydro-*cis*-9,10-di-*n*-propylanthracene (**3**) was prepared by reductive alkylation of anthracene with 1-bromopropane in liquid ammonia and characterized by ^{1}H- and ^{13}C-NMR spectroscopy (see Section 3)[28].

Treatment of 9,10-dihydroanthracene (**2**) with *n*-butyllithium in tetrahydrofuran (THF) gave rise to the monoanion **6**[24,29] which could be subjected to alkylation reactions[9,11]. Thus, **3** was also prepared by successive alkylation of 9,10-dihydroanthracene (**2**) with 1-bromopropane. Deprotonation of 9,10-dihydroanthracene (**2**) with 1.2 equivalents of *n*-butyllithium in THF and alkylation with 1.2 equivalents of 1-bromopropane gave, after five repetitions of the reaction sequence, a crude product (94%) which contained a monopropyl (8%) and two different dipropyl (79%, 13%) derivatives. The major (minor) dipropyl adduct could be identified as possessing a *cis* (*trans*) configuration of the substituents at C-9 and C-10. Particularly significant is the resonance of 9-H (triplet) at δ 3.89 and δ 4.05 which is due to the *cis*-**3** and *trans* isomer, respectively. When we treated **3** (*cis* configuration) with an excess of *n*-butyllithium (THF) at −78 °C, the ^{1}H-NMR spectra failed to indicate any deprotonation. Ion formation was only observed upon warming the sample to 0 °C (1 h).

If 1,3-dibromopropane in THF was added to a solution of **6** in THF, **9** was obtained in 80% yield. The synthesis of **9** was analogous to a procedure given in the literature[17]. In the ^{1}H-NMR spectrum of **9** the signals of the methylene protons at C-10 (AB systems) appear at δ 4.04 (H_a) and δ 3.81 (H_e) with ^2J = 18.3 Hz (see Figure 1). The assignment of the axial and equatorial protons follows the arguments proposed by Rabideau for alkyl-substituted 9,10-dihydroanthracenes[7,8]. The methine proton at C-9 gives rise to the triplet signal (due to the vicinal coupling [^3J = 7.3 Hz] with the methylene protons of the bridging group) at δ 3.83.

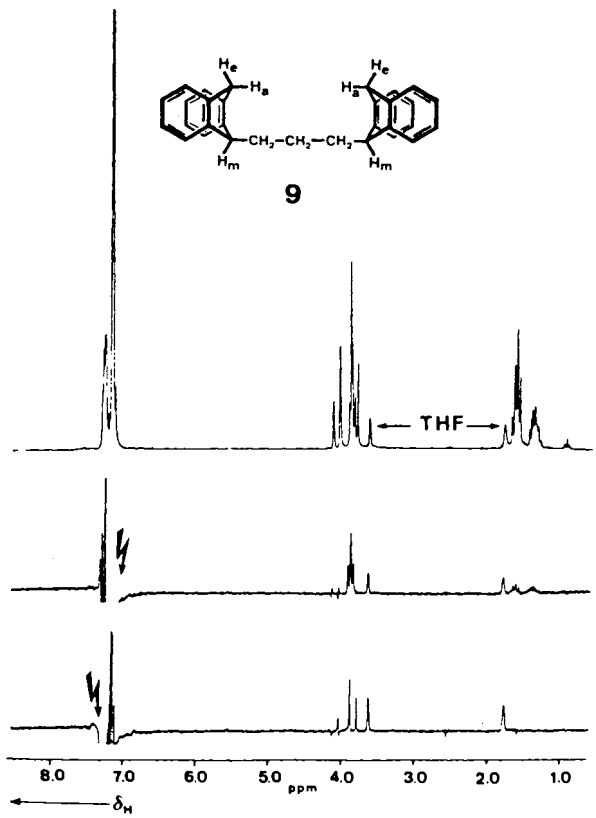

Figure 1. ^{1}H-NMR spectra ([D_8]THF, 200 MHz) of **9**
Top: normal spectrum without decoupling; middle and bottom: difference NOE experiments with irradiation at δ 7.12 and δ 7.23, respectively

When **6** was quenched in reversed order[16], i.e. if the carbanion solution was added dropwise to the 1,3-dibromopropane solution, we obtained **7** in 60% yield. The ^{13}C-NMR signals of **7** were assigned by using **2**, **3**, **9**, and 1-bromopropane as reference compounds.

Compound **7** appeared to be a useful starting material for further synthesis. We first considered the intramolecular cyclization reaction of **7**. Toward that end, a 10^{-1}-molar solution of **7** in THF was slowly added to a suspension of an excess of lithium amide in NH_3/THF (2:1) at −33 °C. The yield of the cyclization product **11** was 62%. In addition, the polymer **4** was produced in 10% yield (see below).

In order to test the regioselectivity of the deprotonation of **9** it was treated with *n*-butyllithium in THF at −78 °C which yielded a deep red solution. Performing the experiment in [D_8]THF allowed us to record the ^{1}H-NMR spectrum of the resulting carbanion. It is clear from the spectrum (aromatic signals at δ 6.4 [d, t], 6.09 [d], 5.82 [t], singlet signal of 10-H at δ 4.09)[12] that the *dianion* **10** has been formed by deprotonation at *both* dihydroanthracene units. Deprotonation of **9** on a preparative scale and quenching with 1-bromopropane at −78 °C gave a crude product which contained about 85% of **13**. Just as in the analogous dihydroanthracene derivative **3**, we found that the ^{1}H-NMR spectrum points toward (at least) *two* stereoisomeric dipropyl derivatives. It shows two methine proton resonances (9,9′-H, 10,10′-H) at δ 4.03 and δ 3.91. Chromatographic separation (HPLC) (with a loss of material) from the monopropyl derivative and the stereoisomeric dipropyl product gave pure **13** in 44% yield. The assignment of the ^{13}C-NMR signals of **13** follows from a comparison with model compounds such as **3** and **9**. It will appear from Section 3 that the isolated (major) product is *all-cis*-**13**.

