The Stereochemistry of the Trinaphthyl-Terrylene Conversion

Ute Anton, Martin Adam, Manfred Wagner, Zhou Qi-Lin, and Klaus Müllen*

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

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Alkylated terrylenes can be synthesized by a twofold cyclization of an appropriately substituted trinaphthyl[1,11]. In this paper, we consider a special case. The alkyl substitution in the starting material **1** strongly affects the interplanar angle between the naphthalene moieties. After cyclization, the substituents are positioned in the sterically crowded *bay* region of the title structure **2**. The influence of the steric strain on the reactivity of **1** and on the stability of the resulting hydrocarbon **2** is investigated. Special emphasis is placed on the crystal structures of **1** and **2**.

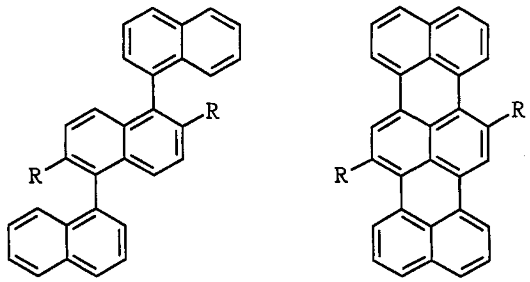
As part of our effort to synthesize larger, two-dimensionally fused π systems, we have recently reported on the synthesis of a novel *n*-hexylated terrylene **2a**[1]. The molecule carries its solubilizing substituents in the sterically crowded *bay* region and leaves the *peri* positions unobstructed. Thus, functionalization of the *peri* positions and a subsequent extension in this direction become possible. The synthesis of **2** proceeds by two cyclization steps of the corresponding trinaphthyl **1**.

To find out more about the steric hindrance induced by the alkyl groups during the cyclization reaction, as well as to understand the effect of the solubilizing group on the planarity of the resulting rylene[2], we have attempted to grow single crystals of **1** and **2**. While the *n*-hexyl group in **1a** and **2a** has a significant solubilizing effect on the parent hydrocarbon, it impedes crystallization; the ethylated analogs **1b** and **2b**, however, readily undergo crystallization.

In this paper we present crystal structure analyses of two diastereomers of **1** as well as that of the *peri*-fused compound **2**. In both cases, a significant steric hindrance is induced by the *n*-alkyl groups causing, in the case of **1**, an unusually large interplanar angle compared with unsubstituted binaphthyl[8]. In the case of **2**, a significant torsion in the rylene skeleton is forced.

Results and Discussion

1 is synthesized by using the transition metal-catalyzed coupling of 1,5-dibromo-2,6-dialkylnaphthalene with 1-(dihydroxyboryl)naphthalene in the presence of tetrakis(triphenylphosphane)palladium(0) as catalyst[3]. The formation of **2** proceeds by two subsequent cyclization steps of the corresponding trinaphthyl **1**. An anionic cyclization of **1** using pyrophoric lithium powder in boiling 1,2-dimethoxyethane leads to the corresponding naphthylperylenes, which are then cyclized to the alkylated terrylenes **2**. This second cyclization is carried out by using a mixture of *aluminium trichloride and* copper(II) chloride. Compared with the alkali metal-induced cyclization of other substituted oligonaphthylenes, **1** shows a significantly reduced reactivity, and the yield of the reaction product is lower[1,4,5]. The steric hindrance induced by the alkyl groups may well be the cause of the trinaphthyl's reluctance to undergo cyclization.



1a: R = $(CH_2)_5CH_3$ 2a: R = $(CH_2)_5CH_3$

1b: R = CH_2CH_3 2b: R = CH_2CH_3

Trinaphthyl **1** possesses two elements of axial chirality, thus, next to a pair of enantiomers of configuration (*R,R*) and (*S,S*), a *meso* form may exist. Recently, Hayashi et al. reported on the synthesis of two methyl-substituted trinaphthyls[6]. The synthesis was carried out by using a chiral nickel catalyst with a ferrocenylphosphane ligand. By this method, optically active trinaphthyls were synthesized in over 95% ee. In the synthesis of **1**, no chiral catalyst is used; thus, a mixture of racemic and *meso* forms is expected.

