A Soluble Benzodifluoranthene Derivative by Dehydration of an Oxygen-Bridged Precursor

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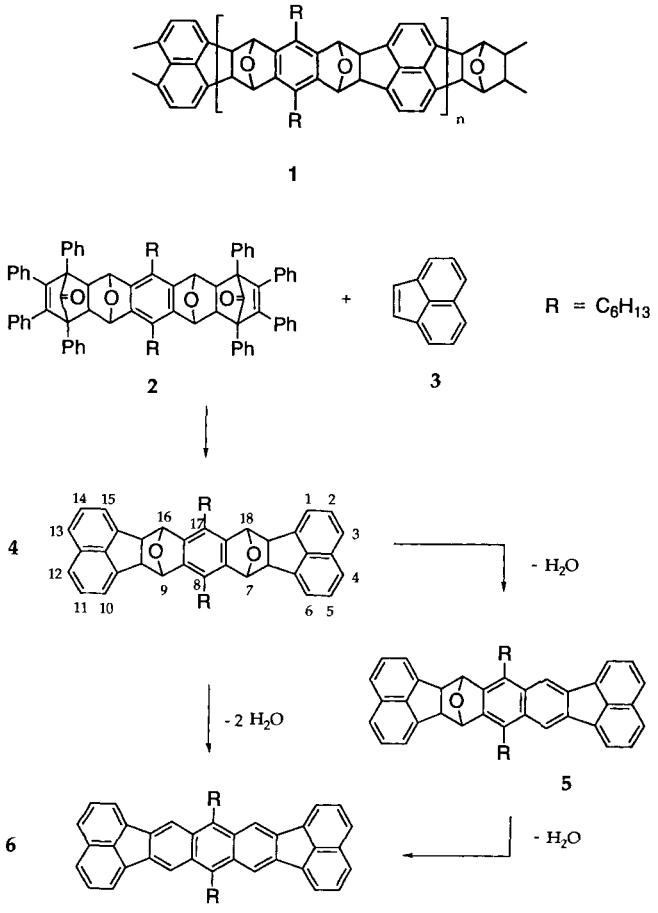
Synthesis and characterization of the alkyl chain-substituted benzodifluoranthene **6** are described. The final synthetic step involves an acid-promoted dehydration whose conversion is determined to be quantitative. The solubilities of compounds **4e**, **5**, and **6** are qualitatively correlated with structural features. The molecular structure of **6** in the crystal is elucidated by an X-ray structure analysis.

The dehydration of oxygen-bridged, partially unsaturated condensed hydrocarbons in one of the most often used methods for the synthesis of compounds with extended π conjugation. Linear, branched, and cyclic precursor molecules have been employed[1]. Dehydration reactions are commonly associated with a limited reproducibility as well as a limited predictability regarding the optimal reagent/reaction conditions. Yields almost never exceed 90%. We are involved in the synthesis of double-stranded (ladder) polymers using Diels-Alder (DA)-type chemistry[2]. A prime goal of this research is to convert these structurally perfect ladder polymers into their unsaturated counterparts, polymers which are of interest for materials science purposes. It seems to us that an endeavor like this is most likely to be accomplished if precursor polymers are used which have (a) already relatively large areas of unsaturation and (b) only oxygen bridges that are amenable to dehydration (no deoxygenation). From this point of view we consider a polymer like **1** a desirable synthetic objective. Since the synthesis of such a polymer requires a considerable effort we first carried out model studies specifically focussing on the question of to what extent dehydration of compounds, representing parts of **1**, can be achieved. In this paper we report on the synthesis of model compounds **4** and their dehydration including (a) a thorough determination of the conversions and (b) an investigation into their dependence on stereochemical features. Finally, we present an X-ray crystallographic structure determination of the benzodifluoranthene derivative **6**.



