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Synthesis of *n*-Alkyl-Substituted Perylenes and Terrylenes via Alkali-Metal Induced Cyclization of Oligonaphthylenes

Ute Anton, Christine Göltner, and Klaus Müllen*

Max-Planck-Institut für Polymerforschung,
Ackermannweg 10, W-6500 Mainz, F.R.G.

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The synthesis of two novel *n*-alkyl- or aryl-substituted perylenes and of an *n*-alkylated terrylene is possible by an alkali-metal induced cyclization of the corresponding bi- or trinaphthyls. Differences in reactivity of the naphthylenes in the ring-closure reaction are caused by the different substitution pattern. UV and fluorescence spectra as well as the stability of the resulting rylenes[2] are discussed as a function of substitution.

Perylene (**1**; $n = 0$; R = H) has been the subject of extensive chemical and physical research. As early as 1954, semiconducting charge-transfer complexes of perylene and bromine or iodine were reported[3]. Perylene derivatives such as Solvent Green or Indanthrene Red have found application as dyes for plastics or resins[4]. Due to their high fluorescence quantum yield and photostability, perylenes are employed in solar collectors and as fluorescence indicators[5].

Conceptually, perylene can be thought of as a central building block for larger, two-dimensionally fused π-systems. While there is appreciable chemical and physical interest in these compounds, research has been limited by the lack of selective and mild synthetic methods, as well as by the intractability of the products. Thus, an extension of the π-system in the "north-south" direction leads to quaterrylene (**1**; $n = 2$; R = H), which was originally prepared by Clar, starting from perylene, in a reaction with aluminum trichloride under drastic conditions[6]. A thorough characterization of the product was prevented by its insolubility and extremely high melting point (> 570°C). When enlarging the π-skeleton in the "east-west" direction, perylene can also serve as a precursor for coronene (**2**) synthesis. The latter has been prepared by the same author in a stepwise Diels-Alder addition of maleic anhydride, followed by decarboxylation and aromatization[7]. Although several investigations have been carried out with **2**, its solubility is still insufficient for many purposes.

Thus, for the synthesis and characterization of larger perylene compounds, the introduction of solubilizing groups is mandatory. In principle, substituted perylenes can be prepared by using two different approaches. One can substitute perylene itself, for instance in an electrophilic substitution, or one can build up the perylene skeleton from appropriate precursors, such as functionalized naphthalenes. For our syntheses, we have chosen the second method for several reasons: (i) the problem of regioisomerism is avoided, (ii) very mild cyclization conditions can be employed, and (iii) the reaction may be extended to the cyclization of appropriately substituted polynaphthylenes.

Using an alkali-metal induced cyclization of alkylated oligonaphthylenes, we have recently succeeded in preparing a homologous series of soluble rylenes (**1**; $n = 0-3$; R = *tert*-butyl)[8]. The homologs owe their solubility to the terminal *tert*-butyl substituents. With increasing size of the molecule, however, a sharp decrease in solubility is observed. Clearly, when considering a further extension in the "north-south" direction, the *peri*-positions of the rylene must remain unobstructed; this requires the inclusion of solubilizing groups in the sterically crowded, so-called *bay*-region of the molecule, as in the title compounds **9**–**11**.

In the case of the Diels-Alder addition, representing an "east-west" extension of the rylene frame, we have found that voluminous *tert*-butyl groups inhibit a reaction with dienophiles such as maleic anhydride, necessitating the introduction of solubilizing groups into the *peri*-position of the rylene as in **12**. The *n*-alkyl group seems to be an appropriate choice in both cases, since while sterically less demanding than the *tert*-butyl group, it should be stable under the cyclization conditions employed.

As part of our continued effort to synthesize extended π-systems, we present here the synthesis of two novel *n*-alkylated terrylenes and perylenes which may serve as building blocks toward larger, two-dimensionally fused aromatic systems. The influence of the position of the *n*-alkyl group on the tendency toward cyclization and of the stability of the resulting hydrocarbon is discussed.

Synthesis of Oligonaphthylenes 5–8

Synthesis of the β-alkyl naphthylenes **3a**[9] and **3b**[10] is accomplished by Ni(0)-induced coupling of 2-bromo-, or 2,6-dibromonaphthalene with *n*-hexylmagnesium bromide. Monobromination of **3a** with tetrachloromethane as solvent

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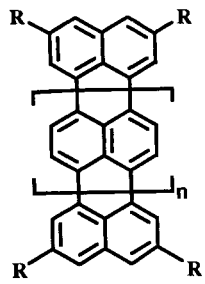

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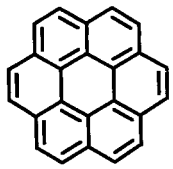

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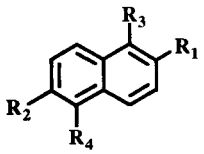
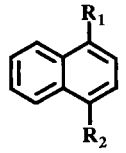