In the ^{13}C-NMR spectrum of **1a** a doubling of certain resonance signals in the aromatic region is observed (see Figure 1a). A double-resonance experiment (DEPT) shows 8 different absorptions of quaternary and 13 of tertiary aromatic carbon atoms (see Figure 1). Assuming a center of inversion in the central naphthalene moiety, we would expect just 6 quaternary and 9 tertiary carbon resonance lines. The larger number of signals must be attributed to the presence of the two diastereomeric forms in solution. A ^{13}C-NMR spectroscopic analysis of **1b** (see Figure 1b) shows just 13 different aromatic resonances, two of which are more intense, indicating that each of these signals is caused by two carbon atoms. No duplication

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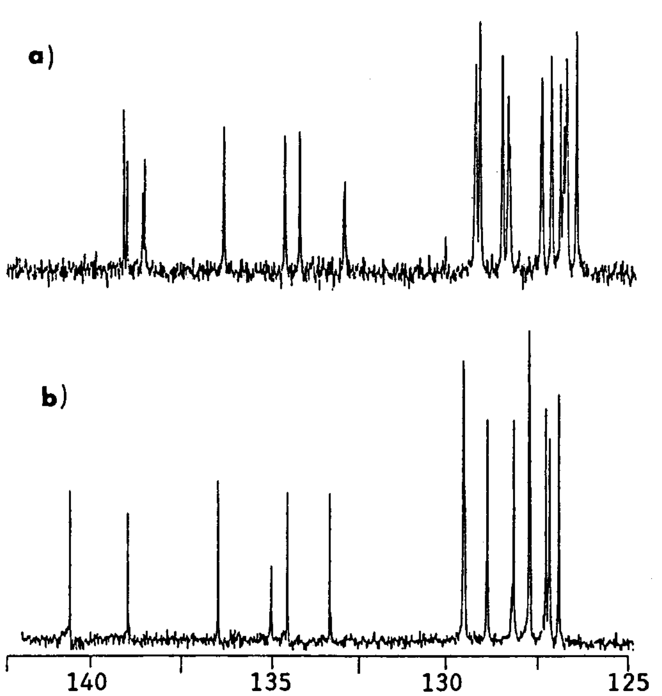

Figure 1. Aromatic region of the ^{13}C-NMR spectrum (125 MHz) of (a) **1a** and (b) **1b**. In both spectra, the resonances $\delta > 130$ result from quaternary carbon atoms, signals $\delta < 130$ from tertiary carbon atoms