Compound **4** was obtained as a mixture of stereoisomers by heating the multicycle **2** to its decomposition temperature in the presence of two equivalents of acenaphthylene (**3**). In this reaction, **2** serves as a synthesis equivalent of benzo[1,2-*c*:4,5-*c'*]difuran[3]. Only four of the six possible stereoisomers were formed in the approximate, relative ratios (in % in parentheses) *endo/anti/endo*-**4** (**4a:** 1.5), *exo/anti/endo*-**4** (**4b:** 12.6), *exo/anti/exo*-**4** (**4c:** 1.6)[4], *endo/syn/endo*-**4** (**4d:** 0), *exo/syn/endo*-**4** (**4e:** 84.5), and *exo/syn/exo*-**4** (**4f:** 0)[4] in an overall yield of 84%. The isomers **4b**, **4c**, and **4e** were isolated by column chromatography. Unfortunately, we have not been able to isolate the remaining isomer. Table 1 contains selected ^{1}H-NMR shifts and coupling constants. The assignment was made by using the Karplus equation[5]

and on the basis of related work[6]. The most conclusive evidence is the fact that the coupling constants between adjacent protons in *exo*-configurated units are zero, whereas those of *endo*-configurated units are 3-4.3 Hz. This is in agreement with ball-and-stick models which show that the dihedral angle between two such protons of *exo*-units is close to 90°.

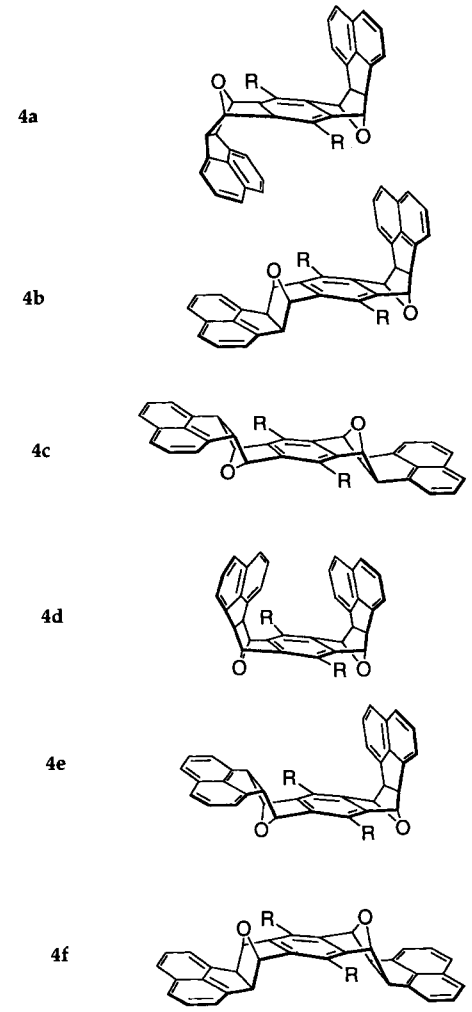


Figure 1. Stereoisomers of compound **4**

Table 1. Selected ^{1}H-NMR shifts and coupling constants [Hz] (in parentheses) of the stereoisomers of **4**

	9a-,15b-H	9-,16-H	7-,18-H	6b-,18a-H
4a	4.36 (3.0)	5.33 (3.6)	5.40 (3.6)	4.45 (3.0)
4b	3.55 (0)	5.00 (0)	5.82 (4.3)	4.60 (3.7)
4c	3.77 (0)	5.49 (0)	5.49 (0)	3.77 (0)
4e	2.58 (0)	5.05 (0)	5.82 (4.0)	4.60 (3.3)

The dehydration studies were carried out with the isomers **4b**, **4c**, and **4e**. The stereochemical features of these isomers are sufficiently different to find out whether there is a dependence of the dehydration reaction on the spatial condition in the vicinity of a given oxygen bridge. *para*-Toluenesulfonic acid (*p*-TsOH) was selected as the dehydrating agent because it allows the use of unpolar solvents like toluene which are necessary to keep the products in solution. This point is of prime importance for the desired polymer-analogous dehydrations. **4e** as the main isomer could easily be obtained on a 1-g scale and was therefore used for preparative scale dehydration studies. In a typical experiment a solution of **4e** and 2.5 equivalents of dehydrating agent were heated to reflux for 1–2 h. In a number of runs the dehydrated product, the benzodifluoranthene **6**, was obtained in isolated yields ranging from 97.5 to 98.6%. This very high yield was indicative of a complete conversion. The absolutely clean course of the dehydration was further proven in NMR-tube experiments employing all three isomers. They were heated to approx. 100°C in sealed NMR tubes in the presence of slightly higher than stoichiometric amounts of *p*-TsOH (2.3 equiv.). The reactions were monitored by ^{1}H-NMR spectroscopy (500 MHz). In all cases, the crude reaction mixtures did not even contain a trace of residual starting material and/or of a side product as judged by visual inspection. From these findings we draw the conclusion that the dehydration of all stereoisomers of **4** is an absolutely clean process, which makes it potentially useful for polymer-analogous applications.

