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8,9-Didehydrofluoranthenes as Building Blocks for the Synthesis of Extended Polycyclic Aromatic Hydrocarbons (PAHs)

Wolf Dietrich Neudorff, Niels Schulte, Dieter Lentz, and A. Dieter Schlüter*

Institut für Chemie, Freie Universität Berlin, Takustrasse 3, D-14195 Berlin, Germany

adschlue@chemie.fu-berlin.de

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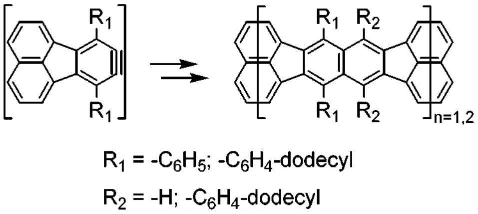
ABSTRACT



The synthesis of phenyl-substituted 8,9-dibromofluoranthene and *p*-dodecylphenyl-substituted 8,9-fluoranthene anthranilic acid is presented. Their synthetic potential as 8,9-didehydrofluoranthene precursors is demonstrated in combination with a new biscyclopentadienone by the synthesis of novel phenyl-substituted PAHs with up to 14 annulated rings. The crystal structure of 7,16-diphenylfluorantheno[8,9-*k*]fluoranthene is given.

Cyclopentene-fused polycyclic aromatic hydrocarbons (CPAH) of the fluoranthene type are a class of nonalternant polycyclic aromatic hydrocarbons (PAH) which have been of considerable interest because of their structural relationship[1] to the extensively investigated fullerenes[2] and because of their potential use in electroluminescent organic devices.[3] This interest is reflected in recent patent literature.[4] Phenyl substitution of some of these CPAHs is discussed in the context of organic quantum effect devices and organic ferromagnets.[5]

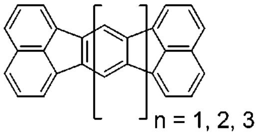


Figure 1. Homologous series of acenaphthene-capped fluoranthenes.

Much is known about acenaphtho[1,2-*k*]fluoranthenes ($n = 1$, Figure 1) and benzo[1,2-*k*:4,5-*k*′]difluoranthenes ($n = 3$), which have even been synthesized as completely aromatic ladder polymers by conventional Diels−Alder reactions[6] and

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[1] Schlüter, A. D.; Löffler, F.; Enkelmann, V. *Nature* **1994**, *368*, 831.

[2] *Fullerenes and Related Structures*; Hirsch, A., Ed.; Springer: Berlin, 1999; Vol. 199.

[3] Dicker, G.; Hohenau, A.; Graupner, W.; Tasch, S.; Graupner, M.; Hermetter, A.; Schlicke, B.; Schulte, N.; Schlüter, A. D.; Scherf, U.; Müllen, K.; Leising, G. *Synth. Met.* **1999**, *102*, 873. List, E. J. W.; Leising, G.; Schulte, N.; Schlüter, A. D.; Scherf, U.; Graupner, W. *Jpn. J. Appl. Phys.* **2000**, *239*, L760.

[4] Ikeda, H.; Hosokawa, C.; Arakane, T. WO 2001023496, 2001. Nakatsuka, M.; Kitamoto, N. JP 2000 07,594, 2000. Nakatsuka, M. Kitamoto, N. JP 11040360, 1999.

[5] Niemz, A.; Cuello, A.; Steffen, L. K.; Plummmer, B. F.; Rotello, V. M. *J. Am. Chem. Soc.* **2000**, *122*, 4798 and references therein.

[6] Schlüter, A. D.; Löffler, M.; Godt, A.; Blatter, K. Perfect Diels−Alder Ladder Polymers: Precursor for Extended π-Conjugation. In *Desk Reference of Functional Polymers Synthesis and Application*; Arshady, R., Ed.; American Chenical Society: Washington, DC, 1997; and references therein.

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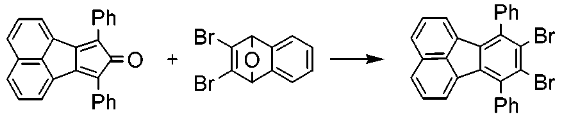
by electropolymerization.[7] Little was known, however, about the synthesis of the homologous fluorantheno[8,9-*k*]fluoranthenes ($n = 2$),[8] which can be seen as planar parts of the C_{60}-fullerene's belt region.