3a: $R_1=(CH_2)_5CH_3$; $R_2=R_3=R_4=H$

3b: $R_1=R_2=(CH_2)_5CH_3$; $R_3=R_4=H$

3c: $R_1=(CH_2)_5CH_3$; $R_3=Br$; $R_2=R_4=H$

3d: $R_1=R_2=(CH_2)_5CH_3$; $R_3=R_4=Br$

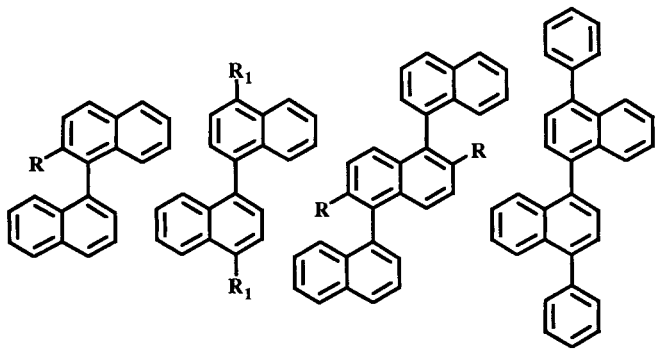


4a: $R_1=(CH_2)_4CH_3$; $R_2=H$

4b: $R_1=(CH_2)_4CH_3$; $R_2=Br$

4c: $R_1=(CH_2)_4CH_3$; $R_2=B(OH)_2$

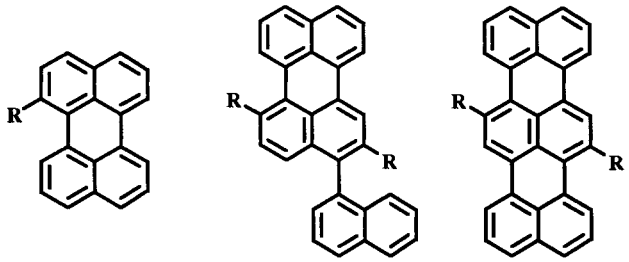
4d: $R_1=B(OH)_2$; $R_2=H$



5 **6** **7** **8**

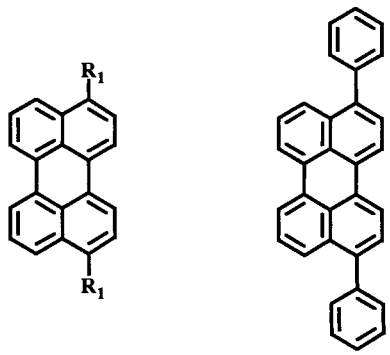
$R=(CH_2)_5CH_3$ $R_1=(CH_2)_4CH_3$

and a catalytic amount of iron turnings leads to **3c** in good yields[11], while dibromination of **3b** is carried out in acetic acid. The napthalene **4a**, which is *n*-alkylated in the α-position, is readily available by Friedel-Crafts acylation of naphthalene followed by Wolff-Kishner reduction of the ketone[12]. The monobromide **4b** is obtained as described above for **3a**[13]. For the formation of the oligonaphthylenes **5**–**8**, the transition-metal-catalyzed coupling of aryl boronic acids with aryl bromides according to Suzuki has proven to be highly efficient[14]. **4b** is transformed into the corresponding boronic acid by lithiation at −78 °C with *n*-butyllithium, followed by treatment with triisopropoxyborane. Similarly, **4d**[15] can be obtained from 1-bromonaphthalene. Preparation of the binaphthyls **5** and **6** is achieved by reacting an equivalent amount of the bromides **3c** or **4b** with the corresponding boronic acids **4d** or **4c** in a two-phase system consisting of boiling toluene and aqueous 2 N potassium carbonate under the influence of 1.5 mol-% tetrakis(triphenylphosphane)palladium(0). When carrying out the coupling reaction with a non-alkylated boronic acid, 1-butanol is added to the boiling reaction mixture, until the acid dissolves in the organic layer. The trinaphthyl **7** is obtained analogously by treating two equivalents of the monoboronic acid **4d** with **3d**. Compound **8** is obtained by coupling two equivalents of dihydroxyborylbenzene with 4,4′-dibromobinaphthyl[8].



9 **10** **11**

$R=(CH_2)_5CH_3$



12 **13**

$R_1=(CH_2)_4CH_3$

Anionic Cyclization

As in the preparation of the *tert*-butylated rylenes[8], an alkali-metal induced cyclization of the linearly connected naphthalenes to the two-dimensionally fused systems represents the key step in the synthetic sequence. Remarkably, treatment of **5** and **6**, respectively, with potassium in 1,2-dimethoxyethane at room temperature leads to quite different results. Reduction of the *peri*-substituted binaphthyl **6** occurs rapidly. Within a few minutes, the green color of the radical monoanion of the oligonaphthylene can be seen. After about two hours, the solution takes on the deep purple color of the perylene dianion. To complete the reaction, the solution is stirred overnight, and then the product is oxidized with anhydrous cadmium chloride. Recrystallization from *n*-heptane yields 82% of **12**. Recently, Vögtle et al. reported on the synthesis of 3,9-dimethylperylene using lithium powder as reducing agent in similarly high yields[16].

1-(*n*-Butyl)perylene was first prepared by Zieger and Rosenkranz in 1964 by alkylating perylene with *n*-butyllithium

at −30°C in THF[17]; other 1-*n*-alkylated perylenes have been prepared since by the same method[18]. Syntheses leading to 1-substituted perylenes which build up the perylene skeleton itself are only knwon in the case of 1,12-dihydroxyperylene, which is obtained in low yields when baking together β-dinaphthol in a sodium chloride/aluminum chloride melt at 170°C, followed by reduction of the quinone formed with zinc dust[19,20]. Thus, by employing an alkali-metal induced cyclization for the synthesis of *bay*-alkylated perylenes, a new synthetic route is presented, which can be extended to higher homologs.