The initial step in the synthesis of higher homologues of **9** was the deprotonation of **9** to produce the dianion **10** (see above) which could then be subjected to a twofold alkylation with **7**. It could be deduced from ^{13}C-NMR and FD mass spectrometry that an isomeric mixture of tetraanthrylene species (**15**) was formed. Analysis of the crude reaction mixture by TLC indicated at least 4 products. Repeated chromatography provided one isomer of the "tetramer" **15** in pure form. While the ^{1}H-NMR spectra of the latter and of the mixture are virtually identical, the corresponding ^{13}C-NMR spectra exhibit significant differences. The assignments of the ^{13}C-NMR signals of the pure compound **15** could be achieved by comparison with the model systems **3**, **9**, and **13**. The ^{1}H-NMR spectrum of **15** (see Figure 2) shows broad lines due to the existence of many overlapping resonances. However, the resonance of the terminal axial

methylene proton (10-H) is clearly separated from those of all other benzylic protons with the correct intensity ratio of 1:4.

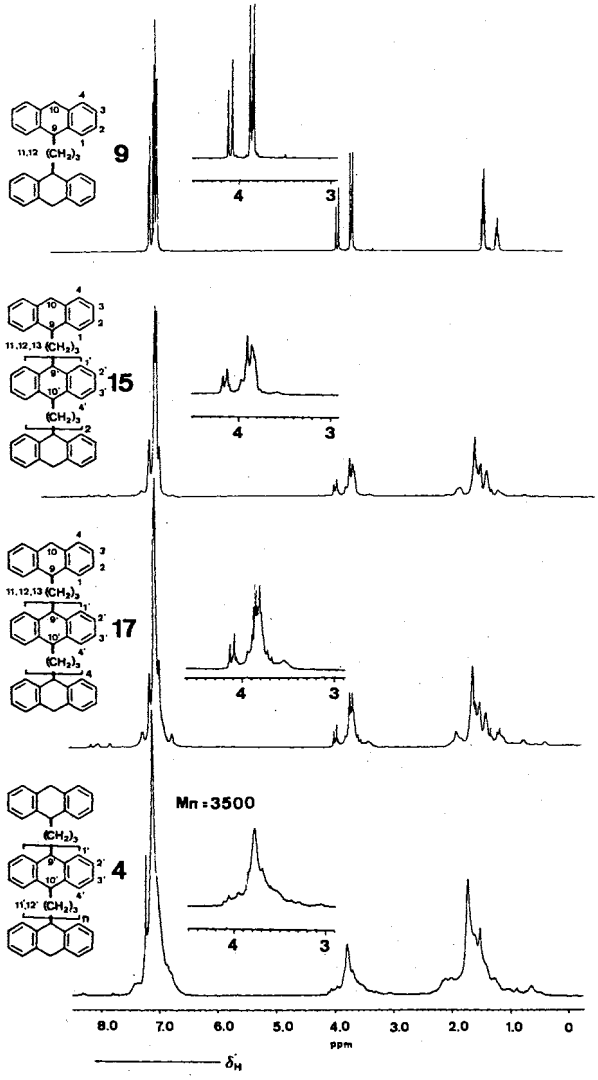

Figure 2. ^{1}H-NMR spectra ($CDCl_3$, 400 MHz) of (from top to bottom) **9**, **15**, **17**, and **4** (M_n = 3500)

For the synthesis of the homologous "hexamer" **17**, we started from the isomeric mixture of the "tetramer", which was subjected to deprotonation at the terminal methylene positions and to subsequent alkylation with **7**. After aqueous workup and repeated column chromatography we isolated a fraction for which the relative intensity of the two benzylic ^{1}H-NMR signals was 1:6 (see Figure 2). The FD mass spectrum indicated that the hexamer **17** contained some pentamer **16** as minor component. Their complete chromatographic separation was not possible.

The synthesis and structural characterization of the polymer **4** have been described by us elsewhere[21]. In order to test its alkylation reaction we chose a sample which, according to vapor-pressure osmometry, had a mean molecular weight of M_n = 1800 g/mol and thus a mean polymerization grade of P_n = 8. Compound **4** (1 eq.) was dissolved in THF and treated with *n*-butyllithium (18 eq.) at −78 °C. This roughly corresponds to 1 eq. of base per benzylic carbon. Upon contact with the base the solution of **4** instantaneously turned deep red. After 2 h the reaction mixture was quenched with 1-bromopropane (18 eq.) in THF. The ^{1}H-NMR spectrum of the product **18** indicated that the signal of the terminal bisbenzylic protons had disappeared. The high-field triplet signal (δ 0.85) of the methyl protons of a propyl group had a relative intensity which indicated that any macromolecule carries two propyl groups (see Figure 3).

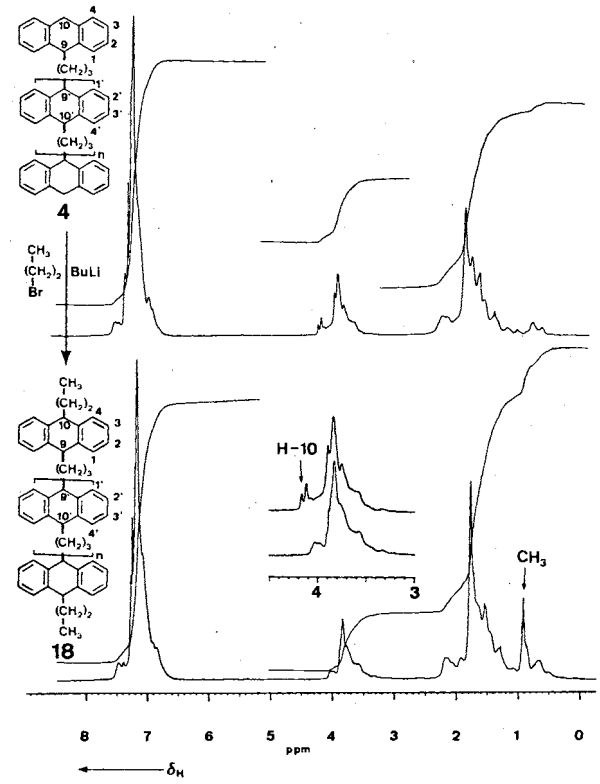

Figure 3. ^{1}H-NMR spectroscopic monitoring of the alkylation of polymer **4**

The above results raise the question if dihydroanthracene compounds such as **9** and **13** can be subjected to peralkylation reactions. When **3** was treated with *n*-butyllithium/tetramethylethylenediamine in THF followed by alkylation with 1-bromopropane the "peralkylated" 9,9,10,10-tetrapropyl derivative **19** was obtained in 40% yield. In the 7-line ^{13}C-NMR spectrum of **19** the signals of the quarternary aliphatic carbons (C-9, C-10) appear at δ 45.1. Particularly characteristic is the resonance line of the α-methylene carbon which in **19** is shifted downfield with respect to **3** by 5.4 ppm.