Compared with parent benzodifluoranthene[7], compound **6** shows considerable solubility (see below) due to its substitution with flexible alkyl chains. This enabled a complete characterization of this compound (see Experimental) and allowed to determine the molecular structure in the crystal. The structure is planar, as we expected (Figure 2).

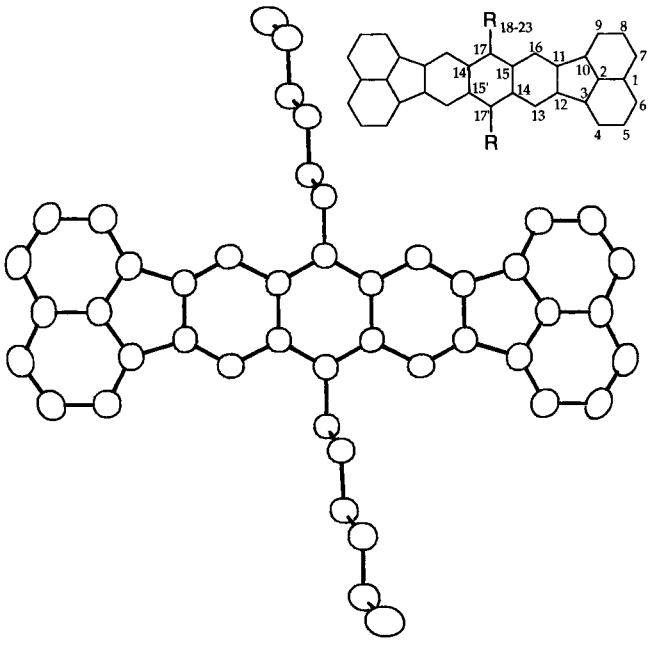


Figure 2. Structure in the crystal of compound **6** (ORTEP); selected bond lengths [Å]: C3–C12 1.474(4), C12–C13 1.352(4), C13–C14 1.435(4), C14–C17 1.406, C11–C12 1.444(4), C14–C15 1.451(4)

In the dehydration experiments it was qualitatively observed that the oxygen bridges of *endo*-configurated frag-

ments are removed significantly faster than of the *exo*-configurated ones, regardless of the relative orientation of the oxygen bridges (*syn* or *anti*). Thus, the reaction of **4b** or **4e** with, for example, 0.5 equivalents of *p*-TsOH gave to approx. 100% (NMR) the same monodehydrated product, the *exo*-configurated **5**. No starting material could be observed. If this selectivity holds true in the polymer-analogous case, it would allow a stepwise unfolding (aromatization) of the polymer and thus a more continuous generation of a double-stranded polymer with a fully conjugated backbone. Compound **5** was also synthesized on a preparative scale.

Finally, the solubilities of compounds **4e**, **5**, and **6** were determined quantitatively. The data show that the kinks in the structures, caused by the oxygen bridges and sites of saturation, lead to a remarkable increase in solubility (Table 2). Two kinks seem to exert a larger effect than one. Considering the significant drop in solubility on going from **4e** and **5** to **6** it becomes evident that one cannot expect a complete dehydration of polymer **1** resulting in the formation of a soluble material.

Table 2. Solubility data (±10%) of compounds **4e**, **5**, and **6** in chloroform at room temperature in g/l and mol/l

Compound	g/l	mol/l
4e	114	0.18
5	66	0.11
6	3.6	0.0065

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Experimental

All experiments were carried out under N_2. Compound **2** was prepared according to ref.[3]. The reaction time of the bromination step was reduced to 24 h by the addition of Fe powder. Commercial acenaphthylene (**3**) was purified by column chromatography. Only those ^{1}H-NMR data are listed that are not contained in Table 1. – Melting points: uncorrected. – UV: Beckmann DU-7 Spectrophotometer. – ^{1}H and ^{13}C NMR: Bruker WH 270/AC 500. – MS: Varian MAT 771 (80 eV). – Elemental analysis: Perkin-Elmer EA 240.