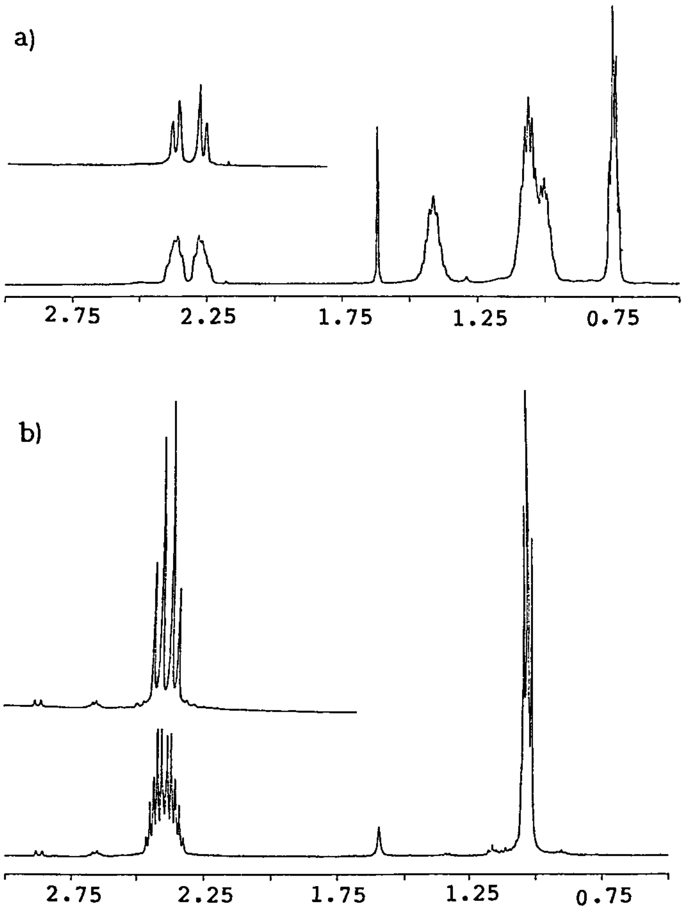

Figure 2. ^1H-NMR spectrum and decoupling experiment of the benzylic region of (a) **1a** and (b) **1b**

of signals is observable; thus, in this case the diastereomers cannot be distinguished.

In the ^1H-NMR spectrum, the benzylic protons of **1a** appear as two separate multiplets centered at $\delta = 2.29$ and 2.39, respectively, with an integration ratio of 1:1. The complex shape of the two multiplets is the result of the diastereotopicity of the benzylic CH_2 protons. For this phenomenon two interpretations are possible: (1) each multiplet is an AB spin system stemming from two diastereomers, which exist in a 1:1 ratio, or (2) the multiplets are the A and B part of an AB spin system, and the complex shape of each is due to the combination of a geminal and a vicinal coupling. To distinguish between the two possibilities, a homonuclear decoupling experiment is performed. Irradiation into the β-CH_2 group leads to two doublets (^2J = 1.04; see Figure 2a), as is expected for an AB spin system of diastereotopic benzylic protons. Thus, the second possibility (b) is correct, the two multiplets are the result of a geminal coupling of the benzylic CH_2 protons.

The benzylic protons of **1b** appear as one broad multiplet centered at $\delta = 2.31$. As above, a decoupling experiment is carried out (see Figure 2b). Irradiation into the lines of the neighboring CH_3 group again leads to two doublets, each with ^2J = 1.3 Hz.

In compound **1**, two centers of chirality exist, thus 2^n stereoisomers arise, an achiral *meso* form (*R,S* or *S,R* configuration at the chiral centers) and a pair of enantiomers. Studies on the racemization of optically active samples of 1,1′-binaphthyl gave an activation barrier of 92 kJ/mol[7] for the rotation of the naphthalene subunits, which interconverts the enantiomers. This value is high enough to allow the detection of the rotamers in solution at room temperature. In the trinaphthyls **1**, the naphthalene-naphthalene rotation should be rendered significantly more difficult by the *n*-alkyl group, thus it should certainly be slow on an NMR time-scale. The failure to detect the different isomers of **1b** NMR-spectroscopically must be attributed either to a coincidental isochromism of the signals or to the existence of just one rotamer in solution within the detection limits of the experiments.

Although the different atropisomers cannot be detected by NMR spectroscopy, crystallization affords single crystals of each diastereomer. They are easily distinguishable; while *meso*-**1b** crystallizes as monoclinic quasi-octahedra from ethyl acetate, the *d,l*-isomer can be obtained as prisms from benzene (Figure 3). *meso*-**1b** is located at a center of inversion, and the naphthalene subunits are planar within the limits of error. The dihedral angle between the central naphthalene system and its neighbors is 98°, which is considerably larger than the value of 68.6° found in the crystal structure of a racemic mixture of 1,1′-binaphthyl[8]. A much larger interplanar angle of 103° is reported from a crystal structure analysis of optically active 1,1′-binaphthyl[9]. The angle of 98° found in this work indicates a complete electronic decoupling of the naphthalene rings. For this reason, the length of the C(1)–C(11) bond (1.54 Å) corresponds to that of a single bond.