Reduction of **5** with potassium is quite slow. The green color of the radical monoanion appears after several hours, but the deep violet color of the perylene dianion does not develop. After oxidation and chromatography over aluminium oxide, less than 5% of the desired cyclized product can be isolated. Moreover, no starting material is recovered. Apparently, due to the sterically crowded situation at the benzylic position, proton abstraction takes place, and side reactions such as solvent inclusion at this position predominate.

On the other hand, if one carries out the cyclization reaction at higher temperature using pyrophoric lithium powder, a clean reaction is observed. The preparation of perylene from 1,1′-binaphthyl using lithium was first mentioned by Gilman[21]. Later, this method was used to prepare tetramethylperylenes from the corresponding binaphthyls in yields of 36–40%[22]. After addition of lithium powder to a solution of **5** in 1,2-dimethoxyethane, a grey suspension results. Dimethoxyethane has been chosen instead of THF as solvent, because in the latter ether cleavage by lithium has been observed at elevated temperatures[23]. The reaction mixture is heated to 60–70°C, and after ten minutes a color change first to green and shortly afterwards to dark blue is observed. The reaction is allowed to proceed at this temperature for five hours and, after cooling to room temperature and filtering off the reducing agent, the anion is reoxidized by using cadmium chloride. Purification on aluminium oxide leads to the substituted perylene **9** in 30% yield next to unchanged starting material. It is important to note that, by using lithium, the cyclization reaction takes place in spite of the steric hindrance caused by the *n*-alkyl group. In a reduction, lithium has a greater tendency than potassium to form solvent-separated ion pairs, thus a different ion-pair structure may cause the different reactivities in this case.

To ascertain whether the facile cyclization of **6** is solely the result of a favorable geometry, or if the cyclization tendency is influenced by electronic factors as well, we synthesized the phenyl-substituted binaphtyl **8**. Here, the α-position of the naphthalene, which possesses a large AO coefficient in its frontier orbital, is replaced by an electron-withdrawing substituent. A comparison between **6**, which carries an electron-donating substituent, and **8** in the potassium-induced ring-closure reaction shows no differences in reactivity. In both cases, reduction is rapid, the reaction runs to completion in the same time, and the yields lie in the same range (82% for **12** and 90% for **13**). Thus, apparently, the ease of the ring-closure reaction is not influenced by electronic factors, and the comparatively low yields in the cyclization reactions of **9**–**11** can indeed be attributed to steric reasons.

The next higher homologue **7** is treated in a similar fashion. In the reductive treatment of **7** with lithium, naphthylperylene **10** can be isolated in 25% yield. The formation of small amounts of terrylene chromophores is also observed.

Cationic Cyclization

To arrive at the *n*-alkylated terrylene, the cationic cyclization conditions reported earlier are employed[8]. The naphthylperylene **10** is stirred under a nitrogen atmosphere with carbon disulfide as solvent and aluminium trichloride and cooper(II) chloride at room temperature. After eight hours, the blue charge-transfer complex formed is hydrolyzed with dilute aqueous ammonia. Work-up is conducted in the presence of a mild reducing agent. Recrystallization from acetone yields the *bay*-substituted terrylene **11** in 31% yield. Under the very mild conditions employed, no side reactions at the *n*-alkyl groups are observable.

Stability and Structure

Unsubstituted perylene is a planar, high melting, photochemically as well as thermally stable hydrocarbon. How do the different substitutions patterns affect the properties of the parent hydrocarbon? In **9**–**11**, the *bay* substituent causes a significant torsion in the rylene skeleton. An X-ray analysis of **11** shows the angle C(1)–C(16b)–C(16a)–C(16) to be 18°[24]. This deviation from planarity is reflected in the low melting points. Compound **9**, for example, melts at 63°C, while **10** does not crystallize at room temperature. Not surprisingly, the strain in the *bay* region causes a significant destabilization of the hydrocarbon. Decomposition of the rylene in solutions that have not been degassed, especially in the presence of UV light, is rapid. The decomposition is accompanied by a bleaching of the longest-wavelength absorption. Mass spectroscopic analysis of the products shows epoxide formation.

Recently, an X-ray structure of a charge-transfer complex of benzene and a perchlorinated perylene diimide was reported[25]. Torsional angles of 16 to 32° were found for the central perylene ring. In this case, the deviation from planarity is forced by the large chlorine substituents.

A comparison of the UV spectra of perylene and **9**, **12** and **13** shows that in the substituted perylenes, the absorption bands are less structured; the characteristic shape of the longest wavelength ^1L_a absorption, however, remains the same. In **9**, a small hypsochromic shift from λ_{max} = 435 (perylene) to λ_{max} = 427 [1-(*n*-butyl)perylene] of the longest wavelength absorption is observed, while **12** (λ_{max} = 452) and **13** (λ_{max} = 458) show a bathochromic shift relative to the unsubstituted hydrocarbon.

For the terrylene (**11**), the vibrational structure of the longest wavelength absorption is similar to that of the corresponding perylene as well as to that of the tetra-*tert*-butylated terrylene described in ref.[8]. λ_{max} of **11** is 535 nm,

about 30 nm hypsochromically shifted compared with the *tert*-butylated analog (λ_{max} = 568 nm). In both *n*-alkylated perylenes (**9** and **12**) and terrylene (**11**), the fluorescence spectra show a mirror-image symmetry to the longest-wavelength absorption and a small Stoke's shift indicating a negligible change in geometry when going from ground to first excited state. This lack of conformational mobility can be expected for rigid, planar hydrocarbons.