In an attempted peralkylation of **9** the compound was dissolved in NH_3/THF (−33 °C, 2:1) and treated with a large excess of lithium amide (6 eq. per benzylic proton) for 1 h. Under the prevailing conditions the carbanions can be alkylated in situ in the presence of further base which is not possible with the use of *n*-butyllithium[30]. In the ^{13}C-NMR

spectra of the crude product one observes, in addition to the signals of **13**, resonance signals at δ 50.4, 50.3, and 49.2. Column chromatographic separation provided two fractions in a 4:1 ratio. The first one was pure **13**. As could be inferred from ^{13}C-NMR and FD mass spectrometry the second fraction contained small amounts of **13** and isomers of tri- and tetrapropyl adducts.

The tetrahydro-α,α′-dianthryl-*p*-xylene **24** was prepared in a fashion similar to the tetrahydrodianthrylalkanes. Thus, 9,10-dihydroanthracene (**2**) was transformed into the monoanion **6** by deprotonation with *n*-butyllithium in THF and quenched with an excess of the dichloride **22**. Aqueous workup and column chromatography provided **24** in 33% yield. When, on the other hand, the solution of **6** was added to an excess of the alkylating agent **22**, the dialkylation product **24** was obtained in 49% yield. The reason for this improved yield will become clear from a discussion of the potential side reactions in Section 3. The dehydrogenation of **24** with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in xylene at 130°C gave α,α′-dianthryl-*p*-xylene (**26**) in 60% yield. Better yields (80%) were achieved upon treatment of **24** with *n*-butyllithium/TMEDA and cadmium chloride[31].

To further test the alkylation reaction of the carbanion **6**, the quenching agent **22** was replaced by the tetramethyl analogue **23**. Guided by experience from the above alkylation, the quenching of **6** with **23** was first performed under reverse addition conditions. The products obtained were anthracene (**1**), 9,10-dihydroanthracene (**2**), tetrahydro-9,9′-bianthryl (**27**), and compound **28**. More appropriate for a formation of **25** is the alkylation of **6** with the bifunctional electrophile **23** in a *normal* mode (addition of **23** to the carbanion). Thereby, the oxidation product **27** could not be detected and **28** was formed only as a minor product. The major product was **25** which after chromatography and crystallization was isolated in 30% yield.

3. Discussion

There are two reasons why the monomeric and oligomeric 9,10-dihydroanthracene species are important for an understanding of the polymer **4**: (i) their NMR spectra provide information for the structural elucidation of the higher homologues, and (ii) the method of their synthesis sheds light on the formation of the polymer chain. A basic question, therefore, is the regioselectivity of deprotonation/alkylation sequences (see below).

Thereby, the synthesis of **9**, **13**, and **15** sheds light on the mechanism of the polymer forming reaction. The oligomers are built up by an S_N reaction between the electrophiles 1,3-dibromopropane or 9-(3-bromopropyl)-9,10-dihydroanthracene (**7**), and the nuleophiles, the mono- or dianions **6** or **10** (derived by deprotonation of the dihydroanthracene systems **2** or **9**). As expected, the reaction between **6** and 1,3-dibromopropane to yield either **7** or **9** can be controlled by the stoichiometry and the mode (normal/reverse) of the quenching reaction. It is of great value for the synthesis of the oligomers that the intermediate **7** can be obtained in good yield and in high purity.

A crucial question for the preparation of extended *linear* chain structures with more than two dihydroanthracene units is whether **9** can be selectively deprotonated and alkylated at the terminal methylene groups (C-10). It should be recalled in this context that 9-alkyl-9,10-dihydroanthracenes upon deprotonation and subsequent methylation produce the 9-alkyl-10-methyl derivatives[7,11] exclusively.

When the tetrahydrodianthrylpropane **9** is converted into a dianion and subjected to alkylation no attack occurs at the inner benzylic carbons[12]. In the ^{13}C-NMR spectrum of **13** there is no signal of a terminal methylene unit. The formation of **13** indicates the site of deprotonation, i.e. the formation of the dianion **10**, and also excludes equilibration by proton transfer. This synthetic outcome is in accord with the ^{1}H-NMR spectrum of the intermediate dianion **10** which nicely reflects the shielding of the benzene protons due to the charge effect. Particularly significant is the singlet signal of C-10 at δ 4.09.

In view of the polymer forming reaction it is important that the alkylation of **9** does not provide tri- or tetraalkyl products. In order to test an eventual removal of methine protons we have treated *cis*-9,10-di-*n*-propyl-9,10-dihydroanthracene (**3**) with an excess of *n*-butyllithium in [D_8]THF at −78°C and monitored the reaction by ^{1}H-NMR spectroscopy. Under the reaction conditions there is no deprotonation; however, warming the reaction mixture to 0°C for 1 h gives rise to the spectrum of a monoanion. These findings must be contrasted with related results given in the literature[32].

Experience accumulated in the synthesis of **7**, **9**, and **13** allowed us to design a synthesis of the higher oligomers **15** and **17**. In the synthesis of the "tetramer" **15** from **9** and **7** one must work with precisely two equivalents of the base. Excess base may deprotonate the product **15** at the methylene positions resulting in further alkylation. An insufficient amount of base will afford the structurally related trianthryl species **14**.

The concept leading to the synthesis of **15** can be extended to the synthesis of the related "hexamer" **17**. It comprises the selective deprotonation at the terminal methylene groups of **15** and the subsequent alkylation with **7**. The structural identity of the product **17** follows from the relative intensity (1:6) of the two benzylic signals (see Figure 2).