1. *Synthesis of* **4**

a) *8,17-Dihexyl-6b,7,9,9a,15b,16,18,18a-octahydro-7,18:9,16-diepoxybenzo[1,2-k:4,5,k']difluoranthene* (**4**, Mixture of Isomers): A suspension of 3.0 g (3 mmol) of **2** and 980 mg (6.4 mmol) of **3** was refluxed in dry toluene for 48 h. Tetraphenylbenzene that had formed during the reaction was removed by column chromatography (eluent: toluene). Yield: 1.58 g (84%).

b) *Separation of the Stereoisomers of* **4** was achieved by column chromatography on silica gel (eluent: toluene) and subsequent recrystallization from ethanol:

(6bα,7β,9β,9aβ,15bβ,16β,18β,18aα)-8,17-Dihexyl-6b,7,9,9a,15b,16,18,18a-octahydro-7,18:9,16-diepoxybenzo[1,2-k:4,5-k']difluoranthene (*exo/syn/endo*-**4e**): R_f = 0.2, m.p. 158–160°C. – ^{1}H NMR ($CDCl_3$): δ = 0.90 (t, 6H, CH_3), 1.20–1.68 (m, 16H, CH_2), 2.18 (mc, 2H, α-CH_2), 2.50 (mc, 2H, α-CH_2), 7.28 (m, 4H, 1-, 6-, 10-, 15-H), 7.45 (dd, 2H, 2-, 5-, 11-, 14-H), 7.59 (d, 2H, 3-, 4-, 12-, 13-H). – ^{13}C NMR ($CDCl_3$): δ = 144.0 (C-6a, -18b), 143.2 (C-9b, -15a), 142.1 (C-18c), 140.7 (C-15c), 127.7 (C-3a, -12a), 126.9 (C-2, -5, -11, -14), 124.5 (C-7a, -8a, -16a, -17a), 123.3 (C-3, -4, -12, -13), 123.0 (C-1, -6,-10, -15), 119.1 (C-8, -17), 83.0 (C-9, -16), 80.7 (C-7, -18), 77.4 (C-9a, -15b), 76.9 (C-6b, -18a). – MS, *m/z* (%): 630 (0.04) [M^+], 478 (29) [$M^+ - C_{12}H_8$], 326 (100) [$M^+ - C_{24}H_{16}$]. – $C_{46}H_{46}O_2$ (630.9): calcd. C 87.57, H 7.35; found C 87.15, H 7.35.

(6bα,7α,9β,9aβ,15bβ,16β,18α,18aα)-8,17-Dihexyl-6b,7,9,9a,15b,16,18,18a-octahydro-7,18:9,16-diepoxybenzo[1,2-k:4,5-k']difluoranthene (*exo/anti/endo*-**4b**): R_f = 0.25. – ^{1}H NMR ($CDCl_3$): δ = 0.90 (t, 6H, CH_3), 1.25–1.68 (m, 16H, CH_2), 2.28-2.58 (m, 4H, α-CH_2), 7.28 (m, 4H, 1-, 6-, 10-, 15-H), 7.45 (dd, 2H, 2-, 5-, 11-, 14-H), 7.59 (d, 2H, 3-, 4-, 12-, 13-H).

(6bα,7α,9α,9aβ,15bβ,16α,18α,18aα)-8,17-Dihexyl-6b,7,9,9a,15b,16,18,18a-octahydro-7,18:9,16-diepoxybenzo[1,2-k:4,5-k']difluoranthene (*exo/anti/exo*-**4c**): R_f = 0.42. – ^{1}H NMR ($CDCl_3$): δ = 0.95 (t, 6H, CH_3), 1.35–1.90 (m, 16H, CH_2), 2.80 (mc, 2H, α-CH_2), 2.93 (mc, 2H, α-CH_2), 7.28 (m, 4H, 1-, 6-, 10-, 15-H) 7.45 (dd, 2H, 2-, 5-, 11-, 14-H), 7.59 (d, 2H, 3-, 4-, 12-, 13-H).