The racemic form of **1b** also crystallizes in a monoclinic crystal system, however, the molecule loses its center of inversion. The dihedral angle between the central and terminal naphthalene perimeters are 106 and 93°, respectively. Furthermore, the central naphthalene system becomes non-pla-

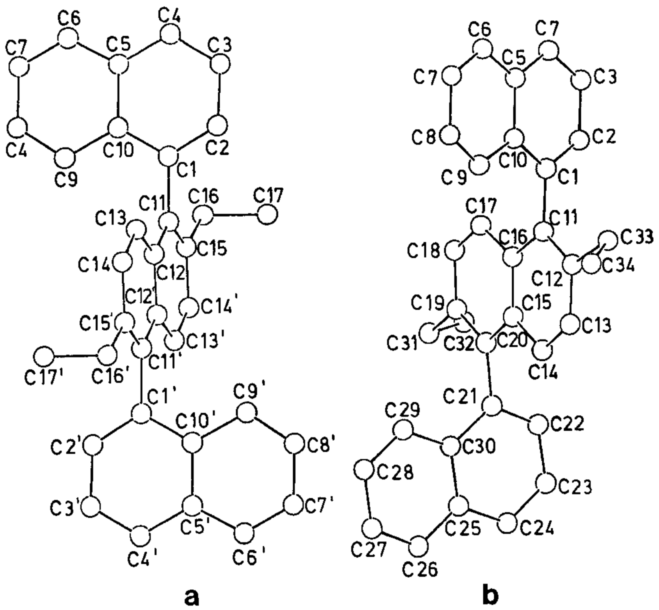

Figure 3. Crystal structure of (a) *meso*-**1b** and (b) enantiomeric **1b**. The numbering scheme in the figure is not in accordance with IUPAC nomenclature

nar, due to the increase in steric hindrance induced by the naphthyl groups.

Using a MOMO molecular mechanics program[10], we have calculated the local minima in **1b** by allowing the energy of several different trial structures to minimize. The experimental and calculated bond angles for the chiral isomer of **1b** are in good agreement. For *meso*-**1b**, the calculated and experimentally determined dihedral angles C(2)−C(1)−C(11)−C(15) differ somewhat. The steric energy[16] calculated for the two atropic isomers is 180 kJ/mol for the chiral isomer and 187 kJ/mol in the case of *meso*-**1b**.

Table 1. Calculated and experimentally determined interplanar angles in **1b**

	meso	
angle	X-ray	calculated
C(2)-C(1)-C(11)-C(15)	98	83
C(2')-C(1')-C(11')-C(15')	98	96
	chiral	
angle	X-ray	calculated
C(2)-C(1)-C(11)-C(12)	93	98
C(22)-C(21)-C(20)-C(19)	106	104

As mentioned above, **2** is formed from **1** in two steps. Neither the large angle between the naphthalene moieties in **1** nor the alkyl substituents prevent the ring-closure reaction. The terrylene derivative **2b** crystallizes from benzene, and, as *meso*-**1b**, it is located at a center of inversion (see Figure 4). Because of the ethyl substituents in the *bay* region of **2b**, the terrylene skeleton significantly deviates from planarity. Using least square planes for the central naphthalene subunit as well as for the outer rings, we observe a dihedral angle of nearly 18°. For this reason, the bond length between the naphthalene segments is increased to 1.47 Å.

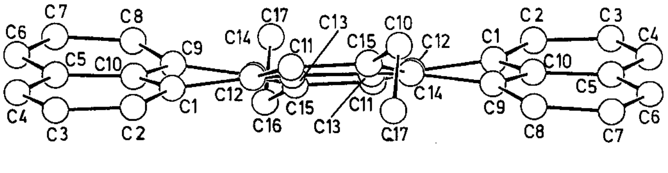

Figure 4. Crystal structure of **2b**

The strain on the system, induced by the alkyl group, is also reflected in the UV absorption spectrum of **2b**. The vibronic structure of the longest wavelength ^1L_a absorption, characterized by four equidistant bands separated by 1400 cm^{-1}, is typical for the rylene series[11]. However, λ_{max} of **2b** is 535 nm, i.e. hypsochromically shifted by about 20 nm compared with 2,4,10,12-tetra-*tert*-butylterrylene[11]. This hypsochromic shift again reflects the out-of-plane distortion in the aromatic frame, which leads to a slight reduction in the overlap of the π orbitals.