In view of the selective alkylation at the terminal benzylic positions of **9** and **15** it is important to test the same reaction for the structurally related poly(dihydroanthrylene) compound in which alkylation at the inner benzylic positions (C-9′, C-10′) should be statistically favoured. Here again, we have first monitored the deprotonation (*n*-butyllithium, [D_8]THF, −78°C) by ^{1}H-NMR spectroscopy. It appears that the reaction at −78°C only gives rise to deprotonation at the terminal methylene groups. Treatment of the resulting metallation product with an excess of 1-bromopropane affords a product which according to the relative ^{1}H-NMR signal intensities of the *n*-propyl group, contains only two substituents (see Figure 3). A comparison of the ^{13}C-NMR spectra of the "alkylated" polymer **18** and the structurally related dipropyl-dianthryl compound **13** indicates the ter-

minal position of the propyl groups in the former. An eventual alkylation at inner benzylic positions of **4** would produce quaternary aliphatic centers.

In order to detect an eventual alkylation "inside" the polymer chain, we can refer to suitable model compounds. In particular, the "peralkylated" dihydroanthracene **19** could provide characteristic resonances of quaternary aliphatic carbons C-9. It appears during the synthesis of **19** that deprotonation of **3** is only possible if bases stronger than *n*-butyllithium are applied. On deprotonation with *n*-butyllithium/tetramethylethylenediamine and subsequent alkylation with 1-bromopropane we, indeed, succeeded in preparing the 9,9,10,10-tetra-*n*-propyl-9,10-dihydroanthracene (**19**). As mentioned in Section 2, both the resonance lines of C-9 (δ 45.1) and $C-CH_2(\alpha)$ (δ 50.2) in **19** are significantly different from those in the precursor **3**. The alkyl substitution in the polymer **18** causes the signals of terminal dihydroanthracene units at δ 136.0, 47.2, 37.2, and 26.1 to disappear while new signals can be detected e. g. at δ 45.1, 28.1, and 14.3. The failure to record resonances at about δ 50 shows that no quaternary carbons have been formed by alkylation at inner benzylic carbon centers.

An attempt has been made to subject **9** to peralkylation. Toward that end, **9** was treated with a large excess of lithium amide in NH_3/THF. Thus, deprotonation could be performed in the presence of 1-bromopropane which was not possible for a deprotonation/alkylation sequence initiated by *n*-butyllithium. The ^{13}C-NMR spectrum of the crude product provides evidence for quatenary aliphatic centers. In particular, the resonances at δ 50.4, 50.3, and 49.2 can be nicely correlated with the absorption of $C-CH_2(\alpha)$ in **19**. Chromatographic purification of the crude product gave a mixture of tri- and tetrapropyl adducts.

Having established the regioselective formation of oligomeric chains we have now to consider the stereochemical aspects of the dihydroanthracene chemistry. The 9,10-di-*n*-propyl-9,10-dihydroanthracene which we isolate upon reductive alkylation of anthracene possesses a *cis* configuration of the substituents[28]. Particularly characteristic in the ^{13}C-NMR spectrum of **3** are the resonances of C-1 and C-2 at δ 128.7 and δ 125.8, respectively; the data closely correspond to those of the 9,10-diethyl analogue (δ 128.6, δ 125.7) whose *cis* configuration has been convincingly established by Rabideau[10]. For the latter case a *trans* substitution is known to cause a significant high-field shift of the signal of C-1. When 9,10-dihydroanthracene is subjected to deprotonation/alkylation processes with *n*-butyllithium and 1-bromopropane at −78 °C (see Section 2) we obtain a reaction mixture which according to its NMR spectra contains neither tri- nor tetrapropyl derivatives, but is composed of two stereoisomeric 9,10-dialkyl derivatives which differ in the configuration of the propyl groups. The *cis* isomer, which may be identified by comparison with an authentic sample of **3**, is the major component (6:1). In addition to the above ^{13}C-NMR spectra one can make use of the fact that the methine proton 9-H of the *cis* isomer resonates upfield ($\Delta\delta_H = 0.16$) with respect to that of the *trans* analogue[28].

The alkyl substituent at C-9 of the tetrahydrodianthrylpropane **9** can be positioned either axial or equatorial with respect to the boat-shaped six-membered 1,4-cyclohexadiene rings of the two dihydroanthracene moieties. The preferential conformation, i. e. the actual position of the alkyl substituent at C-9, could be determined by NOE-difference measurements[7,8]. As is obvious from Figure 1, saturation of the aromatic protons resonating at δ 7.23 causes a significant increase of the signal intensity of H_e (δ 3.81) and only a slight increase of that of H_a. Saturation at δ 7.12 strongly increases the intensity of H_m at δ 3.83. It follows that H_e and H_m are positioned within the plane of the benzenoid π systems. Correspondingly, a NOESY experiment[33] (puls sequence $90-\tau-90-\tau-90$) provides cross-peaks between the methine proton H_m (triplet at δ 3.83) and the aryl protons (multiplet at δ 7.12) and also between methylene proton H_e (doublet at δ 3.81) and the aryl protons (multiplet at δ 7.23). This is only possible when the alkyl substituent is in an axial position.

When proceeding from **9** to its dipropyl derivative **13** one is again faced with a problem of configurational isomerism. Similar to the situation in **3** and its *trans* isomer, the alkyl substituents at C-9 and C-10 can be either *cis* or *trans* so that, in principle, **13** could exist in three different forms. In the ^{1}H-NMR spectrum of the isolated compound **13** the methine protons at C-9 and C-10 give rise to two overlapping triplet signals at δ 3.91. This should be contrasted to the fact that in the related compound **9** proton H_a resonates downfield from H_e by $\Delta\delta_{a,e} = 0.23$. The failure to detect the (downfield) resonance of an axial methine proton in the spectrum of **13** points toward a *cis*-diaxial arrangement of the substituents at C-9 and C-10 in both dihydroanthracene subunits. This is supported by NOE-difference measurements. If one irradiates with the frequency of the aromatic multiplet at δ 7.24, the two overlapping triplets of the methine protons appear in a quite similar fashion as without irradiation. One concludes, that the methine protons are hence positioned close to the aromatic protons and adopt an equatorial position.