Here we report on the synthesis of "monomeric" and "dimeric" phenyl-substituted fluoranthenofluoranthenes via new 8,9-didehydrofluoranthenes and a new biscyclopentadienone serving as an efficient diene in Diels−Alder reaction with one of these didehydrofluoranthenes.

It is difficult to regiospecifically functionalize PAHs by introducing substituents to the parent molecule. Often the only way to do this is to introduce the substituents while building up the aromatic system. To obtain a vicinal difunctionalization in the 8,9-position of fluoranthene, from which the corresponding aryne can be generated, we started from the cyclopentadienone **1a** (Scheme 1).[9] After several unsuccessful attempts to add acetylene derivatives, which should give the aryne precursor either directly or after subsequent transformation, we finally found the new dibromoepoxynaphthaline **2** to be a suitable dibromoacetylene equivalent. It was made from 3,4-dibromofuran[10] and anthranilic acid by a standard procedure in 93% yield.

Scheme 1[a]

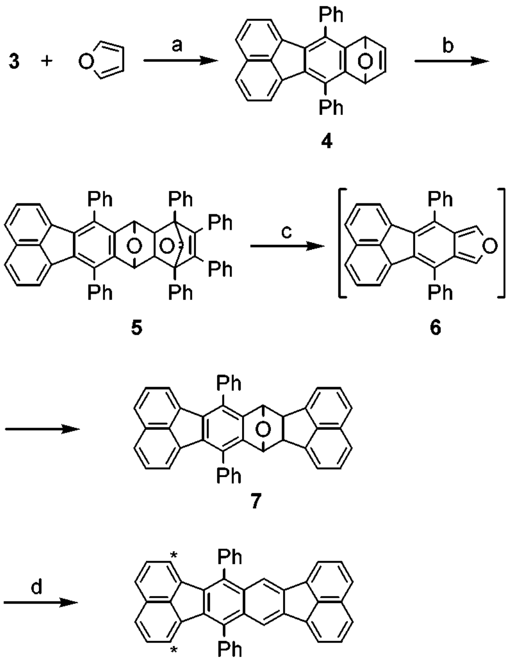


1a **2** **3**

[a] Method A: *o*-xylene, reflux, 20−40%. Method B: melt, 130 °C, 62%.

The synthesis of 8,9-dibromofluoranthene **3** from **1a** and **2** follows the same well-known reaction sequence of Diels−Alder, decarbonylation, and *retro*-Diels−Alder reactions which is normally used to generate isobenzofurans from tetraphenylcyclopentadienone (tetracyclone) and epoxynaphthalines.[11] Isobenzofuran is the side product here, and reaction conditions have to be more drastic due to the bulkiness of the bromo substituents in **2**. For dibromofluoranthene **3**, there was a 20−40% yield, when the reaction was carried out in solution, and up to a 62% yield from a melt of **1a** in **2**. An intermediate structure comparable to **5** (Scheme 2) could not be detected because of the high-temperature conditions required. The comparably low yields are caused by side reactions of **1a** which were not further investigated. The aryne was generated from **3** with butyllithium (BuLi) and in situ trapped by furan to give **4** in 71% yield.[12] Subsequent Diels−Alder reaction of **4** with tetracyclone yielded the isobenzofuran precursor **5** in 88%. Isobenzofuran **6** was generated in situ by heating **5** in toluene and trapping with acenaphthene to give the epoxy-bridged fluoranthenofluoranthene **7** in 82% isolated yield with an *endo*−*exo* ratio of 1:3. The isomers were separated and individually characterized. Finally, diphenylfluoranthenofluoranthene **8** was obtained by dehydration with *p*-toluenesulfonic acid (*p*-TsOH) in 76% isolated yield. The yellow green product showed a strong fluorescence even in the solid state.

Scheme 2[a]



8

[a] (a) BuLi, toluene, −40 °C, 71%, (b) tetracyclone, EtOH, 78 °C, 88%, (c) toluene 112 °C, 82%, (d) *p*-TsOH, toluene, 112 °C, 76%. For chemical shifts (*), see Table 1.