With the syntheses presented, the foundation stone has been laid for the construction of larger, two-dimensionally fused, soluble hydrocarbons. Using two different alkali-metal induced cyclizations, we have synthesized *n*-alkylated perylenes and terrylenes with different substitution patterns. The compounds **9**–**11** are substituted in the sterically crowded *bay*-region, leaving the *peri* positions accessible to an extension in the "north-south" direction. The substituent causes a significant torsion in the rylene, which, not surprisingly, affects the stability of the parent hydrocarbon. Compounds **12** and **13** carry their substituents in the *peri* positions, this time leaving the *bay* region unobstructed. Thus, the dienophilic character of this region makes Diels-Alder additions feasible.

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Experimental

^{1}H NMR: Varian Gemini 200 (200 MHz), Bruker AM 300 (300 MHz). – ^{13}C NMR: Varian Gemini 200 (50.32 MHz), Bruker AM 300 (75.48 MHz). – UV/Vis: Perkin-Elmer Lambda 9. – Fluorescence: Perkin-Elmer MPF 44A. – IR: Nicolet 320 FT-IR. – Melting points (uncorrected): Büchi melting point apparatus. – Thin-layer chromatography: (TLC): Ready-to-use silica gel 60 F_{254} plates (Merck). – Column chromatography: Silica gel, particle size 70–230 mesh (Merck, Geduran Si 60) or aluminium oxide (Merck, Geduran Al 90) with the eluents indicated.

1- and 2-Bromonaphthalene as well as benzeneboronic acid are commercially available, 1-dihydroxyborylnaphthalene[14], 2,6-dibromonaphthalene[26], 4,4′-dibromobinaphthyl[7], 1-pentylnaphthalene[11], and 4-bromo-1-pentylnaphthalene[12] were prepared according to the procedures reported.

2-(n-Hexyl)naphthalene (**3a**): A suspension of 2-bromonaphthalene (25 g, 0.12 mol) and 1.26 g (1 mol-%) of diphenylphosphinoethane-nickel(II) chloride in 300 ml of dry diethyl ether was cooled in an ice bath. To this suspension, 56 ml of a 2 N solution of *n*-hexylmagnesium bromide in diethyl ether was added during 1 h. During the addition, the catalyst went into solution while its color changed from red to yellow. The ice bath was removed and after an induction period of about half an h, the solution began to boil. To complete the reaction, the solution was refluxed for 15 h. Thereafter, the reaction mixture was again cooled with an ice bath and hydrolyzed with water followed by dilute aqueous hydrochloric acid. The layers were separated, the organic layer was dried with $MgSO_4$, filtered and the solvent evaporated. The crude product was distilled under vacuum; B.p. 97°C/10^{-2} Torr; yield: 23 g (92%) of **3a**. – ^{1}H NMR ($CDCl_3$): δ = 7.92–7.84 (m, 3H, aromatic H), 7.72 (s, 1H, aromatic H), 7.56–7.42 (m, 3H, aromatic H), 2.88 (t, *J* = 8 Hz, 2H, CH_2), 1.83 (t, *J* = 7 Hz, 2H, CH_2), 1.46–1.40 (m, 6H, CH_2), 1.02 (m, 3H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 140.6, 133.9, 132.1, 127.9, 127.8, 127.6, 126.4, 125.9, 125.1, 36.3, 32.9, 31.5, 29.2, 22.8, 14.3. – MS (70 eV), *m/z* (%): 212 (87) [M^+], 141 (100) [M^+ – C_5H_{11}], 155 (8) [M^+ – C_4H_9]. – IR (KBr): $\tilde{\nu}$ = 3052 cm^{-1}, 2956, 2627, 2869, 2856, 1508, 1465, 814, 744, 471.

2,6-Di(n-hexyl)naphthalene (**3b**): 10 g (23 mmol) of 2,6-dibromonaphthalene and 210 mg of diphenylphosphinoethane-nickel(II) chloride dissolved in 150 ml of dry diethyl ether were coupled as described above with 44 ml of a 2 N *n*-hexylmagnesium bromide solution in diethyl ether. The crude product was crystallized from ethanol, and 9 g (90%) of pure **3b** was obtained; m.p. 23–25°C. – ^{1}H NMR ($CDCl_3$): δ = 7.70 (d, *J* = 10 Hz, 2H, aromatic H), 7.29 (d, *J* = 10 Hz, 2H, aromatic H), 7.57 (s, 2H, aromatic H), 2.75 (t, *J* = 15 Hz, 4H, CH_2), 1.7 (m, 4H, CH_2), 1.33 (m, 8H, CH_2), 0.89 (t, *J* = 7 Hz, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 140.1, 132.7, 127.9, 127.8, 126.8, 36.7, 32.0, 29.6, 23.2, 14.7. – MS (70 eV), *m/z* (%): 296 (84) [M^+], 225 (100) [M^+ – C_5H_{11}], 154 (48) [M^+ – 2 C_2H_5], 141 [M^+ – C_6H_{13} – C_5H_{11}]. – IR (KBr): $\tilde{\nu}$ = 2962 cm^{-1}, 2953, 2917, 2870, 2849, 1608, 1470, 1462, 891, 870, 813, 718.