The crude reaction product obtained upon alkylation of **9** gives rise to a ^{1}H-NMR spectrum whose methine signals (see Section 2) indicate the existence of (at least) two stereoisomeric dipropyl derivatives. While the major component is the *cis,cis* isomer, the downfield resonance of the methine protons in the minor component points toward an isomer with a *trans* configuration of the substituents in one (or two) of the dihydroanthracenes.

In view of these results it comes as no surprise heat the formation of the "tetramer" **15** by twofold deprotonation of **9** and subsequent alkylation with **7** produces a mixture of configurational isomers. The ^{13}C-NMR spectrum of the crude reaction product shows many more signals than expected for a single stereoisomer. In principle, **15** can exist in 3 isomeric forms depending on whether the configuration of the alkyl substituents at the two inner dihydroanthracene moieties is *cis* or *trans*. The observation of configurational isomerism for **15** does not come unexpectedly since in his studies directed toward the alkylation of 9-alkyl-9,10-dihy-

droanthracenes, Rabideau found a close relationship between the size of the alkyl group introduced and the configuration of the resulting 9,10-dialkyl product[7,11]. By column chromatography of the crude "tetramer" mixture we succeeded in isolating a pure isomer the ^{13}C-NMR resonances of which could be compared with those of the model compound **13** in order to ascertain stereochemical information.

In the pure isomer **15** the resonance of C-1′ within the two inner dihydroanthracene units appears at δ 128.8 and closely corresponds to that of the model system **3** with a *cis* configuration of the alkyl groups. Another significant finding is that the chemical shifts of C-11 (C-11′) and C-12 (C-12′) in the "tetramer" **15** and its model compound **13** are identical. We tentatively conclude that the pure stereoisomer of **15** possesses an *all-cis* configuration of the substituents.

It has been pointed out above that in the reductive polymerization to yield **4** and (after dehydrogenation) **5** the nature of the bridging group can be modified. Varying the chain lengths of the polymethylene linkage or introducing polyoxaethylene units can, indeed, influence the electronic interaction between the anthracene moieties[22,23]. On our way to polymer chains with unsaturated bridging groups – compounds **20** and **21** are typical examples – we considered the synthesis of **24** in analogy to that one of **9**. However, application of the electrophile **22** instead of 1,*n*-dihaloalkanes creates new problems. **22** is known to undergo base-induced deprotonation at the benzylic position; the resulting anion can then serve as a nucleophile and attack a second molecule of **22** and, thus, initiate a polymerization[34]. **22** is also prone to reductive 1,6-dehalogenation followed by polymerization[35,36]. Both polymerization reactions may, in principle, be initiated by the anion **6** which may function either as base or as reducing agent. Not surprisingly, therefore, formation of **24** proceeds in much better yield, when the quenching of **6** with **22** is performed in the reverse manner, i.e. when **6** is added to an excess of the electrophile. Thus, by keeping **6** at low concentration, the above side reactions can be more efficiently suppressed. Still another situation is encountered in the synthesis of the tetramethyl analogue **25** since introduction of the tertiary halide **23** is expected to slow down the S_N process with **6**. Quenching in a reverse mode affords a mixture of **1**, **2**, **27**, and **28**. Clearly, **1** and **27** originate from a redox reaction between **6** and **23**, and **28** is produced by an S_N reaction and by subsequent dehydrobromination. The reaction between **6** and **23** is dominated by an electron transfer. Thereby, the low concentration of **6** (reverse quenching) is further reduced so that a twofold S_N process can no more be achieved. Quenching in a normal mode seems to be more appropriate since compound **27**, the product of an oxidative coupling of **6**, is not formed under the conditions, and the desired product **25** can be isolated in 30% yield.

4. Conclusion

Deprotonation/alkylation reactions of 9,10-dihydroanthracene (**2**) afford a series of oligomeric (di-, tetra-, and hexanthryl) compounds which serve as model system for the structurally related polymer **4**. The successful prolongation of the linear structures is based on the fact that the "dimer" **9** and "tetramer" **15** can be regioselectively alkylated at the terminal methylene groups. While the novel mono- and oligomeric dihydroanthracenes serve as important models for understanding the structure and reactivity of the polymer **4**, an important difference in the methods of their formation should be noted. The oligomers are built up in a stepwise fashion by separate deprotonation and alkylation reactions. During the formation of the polymer **4** by reductive alkylation of **1** with 1,3-dibromopropane, both the carbanions and electrophiles are present simultaneously. As a consequence, the chain propagation can occur by different mechanisms and the chain structures can, in principle, be terminated by different groups.

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Experimental

Alkylation of Poly(9,10-dihydro-9,10-anthrylenetrimethylene) (**4**): 1.1 g of **4** with average molecular weight (M_n) of 1800 was dissolved in 50 ml THF. The solution was cooled to −78 °C and treated with 11 mmol of *n*-butyllithium (as a solution in 10 ml THF). The color of the polymer solution immediately changed to red. After stirring at −78 °C for 2 h, 11 mmol of 1-bromopropane was added dropwise over a period of 5 min. The mixture was allowed to stir for 5 min and quenched with water (2 ml). The solvent was evaporated under reduced pressure and the residue dissolved in $CHCl_3$ (50 ml) and water. The organic layer was washed several times with water and concentrated to 10 ml. The polymer was precipitated by the addition of methanol (200 ml). The white polymer powder was dried for 8 h under vacuum ($1 \cdot 10^{-2}$ mbar).