2. *Dehydration Experiments*

a) *8,17-Dihexylbenzo[1,2-k:4,5-k']difluoranthene* (**6**): To 100 mg (0.15 mmol) of *exo/syn/endo*-**4e** in 100 ml of toluene was added 67 mg (0.375 mmol) of *p*-toluenesulfonic acid monohydrate, and the mixture was refluxed for 1 h. After cooling, the organic layer was washed with 20 ml of water to remove the acid and then dried ($MgSO_4$). Yield 92.6 mg of **6** (98%) as orange crystals. In order to get a realistic figure for the maximum yield, all filter papers and glassware were washed with toluene until the intensive green fluorescence of **6** could not be detected anymore. – UV (THF): λ_{max} = 490.5, 458.0, 431, 358, 342 nm. – ^{1}H NMR ($CDCl_3$): δ = 1.00 (t, 6H, CH_3), 1.61-1.33 (m, 8H, δ-, ε-CH_2), 1.75 (quint, 4H, γ-CH_2), 2.00 (quint, 4H, β-CH_2), 3.78 (t, 4H, α-CH_2), 7.70 (dd, J_1 = 7.5, J_2 = 8.0 Hz, 4H, 2-, 5-, 11-, 14-H), 7.85 (d, J = 8.0 Hz, 4H, 3-, 4-, 12-, 13-H), 8.10 (d, J = 8.0 Hz, 4H, 1-, 6-, 10-, 15-H), 8.78 (s, 4H, 7-, 9-, 16-, 18-H). – ^{13}C NMR ($CDCl_3$): δ = 137.2, 136.9, 136.5, 135.8, 130.7, 129.6, 128.3, 125.9, 118.6, 117.1, 31.8, 31.6, 30.0, 29.7, 28.7, 22.8. – MS (80 eV), *m/z* (%): 594 (100) [M^+], 523 (53) [$M^+ - C_5H_{11}$]. 451 (21) [$M^+ - 2\ C_5H_{11}$], 297 (12) [$M^+/2$]. – $C_{46}H_{42}$ (594.8): calcd. C 92.88, H 7.12; found C 92.40, H 7.07.

b) *8,17-Dihexyl-6b,7,18,18a-tetrahydro-7,18-epoxybenzo[1,2-k:4,5-k']difluoranthene* (**5**): To 200 mg (0.32 mmol) of **4e** in 100 ml of toluene was added 30 mg (0.15 mmol) of *p*-toluenesulfonic acid monohydrate, and the mixture was refluxed for 1 h. Workup as described for **6** and recrystallization afforded 178 mg (91%) of **5** as a yellow powder. Solutions of **5** showed a purple fluorescence. – UV (CH_2Cl_2): λ_{max} = 411, 388, 368, 314, 300, 272, 244 nm. – ^{1}H NMR ($CDCl_3$): δ = 0.95 (t, 6H, CH_3), 1.45–1.55 (m, 8H, δ, ε-CH_2), 1.65 (quint, 4H, γ-CH_2), 1.90 (m, 4H, β-CH_2), 3.28 (t, 4H, α-CH_2), 4.00 (s, 2H, 7-, 18-H), 5.62 (s, 2H, 6b-, 18a-H), 7.45–7.73 (m, 8H, arom.H), 7.85 (d, J = 8.5 Hz, 2H, 10-, 15-H), 8.10 (d, J = 8.0 Hz, 2H, 12-, 13-H), 8.78 (s, 2H, 9, 16-H). – MS (80 eV), *m/z* (%): 612 (1.2) [M^+], 594 (27) [$M^+ - H_2O$], 460 (100) [$M^+ - C_{12}H_8$].

3. *Solubility Measurements*

Procedure: A precisely determined volume (Hamilton syringe) of a chloroform solution of the compound under investigation (saturated at room temp.) was transferred into a weighed Eppendorf micro test tube. The solvent was removed, the cap fully dried and then weighed back. In several runs the accuracy of this method was found to be ±10%.

X-Ray Structure Determination of **6**[8]: Single crystals were grown from THF. Enraf Nonius CAD-4 diffractometer, room temperature, Cu-K_α radiation, $\lambda = 1.5405$ Å, graphite monochromator. The structure was solved by using direct methods (SIR). Empirical absorption correction, anisotropic temperature factors for O and C, refinement of the H atoms in the "riding mode" with fixed isotropic temperature factors: monoclinic, space group $P2_1/n$, $a = 21.190(1)$, $b = 5.1311(4)$, $c = 14.7738(7)$ Å, $\beta = 99.344(4)$, $V = 1585$ Å^3, $Z = 2$, $\varrho_{calcd.} = 1.247$ gcm^{-3}. 2275 reflections, 1511 observed [$I > 3\sigma(I)$], $R = 0.039$, $R_W = 0.038$.

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