1-Bromo-2-(n-hexyl)naphthalene (**3c**): 10 g (47 mmol) of **3a** was dissolved in 60 ml of CCl_4. A solution of 2.41 ml (0.47 mol) of bromine in 10 ml of CCl_4 was added at 0–5°C by means of a dropping funnel over a period of 1 h. During the reaction, light was excluded. After stirring at low temperature for 2 h, the reaction mixture was hydrolyzed with dilute NaOH, the organic layer was separated, dried with $MgSO_4$ and filtered. After distillation (b.p. 121–125°C/10^{-2} Torr) 11.2 g (82%) of **3c** was obtained. – ^{1}H NMR ($CDCl_3$): δ = 8.41 (d, 2H, *J* = 8 Hz, aromatic H), 7.65–7.15 (m, 4H, aromatic H), 3.05 (t, *J* = 11 Hz, 2H, CH_2), 1.79 (m, 2H, CH_2), 1.43 (m, 4H, CH_2), 0.98 (t, *J* = 7 Hz, 3H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 140.6, 133.0, 132.7, 130.0 128.0, 127.8, 127.1, 126.7, 124.9, 123.2, 37.3, 32.0, 30.3, 29.0, 22.4, 19.1. – MS (70 eV), *m/z* (%): 292 (42) [M^+], 221 [M^+ – C_5H_{11}], 212 (11) [M^+ – Br], 141 (100) [M^+ – C_5H_{11} – Br]. – IR (KBr): $\tilde{\nu}$ = 3052 cm^{-1}, 2955, 2927, 2856, 1557, 1501, 1465, 1256, 812, 746, 529.

1,5-Dibromo-2,6-di-(n-hexyl)naphthalene (**3d**): A solution of 12 g of bromine in 50 ml of acetic acid was added during 1 h at room temperature to 10 g (34 mmol) of **3b** in 170 ml of acetic acid. During the addition, light was excluded. After stirring for 8 h, the dibromide was precipitated by adding 100 ml of water. The product was collected, washed with water followed by dilute aqueous sodium thiosulfate solution. Pure **3d** was obtained by recrystallization from $CHCl_3$/CH_3OH (90 ml/30 ml); yield: 5 g (37%) of **3d**; m.p. 63–65°C. – ^{1}H NMR ($CDCl_3$): δ = 8.25 (d, *J* = 10 Hz, 2H, aromatic H), 7.41 (d, *J* = 10 Hz, 2H, aromatic H) 2.89 (t, *J* = 16 Hz, 4H, CH_2), 1.69 (m, 4H, CH_2), 1.36 (m, 8H, CH_2), 0.91 (t, *J* = 7 Hz, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 140.8, 132.7, 129.7, 127.3, 123.9, 37.7, 32.2, 30.5, 29.6, 23.1, 14.5. – MS (70 eV), *m/z* (%): 454 (97) [M^+], 383 (92) [M^+ – C_5H_{11}], 374 (36) [M^+ – Br], 312 (20) [M^+ – 2 C_5H_{11}], 303 (100) [M^+ – C_5H_{11} – Br]. – IR (KBr): $\tilde{\nu}$ = 2952 cm^{-1}, 2921, 2882, 2858, 2849, 1477, 1462, 1331, 1213, 1143, 1113, 814, 730, 697.

$C_{22}H_{30}Br_2$ (454.4) Calcd. C 58.14 H 6.67 Br 35.18
Found C 57.64 H 6.48 Br 35.88

1-Dihydroxyboryl-4-(n-pentyl)naphthalene (**4c**): 11 g (40 mmol) of 1-bromo-4-(*n*-pentyl)naphthalene (**4b**) was dissolved in 100 ml of dry diethyl ether under nitrogen. The mixture was cooled to –78°C, and during 1 h 29.5 ml of a 1.6 N solution of *n*-butyllithium in *n*-hexane (47 mmol) was added. The resulting solution was transferred into a solution of 25 g (3 equiv.) of triisopropoxyborane in 250 ml of diethyl ether via a canula. The mixture was allowed to warm to room temperature and stirred overnight. Thereafter, the boronic acid ester formed was hydrolyzed with 300 ml of 2 N HCl. The layers were separated, the organic layer was washed with water, dried with $MgSO_4$, filtered and the solvent was evaporated. Finally,

20 ml of pentane and 50 ml of water were added to the crude product and the mixture was stirred for 12 h. The crystalline product was obtained by filtration. – ^{1}H NMR ([D$_6$]acetone): δ = 8.61–8.67 (m, 1H, aromatic H), 8.02–8.18 (m, 1H, aromatic H), 7.82 (d, J = 10 Hz, 1H, aromatic H), 7.40–7.54 (m, 2H, aromatic H), 7.33 (d, J = 10 Hz, 1H, aromatic H), 7.28 (s, 2H, OH), 3.08 (t, J = 8 Hz, 2H, CH_2), 1.65–1.82 (m, 2H, CH_2), 1.25–1.50 (m, 4H, CH_2). – ^{13}C NMR ([D$_6$]acetone): δ = 141.8, 138.2, 133.9, 133.1, 130.9, 126.4, 126.3, 125.1, 33.0, 31.7, 31.4, 23.6, 14.7.

$C_{15}H_{19}BO_2$ (242.0) Calcd. C 74.40 H 7.91
Found C 73.38 H 7.51

General Procedure 1. – Palladium-Catalyzed Coupling Reaction: All reactions were carried out under an inert atmosphere and in the dark. The coupling partners and 1.5 mol-% tetrakis-(triphenylphosphane)palladium(0) were suspended in the specified volume of toluene, then an aqueous 2 N solution of K_2CO_3 and, if specified, 1-butanol was added. The mixture was refluxed for 2 d. After cooling, the layers were separated, the organic layer was extracted several times with $CHCl_3$. The combined extracts were dried with $MgSO_4$, filtered and the solvent was removed. Chromatography on silica gel (petroleum ether) gave the purified products.