9,10-Dihydro-cis-9,10-di-n-propylanthracene (**3**): a) To a stirred solution of 0.18 g (26 mmol) of lithium and 250 ml of dry ammonia were added under argon atmosphere 1.7 g (10 mmol) of anthracene and 90 ml of THF. The resulting red-brown mixture was kept at −33 °C for 1 h. A solution of 2.5 g (20.3 mmol) of 1-bromopropane in 50 ml of THF was added dropwise over a period of 15 min. Upon the addition of the electrophile the color of the carbanion solution changed from red-brown to orange-yellow and finally faded. The reaction mixture was allowed to stir at −33 °C for 1 h and the ammonia was evaporated. THF was removed under reduced pressure and the residue dissolved in toluene/water. The organic layer was washed with water and dried over magnesium sulfate. The solvent was evaporated and the residue chromatographed over silica gel (L = 50 cm, ∅ = 3.5 cm, hexane). Recrystallisation of the eluted product from methanol yielded 1.80 g (68%) of white needles. – **3**: (68%); m.p. 66 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 and 7.20 (AA′BB′, 8H, 1,8-H), 3.89 (t, 2H, 9,10-H), 1.76 (m, 4H), 1.55 (m, 4H), 0.96 (t, 6H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.1 (C-4a,8a,9a,10a), 128.7 (C-1,4,5,8), 125.8 (C-2,3,6,7), 46.5 (C-9, 10), 44.8 (CH_2R), 21.7, 14.1 (CH_3). – MS (70 eV): m/z (%) = 264 (11, M^+), 221 (100), 178 (96).

$C_{20}H_{24}$ (264.4) Calcd. C 90.85 H 9.15
Found C 90.78 H 9.20

b) 3.6 g (20 mmol) of **2** in 250 ml of THF was treated with 12 mmol (8.6 ml) of *n*-butyllithium in hexane at −78 °C (under argon). The resultant red solution which was stirred for 1 h. 1.46 g (12 mmol) of *n*-propyl bromide in 10 ml of THF was added dropwise over a period of 10 min. After 5 min, the reaction sequence

was repeated another four times. The reaction mixture was quenched with water, and THF was removed under reduced pressure. The residue was dissolved in $CHCl_3/H_2O$, and the organic layer was washed with water, dried (Na_2SO_4), and evaporated to give 4.99 g (94%) of an amorphous solid, m.p. 63°C (spectroscopic characterization see above).

9-(3-Bromopropyl)-9,10-dihydroanthracene (**7**): A solution of 3.6 g (20 mmol) of 9,10-dihydroanthracene (**2**) in 250 ml of THF was mixed at −78°C under argon with 22.5 mmol (15 ml) of a solution of *n*-butyllithium in hexane. The formation of the monoanion could be detected by the deep red color. In order to complete the metallation reaction the mixture was kept at −78°C for 2 h. The solution of **6** was added dropwise over a period of 2 h to a vigorously stirred solution of 20.2 g (100 mmol) of 1,3-dibromopropane in 20 ml of THF at −20°C. After the addition was complete the THF and the excess of 1,3-dibromopropane were removed under reduced pressure. Water and chloroform were added to the residue. The organic layer was washed several times with water under an argon atmosphere and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue chromatographed over silica gel under an argon atmosphere (L = 50 cm, ∅ = 4.5 cm, light petroleum/$CHCl_3$, gradient 100−85%). The resulting colorless oil, 3.6 g (60%), crystallised on cooling. − **7**: (60%); m.p. 47°C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 to 7.20 (m, 8H, 1,8-H), 4.15 (d, 1H, 10-H), 3.94 (t, 1H, 9-H), 3.88 (d, 1H, 10-H), 3.32 (t, 2H, CH_2Br), 1.84 (m, 2H), 1.77 (m, 2H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.0 (C-8a,9a), 136.1 (C-4a,10a), 127.9 (C-1,4,5,8), 126.2 (C-2,3,7), 46.6 (C-9), 36.2, 35.2 (C-10), 33.4 (CH_2Br), 30.7. − MS (70 eV): *m/z* (%) = 301 (8.6), 300 (5.7), 299 (8.7), 180 (19), 179 (100), 178 (54).

$C_{17}H_{17}Br$ (301.2) Calcd. C 67.78 H 5.68 Br 26.53
Found C 67.96 H 5.70 Br 26.35

1,3-Bis(9,10-dihydro-9-anthryl)propane (**9**): To a solution of 3.6 g (20 mmol) of **2** in 250 ml of THF at −78°C was added 22.5 mmol (15 ml) of *n*-butyllithium in hexane within 1 min. The reaction mixture was allowed to stir at −78°C for 2 h, and a 0.5 M solution of 1,3-dibromopropane (4.5 g, 22 mmol) in THF was added dropwise over a period of 2 h. The solution was allowed to stir at −78°C for 30 min, then water was added (5 ml). The solution was concentrated under reduced pressure, and chloroform and water were added to the oily residue. The organic layer was washed with water and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue chromatographed over silica gel (L = 40 cm, ∅ = 4.5 cm, light petroleum/$CHCl_3$, 5:1). Recrystallisation of the eluted product from $CHCl_3$/methanol provided 3.2 g (80%) of **9** as white needles. − **9**: (80%); m.p. 138°C. − ^{1}H NMR (400 MHz, [D_8]THF): δ = 7.23 (m, 4H), 7.12 (m, 12H), 4.04 (d, 2H, 10-H), 3.83 (t, 2H, 9-H), 3.81 (d, 2H, 10.H), 1.57 (m, 4H), 1.32 (m, 2H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.6 (C-8a,9a), 136.1 (C-4a,10a), 127.9 and 127.8 (C-1,4,5,8), 126.1 and 126.0 (C-2,3,6,7), 47.1 (C-9), 37.0 (C-11), 35.2 (C-10), 25.2 (C-12).

1,3-Bis(9,10-dihydro-10-n-propyl-9-anthryl)propane (**13**): 5.5 mmol (4 ml) of *n*-butyllithium in hexane was added to a solution of 0.5 g (1.25 mmol) of **9** in 30 ml of THF at −78°C under argon. After stirring at −78°C for 2 h, 5 mmol of 1-bromopropane (0.25 M in THF) was added dropwise over a period of 2 h. The mixture was allowed to stir for 0.5 h and quenched with methanol. The solvent was removed under reduced pressure and the remaining oil chromatographed over silica gel (L = 60 cm, ∅ = 3 cm, light petroleum). A colorless oil was obtained which was subjected to a second purification by HPLC over silica gel. 266 mg (44%) of *cis,cis*-**13** and 47 mg (8%) of a 10-*n*-propyl derivative was thus obtained. − **13**: (44%); colorless oil. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30−7.20 (m, 16H, 1,8-H), 3.91 (m, 4H, 9,10-H), 1.78 (m, 8H), 1.55 (m, 6H), 0.98 (t, 6H, CH_3). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.3 and 140.0 (C-4a,8a,9a,10a), 128.8 (C-1,4,5,8), 125.9 (C-2,3,6,7), 46.5 and 46.4 (C-9,10), 44.9 (CH_2R), 42.3 (C-11), 27.2 (C-12), 21.7, 14.1 (CH_3). − FDMS: *m/z* (%) = 484 (100, M^+), 456 (30), 441 (25).