The crystal structure of unsubstituted terrylene is unknown, but should be similar to the known structures of perylene[12] and quaterrylene[13]. Both crystallize in a sandwich herringbone structure. From this information, Desiraju and Gavezzotti predicted that unsubstituted terrylene adopts a sandwich packing in the space group $P2_1/a$[14]. Our terrylene derivative does not exhibit a sandwich packing, but crystallizes along the *c* axis in a crosswise manner due to the twofold axis.

Experimental

^{1}H NMR: Varian Gemini 200 (200 MHz), Bruker AM 300 (300 MHz), Bruker AMX 500 (500 MHz). − ^{13}C NMR: Varian Gemini 200 (50 MHz), Bruker AM 300 (75 MHz), Bruker AMX 500 (125 MHz); all spectra were recorded at room temperature. − 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): 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. − **1a** and **2a** were prepared as reported previously[1]. The synthesis of 2,6-diethylnaphthalene is described in ref.[15]

X-Ray Structure Analyses: The single crystals were measured on an Enraf Nonius CAD-4 diffractometer with Cu-K_α radiation, ω/2Θ technique. Lattice parameters were derived by least square refinement of the scattering angles of 25 reflections. During the measurement, three standard reflections were measured every 8000 s. All structures were solved by direct methods (MULTAN). H atoms were placed into their computed positions by using known geometries (C−H distance 0.95 Å) and were refined in the riding mode with isotropic temperature coefficients. Empirical absorption corrections were applied. During the last full-matrix refinement, anisotropic temperature coefficients were calculated for the carbon atoms. Crystallographic data and positional parameters see Tables 2–5.

Table 2. Crystallographic data for compound **1b** (*meso*), **1b** (chiral), and **2b**[a]

Compound	**1b** (*meso*)	**1b** (*chiral*)	**2b**
Formula	$C_{34}H_{28}$	$C_{34}H_{28}$	$C_{34}H_{24}$
Crystal size [mm^3]	0.25 × 0.25 × 0.3	0.32 × 0.25 × 0.48	0.28 × 0.25 × 0.51
Space group	$P2_1/n$	$P2_1/n$	$C2/c$
a [Å]	8.290(4)	14.918(1)	24.098(2)
b [Å]	10.048(8)	7.8437(7)	6.442(2)
c [Å]	14.470(5)	20.835(2)	13.819(1)
β [°]	90.22(3)	90.909(6)	97.853(6)
V [$Å^3$]	1205(2)	2437(1)	2125(1)
Z	2	4	4
D_x [$g\ cm^{-3}$]	1.203	1.190	1.352
μ [cm^{-1}]	4.7	4.7	5.4
min. transmission	0.763	0.778	0.849
max. transmission	1.370	1.181	1.288
Θ_{max}	45	60	55
No. of reflections			
measured	1151	3919	1535
unique	955	3919	1413
observed [$I > 3\sigma(I)$]	711	2879	877
R	0.048	0.051	0.039
R_w	0.045	0.042	0.037
No. of parameters	210	419	202

[a] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-56552, the names of the authors, and the journal citation.

Table 3. Positional parameters and their estimated standard deviations of **1b** (*meso*). Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) \cdot [a^2 \cdot B(1,1) + b^2 \cdot B(2,2) + c^2 \cdot B(3,3) + ab(\cos\gamma) \cdot B(1,2) + ac(\cos\beta) \cdot B(1,3) + bc(\cos\alpha) \cdot B(2,3)]$