2-(n-Hexyl)-1,1'-binaphthyl (**5**): 5.82 g (20 mmol) of 1-Bromo-2-hexylnaphthalene (**3c**) and 4.3 g (25 mmol) of 1-dihydroxyborylnaphthalene (**4d**) as well as 485 mg of the catalyst were allowed to react in 20 ml of toluene, 20 ml of 2 N aqueous K_2CO_3 and 10 ml of 1-butanol according to the general procedure 1. Chromatography afforded **5** as a colorless oil; yield: 5.4 g (81%) of **5**. – ^{1}H NMR ($CDCl_3$): δ = 7.85 (m, 4H, aromatic H), 7.40 (m, 5H, aromatic H), 7.15 (m, 4H, aromatic H), 2.25 (m, 2H, CH_2), 1.36 (m, 2H, CH_2), 0.98 (m, 4H, CH_2), 0.62 (t, 3H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 139.3, 137.3, 135.7, 133.72, 132.0, 128.2, 127.8, 126.6, 126.4, 126.0, 125.9, 125.5, 124.9, 33.9, 31.5, 31.2, 29.1, 22.4, 14.0. – MS (70 eV), m/z (%): 338 (100) [M^+], 267 (77) [$M^+ - C_5H_{11}$], 252 [$M^+ - C_6H_{13}$]. – IR (KBr): $\tilde{\nu}$ = 3061 cm^{-1}, 2953, 2926, 2870, 2855, 1515, 1467, 1460, 810, 745.

$C_{26}H_{26}$ (338.5) Calcd. 338.2034 Found 338.2034 (MS)

4,4'-(n-Pentyl)-1,1'-binaphthyl (**6a**): 3.0 g (12.4 mmol) of **4c**, 3.6 g (13 mmol) of **4b** and 400 mg of the catalyst were allowed to react in 30 ml of toluene and 10 ml of 2 N aqueous K_2CO_3 according to the general procedure 1. Compound **6a** was obtained by chromatography (pentane) as white, soft crystals, yield: 3.5 g (71%) of **6a**, m.p. 56–57°C. – ^{1}H NMR ($CDCl_3$): δ = 8.17 (d, J = 10 Hz, 2H, aromatic H), 7.42–7.56 (m, 8H, aromatic H), 7.23–7.34 (m, 2H, aromatic H), 3.20 (t, J = 8 Hz, 4H, CH_2), 1.80–2.00 (m, 4H, CH_2), 1.40–1.64 (m, 8H, CH_2), 1.02 (t, J = 8 Hz, 6H, 2 CH_3). – ^{13}C NMR ($CDCl_3$): δ = 139.2, 137.6, 134.0, 132.5, 128.2, 128.1, 126.0, 125.9, 125.8, 124.6, 33.8, 32.7, 31.2, 23.2, 14.7. – MS (70 eV), m/z (%): 394 (100) [M^+], 337 (60) [$M^+ - C_4H_9$], 280 (16) [$M^+ - 2\ C_4H_9$].

$C_{30}H_{34}$ (397.4) Calcd. C 91.31 H 8.69
Found C 91.34 H 8.58

4,4'-Diphenyl-1,1'-binaphthyl (**6b**): 5.9 g (48 mmol) of phenylboronic acid and 8.2 g of 4,4'-dibromo-1,1'-binaphthyl were allowed to react in 30 ml of toluene, 10 ml of 2 N aqueous K_2CO_3 and 20 ml of butanol according to general procedure 1. Chromatography afforded 5.3 g of **6b** (65%); m.p. 185–187°C. – ^{1}H NMR ($CDCl_3$): δ = 8.04 (dd, J = 10 Hz, 2 Hz, 2H, aromatic H), 7.68–7.31 (m, 20H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 141.4, 140.2, 138.6, 133.8, 132.3, 130.7, 128.3, 127.9, 127.8, 127.0, 126.8, 126.4, 126.3. – MS (70 eV), m/z (%): 406 (100%) [M^+], 329 (26) [$M^+ - C_6H_6$], 202 (16) [$M^+/2$]. – IR (KBr): $\tilde{\nu}$ = 3031 cm^{-1}, 1510, 1381, 1096, 1029, 834, 705.

$C_{32}H_{22}$ (406.2) Calcd. 406.1707 Found 406.1722 (MS)

2',6'-Di-(n-hexyl)-1,1':5',1''-ternaphthyl (**7**): 4.0 g (8.8 mmol) of **3d**, 3.8 g (22 mmol) of **4d** and 280 mg of the catalyst were allowed to react in 20 ml of toluene, 20 ml of 2 N aqueous K_2CO_3 and 10 ml of 1-butanol according to the general procedure 1. Chromatography afforded **7** as a colorless oil, which crystallized upon standing; yield: 4.2 g (86%) of **7**; m.p. 154–156°C. – ^{1}H NMR ($CDCl_3$): δ = 8.00 (d, J = 8 Hz, 4H, aromatic H), 7.68–7.19 (m, 18H, aromatic H), 2.3 (m, 4H, CH_2), 1.40 (m, 4H, CH_2), 1.09 (m, 12H, CH_2), 0.74 (m, 6H, CH_3). – ^{13}C NMR ($CDCl_3$) δ = 138.7, 138.6, 138.2, 135.9, 134.2, 133.8, 132.5, 128.7, 128.7, 128.1, 128.0, 127.1, 126.8, 126.5, 126.4, 126.3 125.9, 34.2, 31.9, 31.6, 29.5, 22.8, 14.5. – MS (70 eV), m/z (%): 548 (100) [M^+], 477 (5) [$M^+ - C_5H_{11}$], 391 (19) [$M^+ - C_5H_{11} - C_6H_{13}$]. – IR (KBr): $\tilde{\nu}$ = 2952 cm^{-1}, 1920, 2848, 1544, 1456, 1376, 816, 784. – UV (cyclohexane): λ_{max} (lg ε) = 299 (4.71).