$C_{37}H_{40}$ (484.7) Calcd. C 91.68 H 8.32
Found C 91.41 H 8.37

"Tetramer" **15**: A solution of 1.1 g (2.75 mmol) of **9** in 100 ml of THF was treated under argon at −78°C with 5.5 mmol (5 ml) of *n*-butyllithium/hexane. The deep red reaction mixture was kept at −78°C for 3 h and then added dropwise to a solution of 1.66 g (5.5 mmol) of **7** in 30 ml of THF over a period of 45 min. After stirring at −78°C for 4 h, 1 ml of water was added and the solvent evaporated. Water and chloroform were added to the residue, and the organic layer was washed with water. The solvent was evaporated and the residue chromatographed over silica gel (L = 70 cm, ∅ = 3.5 cm, $CHCl_3$/hexane, 1:4, argon) to give 1.8 g (79%) of a colorless solid. Analysis by TLC indicates the presence of four compounds with very similar R_f values. The crude reaction mixture (1 g) was subjected to a second column chromatography (L = 80 cm, ∅ = 3 cm, silica gel, $CHCl_3$/hexane, gradient 1:5−1:4) to give 100 mg of a pure configuration isomer of **15**. − **15**: Crude mixture: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30−7.05 (m, 32H, 1−8-H, 1′−8′-H), 4.13 (d, 2H, 10-H), 3.95−3.70 (m, 8H, 9,10-H, 9′,10′-H), 2.10−1.20 (m, 18H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.60, 140.51, 139.87, 139.80, 139.64, 135.98, 135.94, 128.68, 128.62, 127.90, 127.86, 127.73, 127.69, 126.59, 126.08, 126.01, 125.96, 125.86, 47.13, 46.16, 46.04, 43.30, 43.19, 42.78, 42.18, 42.09, 37.65, 37.18, 35.25, 32.85, 32.75, 27.05, 26.08, 24.88, 24.82, 23.91.

Isolated isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30−7.10 (m, 32H, 1−8-H, 1′−8′-H), 4.15 (d, 2H, 10-H), 4.00−3.75 (m, 8H, 9,10-H, 9′,10′-H), 2.20−1.20 (m, 18H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.67 (C-8a,9a), 139.94 and 139.91 (C-4′a,8′a,9′a,10′a), 136.13 (C-4a,10a), 128.80 (C-1′,4′,5′,8′), 128.03 and 127.84 (C-1,4,5,8), 126.20 and 126.08 (C-2,3,6,7), 125.98 (C-2′,3′,6′,7′), 47.26 (C-9), 46.29 and 46.16 (C-9′,10′), 42.26 and 42.17 (C-11′,13′), 37.22 (C-11), 35.36 (C-10), 27.20 (C-12′), 26.22 (C-12′). − FDMS: *m/z* (%) = 840 (100), 660 (19).

$C_{65}H_{60}$ (841.2) Calcd. C 92.81 H 7.19
Found C 92.74 H 7.39

"Hexamer" **17**: A solution of 800 mg (0.95 mmol) of **15** (mixture of configurational isomers) in 100 ml of THF was subjected to twofold deprotonation with *n*-butyllithium and subsequent alkylation with **7** (THF) according to the procedure described for the formation of **15**. Aqueous workup and chromatography of the crude reaction mixture under argon (L = 80 cm, ∅ = 3.5 cm, silica gel, $CHCl_3$/hexane, gradient 1:5−1:4 afforded a fraction whose R_f value was sligthly smaller than that of **15**. Upon subsequent chromatography of the resulting material (300 mg) three fractions were eluted. From the second fraction a compound was obtained the ^{1}H-NMR spectrum of which is in accord with the structure of a "hexamer" **17**. The signals of the axial benzylic protons of the terminal methylene groups and of the other bisbenzylic protons exhibit the expected intensity ratio of 1:6. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45−7.0 (m, 48H, 1−8-H, 1′−8′-H), 4.15 (d, 2H, 10-H), 4.0−3.50 (m, 12H, 9,10-H, 9′,10′-H), 2.15−1.20 (m, 30H). − FDMS: *m/z* (%) = 1281 (25), 1061 (45), 841 (24), 840 (28), 620 (18), 400 (20), 180 (100).

9,10-Dihydro-9,9,10,10-tetra-n-propylanthracene (**19**): A mixture of 170 mg (0.65 mmol) of **3**, 3 mmol of *n*-butyllithium (2 ml of a 1.5 N solution in hexane), 3 ml of cyclohexane, and 3 ml of tetra-

methylethylenediamine was heated under reflux for 1 h. The solution was allowed to cool for 5 min, and 1.5 ml of a 2 M solution of 1-bromopropane and cyclohexane was added dropwise. The solvent was removed under vacuum, and water and chloroform were added. The organic layer was washed with 1 N hydrochloric acid and water. Evaporation of the solvent and chromatography of the oily residue over silica gel (L = 40 cm, $\varnothing$ = 2 cm, hexane) gave 59 mg of **19** as a colorless oil which was crystallized from chloroform/methanol to yield 90 mg (40%) of white crystals. – **19**: (40%); m.p. 176°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 and 7.21 (AA'BB', 8H, 1–8-H), 1.98 (t, 8H, CH_2R), 0.66 (m, 20H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.7 (C-4a,8a,9a,10a), 125.9 and 125.8 (C-1,8), 50.2 (CH_2R), 45.1 (C-9,10), 18.5, 14.6. – MS (70 eV): m/z (%) = 348 (4.6), 347 (13.7), 305 (100), 262 (28), 233 (26).