Atom	x	y	z	B (Å²)
C1	0.7889(6)	0.2346(5)	0.0039(4)	4.1(1)
C2	0.8117(7)	0.1368(5)	-0.0596(4)	4.8(1)
C3	0.7691(7)	0.0024(6)	-0.0449(4)	5.3(2)
C4	0.6988(7)	-0.0304(6)	0.0384(4)	5.5(2)
C5	0.6719(6)	0.0672(5)	0.1074(3)	3.9(1)
C6	0.5989(7)	0.0406(6)	0.1911(4)	5.8(2)
C7	0.5750(7)	0.1320(6)	0.2559(4)	6.3(2)
C8	0.6242(7)	0.2637(6)	0.2404(4)	4.9(1)
C9	0.6946(6)	0.3009(6)	0.1601(3)	3.7(1)
C10	0.7190(6)	0.2033(6)	0.0890(3)	3.9(1)
C11	0.8293(6)	0.3793(5)	-0.0180(3)	3.3(1)
C12	0.9789(6)	0.4340(4)	0.0124(3)	2.7(1)
C13	1.0886(6)	0.3608(5)	0.0666(3)	3.7(1)
C14	1.2316(6)	0.4159(5)	0.0949(4)	4.0(1)
C15	0.7241(6)	0.4528(5)	-0.0711(3)	3.2(1)
C16	0.5644(6)	0.4000(5)	-0.1062(3)	4.2(1)
C17	0.5687(8)	0.3698(6)	-0.2085(4)	6.7(2)

1,5-Dibromo-2,6-diethylnaphthalene: 2,6-Diethylnaphthalene (6.44 g, 35 mmol) was suspended in 170 ml of acetic acid. To this suspension 12.8 g of bromine dissolved in 30 ml of acetic acid was added at room temp. over a period of 2 h. The reaction mixture was stirred overnight, then 200 ml of water was added. The crude product was separated by filtration and recrystallized from chloroform/methanol. Yield: 5.5 g (46%), m.p. 100–102°C. – ^1H NMR ($CDCl_3$): δ = 8.29 (d, J = 10 Hz, 2H, arom. H), 7.47 (d, J = 10 Hz, 2H, arom. H), 3.05 (q, 4H, CH_2), 1.35 (t, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 141.4, 132.1, 128.5, 127.0, 123.2, 30.5, 14.3. – MS (70 eV), m/z (%): 342 (89) [M^+], 327 (81) [$M^+ - CH_3$], 261 (13) [M^+ – Br], 152 (100) [M^+ – 2 Br – C_2H_5].

$C_{14}H_{14}Br_2$ (342.1)
Calcd. C 49.15 H 4.13 Br 46.72
Found C 48.87 H 4.03 Br 46.25

Table 4. Positional parameters and their estimated standard deviations of **1b** (chiral). For B see Table 3

Atom	x	y	z	B (Å²)
C1	0.1858(2)	-0.0182(4)	0.3784(1)	4.33(6)
C2	0.2462(2)	-0.0510(4)	0.3315(1)	5.68(7)
C3	0.2216(2)	-0.1443(5)	0.2757(1)	7.38(9)
C4	0.1352(2)	-0.2029(5)	0.2682(1)	6.73(8)
C5	0.0713(2)	-0.1697(4)	0.3146(1)	4.82(6)
C6	-0.0187(2)	-0.2253(4)	0.3077(1)	5.73(7)
C7	-0.0815(2)	-0.1901(4)	0.3522(1)	6.09(7)
C8	-0.0567(2)	-0.0997(4)	0.4070(1)	5.58(7)
C9	0.0293(2)	-0.0454(4)	0.4168(1)	4.60(6)
C10	0.0968(2)	-0.0762(3)	0.3706(1)	4.13(5)
C11	0.2167(2)	0.0746(3)	0.4379(1)	3.95(5)
C12	0.1970(2)	0.2450(4)	0.4474(1)	4.45(6)
C13	0.2317(2)	0.3273(3)	0.5028(1)	4.65(6)
C14	0.2865(2)	0.2463(3)	0.5460(1)	4.26(5)
C15	0.3095(2)	0.0720(3)	0.5375(1)	3.59(5)
C16	0.2714(2)	-0.0146(3)	0.4837(1)	3.67(5)
C17	0.2911(2)	-0.1910(3)	0.4774(1)	4.12(5)
C18	0.3470(2)	-0.2706(3)	0.5197(1)	4.24(6)
C19	0.3882(2)	-0.1844(3)	0.5715(1)	3.93(5)
C20	0.3697(2)	-0.0138(3)	0.5804(1)	3.75(5)
C21	0.4156(2)	0.0855(3)	0.6329(1)	4.05(5)
C22	0.4939(2)	0.1700(4)	0.6200(1)	5.26(7)
C23	0.5392(2)	0.2643(4)	0.6681(2)	6.53(8)
C24	0.5061(2)	0.2721(4)	0.7288(2)	6.34(7)
C25	0.4256(2)	0.1880(3)	0.7441(1)	4.98(6)
C26	0.3887(2)	0.1949(4)	0.8063(1)	6.64(8)
C27	0.3110(2)	0.1122(4)	0.8201(1)	6.96(8)
C28	0.2653(2)	0.0207(4)	0.7725(1)	6.11(8)
C29	0.2983(2)	0.0109(4)	0.7116(1)	4.74(6)
C30	0.3791(2)	0.0937(3)	0.6956(1)	4.12(5)
C31	0.4537(2)	-0.2816(4)	0.6135(1)	4.96(6)
C32	0.5447(2)	-0.3025(5)	0.5821(2)	7.10(9)
C33	0.1431(2)	0.3516(4)	0.3993(1)	6.11(7)
C34	0.0648(2)	0.4364(5)	0.4297(2)	9.3(1)