$C_{42}H_{44}$ (548.9) Calcd. C 91.90 H 8.10
Found C 91.86 H 8.04

General Procedure 2. – Potassium-Induced Cylizations: All reactions were carried out under argon and with rigorous exclusion of moisture. The starting material was placed into a Schlenk reaction flask and dissolved in absolute 1,2-dimethoxyethane. Potassium, which had been freed from its oxide layer, was cut into small pieces and added to the solution in an argon counterflow. The flask was closed, and the mixture was stirred at room temperature for 3 d.

3,10-Di(n-pentyl)perylene (**12**): 1.0 g (2.5 mmol) of **6** was treated with 1.0 g of potassium in 150 ml of 1,2-dimethoxyethane according to the general procedure 2. The potassium was removed and the formed dianionic species reoxidized by addition of 1.0 g of anhydrous $CdCl_2$. The mixture was stirred until the color of the solution remained constant. Thereafter, 10 g of aluminum oxide was added and the solvent was evaporated. After drying the residue under vacuum it was extracted with heptane to afford 820 mg (82%) of **12**; m.p. 145°C. – ^{1}H NMR ($CDCl_3$): δ = 8.21 (d, J = 10 Hz, 2H, aromatic H), 8.12 (d, J = 10 Hz, 2H, aromatic H), 7.88 (d, J = 10 Hz, 2H, aromatric H), 7.50 (dd, J = 10 Hz, 2H, aromatic H), 7.30 (d, J = 10 Hz, 2H, aromatic H), 3.00 (t, J = 8 Hz, 4H, CH_2), 1.70–1.88 (m, 4H, CH_2), 1.35–1.52 (m, 8H, CH_2), 0.95 (t, J = 8 Hz, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 138.9, 133.5, 132.5, 130.2, 127.2, 126.6, 124.2, 120.4, 120.3, 120.0, 33.8, 32.5, 30.7, 23.1, 14.5, – MS (70 eV), m/z (%): 392 (98) [M^+], 335 (92) [$M^+ - C_4H_9$], 278 (100) [$M^+ - 2\ C_4H_9$].

$C_{30}H_{32}$ (392.3) Calcd. 392.2495 Found 392.2504 (MS)

3,10-Diphenylperylene (**13**): 500 mg of **8** was treated with 500 mg of potassium in 50 ml of dimethoxyethane. After 3 d, the potassium was removed and 500 mg of anhydrous $CdCl_2$ was added. The mixture was stirred for 1 h at room temperature, then 8 g of aluminum oxide was added and the solvent evaporated. The residue was extracted with heptane to afford 460 mg (92%) of crystalline **13**; m.p. >300°C. – ^{1}H NMR ([D$_2$]tetrachloroethane): δ = 8.20–8.30 (m, 4H, aromatic H), 7.82 (d, J = 10 Hz, 2H, aromatic H), 7.49–7.57 (m, 14H, aromatic H). – MS (70 eV), m/z (%): 404 (100) [M^+], 326 (12) [$M^+ - C_6H_6$], 202 (22) [$M^+/2$].

$C_{32}H_{40}$ (404.2) Calcd. 404.1565 Found 404.1545 (MS)

General Procedure 3. – Lithium-Induced Cyclization: The entire reaction was carried out under purified argon and with rigorous exclusion of moisture. The compound to be cyclized and pyrophoric lithium powder (–325 mesh) were placed in a Schlenk reaction flask. After the addition of dry 1,2-dimethoxyethane, a reflux condenser was connected to the flask. The vigorously stirred mixture was heated to 60–70°C. After 5 h, the deep-colored solution was cooled to room temperature, filtered to remove excess lithium and

oxidized with anhydrous cadmium chloride. To complete the reaction, the mixture was stirred for 1 h. After filtration, the solution was concentrated to dryness and the residue was chromatographed on aluminum oxide.

1-(n-Hexyl)perylene (**9**): 420 mg (1.2 mmol) of **5**, 500 mg of lithium and 90 ml of 1,2-dimethoxyethane were allowed to react according to the general procedure 3. Pure **9** (121 mg, 30%) was obtained after chromatography with cyclohexane as eluent. – ^{1}H NMR ($CDCl_3$): δ = 8.20 (d, *J* = 8 Hz, 2H, aromatic H), 7.88 (d, *J* = 8 Hz, 1H, aromatic H), 7.64 (m, 4H, aromatic H), 7.46 (m, 4H, aromatic H), 3.15 (t, 2H, CH_2), 1.87 (m, 2H, CH_2), 1.43 (m, 4H, CH_2), 8.7 (t, 3H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 137.9, 134.1, 132.6, 131.0, 130.8, 130.6, 130.1, 129.7, 129.1, 126.7, 126.8, 126.5, 125.9, 125.7, 125.2, 125.1, 120.4, 119.6, 35.6, 31.3, 30.5, 29.1, 22.2, 13.1. – MS (70 eV), *m/z* (%): 336 (100) [M^+], 293 (26), [$M^+ - C_3H_7$], 265 (72) [$M^+ - C_5H_{11}$]. – IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 2826, 2910, 840, 825, 770. – UV (cyclohexane): λ_{max} (lg ε) = 427 (4.27).