$C_{26}H_{36}$ (348.6) Calcd. C 89.59 H 10.41
Found C 89.47 H 10.58

α,α'-Bis(9,10-dihydro-9-anthryl)-p-xylene (**24**): From a solution of 3 g (17 mmol) of **2** in 200 ml of THF at –78°C under argon, the anion **6** was produced by the addition of 20 mmol (16.7 ml) of *n*-butyllithium in hexane. The solution was kept at –78°C for 3 h and added dropwise to a solution of 1.6 g (9 mmol) of α,α'-dichloro-*p*-xylene (**22**) in 50 ml of THF at –78°C over a period of 1.5 h. The reaction mixture was stirred for 1 h and quenched with water. The organic layer was washed with water and evaporated. Chromatography of the residue over silica gel (light petroleum/chloroform, 0–20%) gave 1.9 g (49%) of **24**. – **24**: Yield 49%, amorphous white crystals; m.p. 231°C. – ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ = 7.22 (d, 4H), 7.15 (q, 8H), 7.00 (d, 4H), 6.50 (s, 4H), 4.08 (t, 2H), 3.77 (AB, 4H), 2.81 (d, 4H). – ^{13}C NMR (100 MHz, $C_2D_2Cl_4$): δ = 139.60 (C-8a,9a), 137.09 (C-14a), 136.62 (C-4a,10a), 129.50 (C-11,14), 128.52 (C-4,5), 127.97 (C-1,8), 126.44 (C-3,6), 126.32 (C-2,7), 49.74 (C-9), 44.37 (C-10), 35.39 (CH_2).

$C_{36}H_{30}$ (462.6) Calcd. C 93.46 H 6.54
Found C 93.33 H 6.60

α,α'-Di(9-anthryl)-p-xylene (**26**): To a solution of 900 mg (1.9 mmol) of **24** in 25 ml of cyclohexane and 16 ml of tetramethylethylenediamine, 16 mmol (12.3 ml) of *n*-butyllithium in hexane was added. Heating to 90°C for 2 h gave rise to a deep violet suspension which was subjected to oxidation with 2.9 g (16 mmol) of cadmium chloride. Black cadmium was precipitated. The oxidation was complete when the violet color of the solution disappeared. Then the cadmium was dissolved by addition of 100 ml of 2 N hydrochloric acid. The organic layer was washed with hydrochloric acid and water. Evaporation of the solvent gave an amorphous light yellow solid residue which was recrystallized from toluene. – **26**: (80%); m.p. 266°C. – ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ = 8.33 (s, 2H), 8.12 (m, 4H), 7.95 (m, 4H), 7.38 (m, 8H), 6.91 (s, 4H), 4.82 (s, 4H). – ^{13}C NMR (100 MHz, $C_2D_2Cl_4$): δ = 138.69 (C-14a), 132.43 (C-9), 131.85 (C-8a,9a), 130.63 (C-4a,10a), 129.39 (C-11–14), 128.54 (C-4,5), 126.80 (C-10), 126.21 (C-1,8), 125.25 (C-3,6), 125.10 (C-2,8), 33.33 (CH_2).

$C_{36}H_{26}$ (458.6) Calcd. C 94.29 H 5.71
Found C 94.29 H 5.85

1,4-Bis[1-(9-anthryl)-1-methylethyl]benzene (**25**): a) Reverse quenching: A solution of **6** in 250 ml of THF was prepared from 3 g (17 mmol) of **2** as described above and added dropwise to a solution of 3.9 g (12 mmol) of **23** in 50 ml of THF at –20°C over a period of 1.5 h. The organic layer was washed with water and evaporated. Chromatography of the remaining solid residue over silica gel (light petroleum/chloroform, 0–30%) led to the isolation of *anthracene* (**1**), *dihydroanthracene* (**2**), *9,9',10,10'-tetrahydro-9,9'-bianthryl* (**27**), and *9,10-dihydro-9-(1-methyl-1-[4-(1-methylethenyl)-phenyl]ethyl)anthracene* (**28**). Analysis of the crude product by ^{1}H-NMR spectroscopy showed that the products **1**, **2**, **27**, and **28** were formed in a 2.3:4.1:2.5:1 ratio.

b) Normal quenching: 3.5 g (19 mmol) of **2** in 500 ml of THF were transformed into the anion **6** by deprotonation with *n*-butyllithium as described above. The solution of **6** was stirred at –78°C for 3 h. A solution of 3.8 g (12 mmol) of the dibromide **23** in 100 ml of THF was added dropwise over a period of 2 h. The organic layer was washed with water and evaporated. Chromatography of the residue over silica gel (light petroleum/chloroform, 0–30%) gave 1.5 g (30%) of **25** as white amorphous crystals. – **25**: (30%); m.p. 196°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18 (m, 8H), 7.08 (m, 4H), 6.99 (m, 4H), 6.82 (s, 4H), 4.10 (s, 2H), 3.58 (s, 4H), 1.26 (s, 12H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.91 (C-14a), 138.03 (C-8a,9a), 137.26 (C-4a,10a), 130.57 (C-11–14), 127.53 (C-4,5), 126.36 (C-1,8), 125.98 (C-3,6), 124.78 (C-2,7), 58.16 [$C(CH_3)_2$], 45.29 (C-9), 36.58 (C-10), 27.01 (CH_3).

$C_{40}H_{38}$ (518.7) Calcd. C 92.62 H 7.38
Found C 92.50 H 7.44

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1: 120-12-7 / **2**: 613-31-0 / **3**: 101905-40-2 / **4**: 113475-26-6 / **7**: 63820-36-0 / **9**: 63934-08-7 / **9** (10-*n*-propyl): 113475-17-5 / **13**: 113475-18-6 / **15**: 113475-19-7 / **17**: 113475-20-0 / **19**: 113475-21-1 / **22**: 623-25-6 / **23**: 35086-20-5 / **24**: 113475-22-2 / **25**: 113475-23-3 / **26**: 113475-24-4 / **27**: 10349-31-2 / **28**: 113475-25-5 / $Br(CH_2)_2CH_3$: 106-94-5 / $Br(CH_2)_3Br$: 109-64-8

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