Table 5. Positional parameters and their estimated standard deviations of **2b**. For B see Table 3

Atom	x	y	z	B (Å²)
C1	0.5502(1)	0.1069(5)	0.1130(2)	2.99(7)
C2	0.5364(1)	-0.0803(5)	0.1526(2)	3.49(7)
C3	0.5778(1)	-0.2191(5)	0.1931(2)	3.86(8)
C4	0.6334(1)	-0.1696(5)	0.1948(2)	3.92(8)
C5	0.6493(1)	0.0160(5)	0.1524(2)	3.31(7)
C6	0.7062(1)	0.0705(5)	0.1554(2)	3.91(8)
C7	0.7202(1)	0.2523(6)	0.1153(2)	4.11(8)
C8	0.6789(1)	0.3831(5)	0.0653(2)	3.62(8)
C9	0.6224(1)	0.3320(5)	0.0557(2)	2.94(7)
C10	0.6074(1)	0.1511(5)	0.1062(2)	2.94(7)
C11	0.4557(1)	0.2630(5)	0.1094(2)	3.22(7)
C12	0.5084(1)	0.2665(5)	0.0802(2)	2.84(7)
C13	0.5219(1)	0.4319(5)	0.0198(2)	2.73(6)
C14	0.5783(1)	0.4586(5)	-0.0014(2)	2.85(7)
C15	0.5875(1)	0.6015(5)	-0.0734(2)	3.02(7)
C16	0.6404(1)	0.6233(5)	-0.1213(2)	3.48(7)
C17	0.6747(1)	0.8182(6)	-0.0892(2)	4.29(8)

2′,6′-Diethyl-1,1′:5′,1″-trinaphthyl (**1b**): The reaction was carried out under argon. 1,5-Dibromo-2,6-diethylnaphthalene (4.1 g, 12 mmol), 1-(dihydroxyboryl)naphthalene (6.2 g, 30 mmol), and tetrakis(triphenylphosphane)palladium(0) (600 mg) were dissolved in a mixture of 40 ml of toluene, 20 ml of *n*-butanol, and 40 ml of 2 N aqueous K_2CO_3. The reaction mixture was refluxed for 2 d. After cooling, the layers were separated, and the organic layer was extracted several times with chloroform. The combined extracts were dried with $MgSO_4$, and the solvent was removed. Recrystallization from chloroform/ethanol (5:1) afforded 4.4 g (84%) of **2b** as colorless crystals, m.p. 244–247°C. – ^{1}H NMR ($CDCl_3$): δ = 7.98 (d, J = 10 Hz, 4H, arom. H), 7.65–7.20 (m, 18H, arom. H), 2.36 (m, 4H), 1.02 (t, J = 15 Hz, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 139.9, 138.1, 135.7, 134.2, 133.8, 132.4, 128.3, 128.0, 127.7, 127.1, 126.6, 126.1, 28.0, 16.1. – MS (70 eV), *m/z* (%): 436 (100) [M^+], 391 (26) [$M^+ - C_3H_8$]. – UV (cyclohexane): λ_{max} (lg ε) = 296 nm (4.28).