$C_{26}H_{24}$ (336.2) Calcd. 336.1879 Found 336.1874 (MS)

1,5-Di-(n-hexyl)-4-(1'-naphthyl)perylene (**10**): 1.00 g (1.8 mmol) of **7**, 1 g of lithium powder and 150 ml of 1,2-dimethoxyethane were allowed to react according to the general procedure 3. After chromatography (cyclohexane/toluene, 7:3) 248 mg (25%) of **10** was isolated as a yellow oil. – ^{1}H NMR (CD_2Cl_2): δ = 8.30 (d, *J* = 8 Hz, 1H, aromatic H), 8.25 (s, 1H, aromatic H), 8.00 (dd, *J* = 8 Hz, 2 Hz, 2H, aromatic H), 7.9 (d, *J* = 8 Hz, 1H, aromatic H), 7.81 (m, 2H, aromatic H), 7.56 (m, 5H, aromatic H), 7.25 (m, 2H, aromatic H), 7.21 (d, *J* = 9 Hz, 1H, aromatic H), 6.92 (d, *J* = 9 Hz, 1H, aromatic H), 3.15 (t, 2H, CH_2), 2.41 (m, 2H, CH_2), 1.85 (m, 2H, CH_2), 1.48 (m, 2H, CH_2), 1.26 (m, 4H, CH_2), 1.08 (m, 4H, CH_2), 0.86 (m, 3H, CH_3), 0.74 (m, 3H, CH_3). – ^{13}C NMR ([D_8]THF): δ = 138.4, 137.1, 137.0, 135.2, 134.1, 133.7, 133.0, 132.5, 131.2, 130.9, 130.3, 130.1, 129.7, 129.0, 128.4, 127.8, 127.4, 127.3, 127.3, 127.2, 127.1, 127.0, 126.8, 126.7, 126.6, 126.3, 126.0, 125.9, 125.6, 125.4, 125.3, 125.3, 125.0, 124.4, 122.2, 119.5, 35.5, 35.1, 33.5, 31.4, 31.0, 30.9, 30.8, 30.7, 30.6, 29.2, 28.7, 22.3, 22.0, 13.2, 13.2, 13.1. – MS (70 eV), *m/z* (%): 546 (100) [M^+], 475 (11) [$M^+ - C_5H_{11}$], 390 (26) [$M^+ - C_{11}H_{24}$], 256 (11) [$M^+ - C_{21}H_{14}$]. – IR (KBr): λ = 3449 cm^{-1}, 2961, 2925, 2920, 1261, 1095, 1023, 802, 782, 768. – UV (dioxane): λ_{max} (lg ε) = 436 (4.26).

$C_{42}H_{42}$ (546.6) Calcd. 546.3286 Found 546.3280 (MS)

1,9-Di-(n-hexyl)terrylene (**11**): 100 mg (0.18 mmol) of the naphthylperylene **10** was dissolved in 15 ml of CS_2. To the resulting solution, 100 mg of $AlCl_3$ and 100 mg of $CuCl_2$ were added, and the mixture was stirred under argon at room temperature. After 8 h, the solvent was decanted, and the remaining charge-transfer complex was hydrolyzed with dilute aqueous NH_3 to which a small amount of $Na_2S_2O_4$ had been added. The suspension was extracted repeatedly with toluene, the combined extracts were dried with $MgSO_4$, filtered, and the solvent was removed. The residue was chromatographed on aluminum oxide. The starting material could be removed by using cyclohexane as the solvent. By increasing the polarity of the solvent (cyclohexane/toluene, 7:3), the product was isolated. Recrystallization from acetone gave 30 mg (31%) of **11**; m.p. 189–191 °C. – ^{1}H NMR (C_6D_6): δ = 8.19 (s, 2H, aromatic H), 8.15 (d, *J* = 8 Hz, 2H, aromatic H), 7.98 (d, *J* = 7 Hz, 2H, aromatic H), 7.60 (m, 4H, aromatic H), 7.42 (m, 4H, aromatic H), 3.18 (t, 4H, CH_2), 1.86 (m, 4H, CH_2), 1.35 (m, 8H, CH_2), 0.89 (m, 6H, CH_3). – ^{13}C NMR ([D_8]THF): δ = 138.8, 135.2, 132.1, 131.7, 130.5, 130.4, 130.0, 128.0, 127.7, 127.1, 127.0, 126.6, 126.49, 120.9, 36.9, 32.58, 31.9, 30.4, 23.5, 14.3. – MS (70 eV), *m/z* (%): 544 (100) [M^+], 473 [$M^+ - C_5H_{11}$], 400 [$M^+ - C_{10}H_{24}$], 388 [$M^+ - C_{11}H_{24}$]. – IR (KBr): $\tilde{\nu}$ = 2958 cm^{-1}, 2918, 2851, 1261, 1096, 1060, 1040, 1021, 828, 802, 769. – UV (cyclohexane): λ_{max} (lg ε) = 535 (4.79).

$C_{42}H_{40}$ (544.4) Calcd. 544.3130 Found 544.3125 (MS)

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