$C_{34}H_{28}$ (436.6) Calcd. C 93.52 H 6.48
Found C 93.09 H 6.36

1,5-Diethyl-4-(1-naphthyl)perylene: The entire reaction was carried out under argon and with rigorous exclusion of moisture. **1b** (872 mg, 2 mmol) and pyrophoric lithium powder (325 mesh, 1 g) were placed in a Schlenk reaction flask. After the addition of 80 ml of absol. 1,2-dimethoxyethane, a reflux condenser was connected to the flask. The vigrously stirred mixture was heated to 60–70°C. After 5 h, the deeply colored solution was cooled to room temp., filtered under argon to remove excess lithium powder, and oxidized with anhydrous $CdCl_2$. To complete the reaction, the mixture was stirred for 1 h. After filtration, the solution was evaporated to dryness and the residue chromatographed on aluminium oxide (cyclohexane/toluene, 7:3). Yield: 210 mg (24%) of yellow crystals. – ^{1}H NMR ([D$_6$]benzene): δ = 8.43 (s, 1H, arom. H), 8.18 (d, J = 10 Hz, arom. H), 7.94–7.76 (m, 4H, arom. H), 7.70–6.96 (m, 10H, arom. H), 3.02 (q, 2H, CH_2), 2.51 (m, 2H, CH_2), 1.60 (t, J = 15 Hz, CH_3), 1.07 (t, J = 13 Hz, CH_3). – ^{13}C NMR ([D$_6$]benzene): δ = 140.5, 139.1, 138.1, 135.8, 134.9, 134.5, 134.0, 133.9, 133.4, 132.3, 131.9, 131.5, 130.0, 129.5, 127.9, 127.5, 127.4, 127.3, 126.9, 126.7, 126.6, 126.5, 126.4, 125.9, 125.5, 122.5, 120.4, 120.4, 120.2, 29.0, 27.6, 16.0, 15.5. – MS (70 eV), *m/z* (%): 434 (100) [M^+], 390 (20) [$M^+ - C_3H_7$]. – UV (cyclohexane): λ_{max} (lg ε) = 441 nm (4.30).

$C_{34}H_{26}$ Calcd. 434.2034 Found 434.2030 (MS)

7,15-Diethylterrylene (**2b**): **1b** (66 mg, 0.15 mmol) was dissolved in 60 ml of CS_2. To the resulting solution 70 mg of aluminium trichloride and 70 mg of copper(II) chloride were added in one portion, and the mixture was stirred under argon at room temp. After 8 h, the solvent was decanted, and the remaining charge-transfer complex was hydrolyzed with dilute aqueous NH_3. The suspension was extracted repeatedly with toluene, the extracts were dried with $MgSO_4$, and the solvent was removed. The residue was chromatographed on aluminium oxide (cyclohexane/toluene, 10:3). After crystallization from benzene, 20 mg (31%) of **2b** was obtained, m.p. >250°C. – ^{1}H NMR ([D$_6$]benzene): δ = 8.16 (s, 2H, arom. H), 8.07 (s, 2H, arom. H), 7.92 (d, J = 2 Hz, 2H, arom. H), 7.55 (m, 4H, arom. H), 2.35 (q, 4H, CH_2), 0.83 (t, J = 15 Hz, 6H, CH_3). – MS (70 eV), *m/z* (%): 432 (84) [M^+], 388 (21) [$M^+ - C_3H_7$], 193 (100). – UV (cyclohexane): λ_{max} (lg ε) = 543 nm (4.84).

$C_{34}H_{24}$ Calcd. 432.1878 Found 432.1871 (MS)

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CAS Registry Numbers

1a: 143076-95-3 / **1b** (*meso*): 143790-91-4 / **1b** (*chiral*): 143790-94-7 / **2b**: 143790-93-6 / 1,5-Dibromo-2,6-diethylnaphthalene: 143790-90-3 / 2,6-Diethylnaphthalene: 59919-41-4 / 1-(Dihydroxyboryl)naphthalene: 13922-41-3 / 1,5-Diethyl-4-(1-naphthyl)perylene: 143790-92-5