A crystal structure analysis was performed for **8**.[13] Figure 2 shows a pair of molecules in the crystal. The phenyl groups are almost perpendicular to the main plane of the molecule as expected[14] and slightly bent toward the neighboring acenaphthene unit. The latter is assigned to a packaging effect originating from an intermolecular repulsion of the phenyl

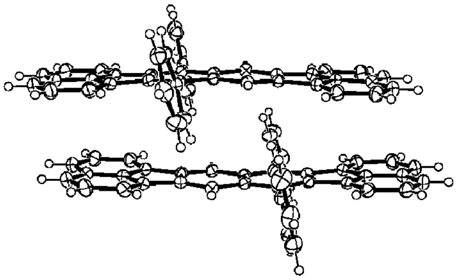


Figure 2. Structure of **8** in the crystal (ORTEP plot).

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[7] Debad, J. D.; Bard, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 2476.
[8] Clar, E.; Stephen, J. F. *Tetrahedron* **1964**, *20*, 1559.
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[11] Fieser, L. F.; Haddadin, M. J. *Can. J. Chem.* **1965**, *43*, 1599.
[12] Hart, H.; Lai, C.-Y.; Godson, C. N.; Shamouil, S. *Tetrahedron* **1987**, *43*, 5203.

groups. This effect should not be present in solution which becomes apparent from molecular mechanics simulations.[15] UV/vis data are given in Table 1.

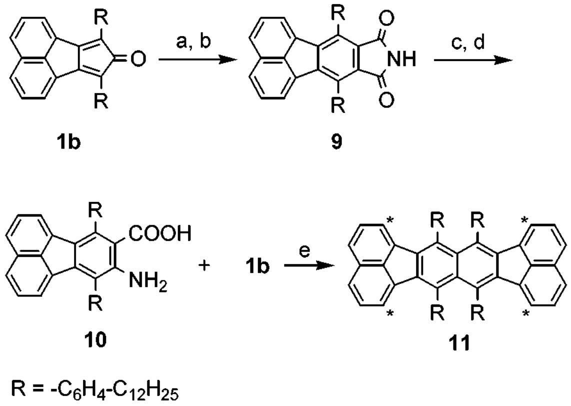
Table 1. Selected UV/Vis and Proton NMR Data

	absorption λ_{max} [nm]	emission λ_{max} [nm]	Stokes shif [nm]	chemical shift^c δ [ppm]
8	454^a	455^a	1	*6.6^d
11	469^b	475^b	6	*5.6
15	542^b	550^b	8	**5.15/*5.7

^{a} $CHCl_3$. ^{b} CH_2Cl_2. ^{c} **8**, 270 MHz/$CDCl_3$; **11**, 15 250 MHz/$CDCl_3$. ^{d} Asterisks assign the marked protons in Schemes 2−4.

A limitation in generating arynes from vicinal dibromides with BuLi is this method's intolerance to strong electrophilic groups. Therefore, we used the method of Pascal Jr.[16] to obtain the fluoranthene anthranilic acid **10** (Scheme 3).

Scheme 3^a

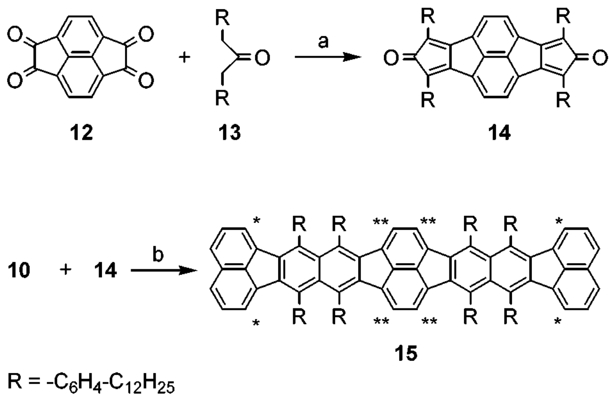


^{a} (a) Maleimide, C_6H_5Br, reflux; (b) C_6H_5Br, Br_2, rt, 78%; (c) MeOH, NaOH, NaOCl, reflux; (d) propanol, KOH, reflux, 62%; (e) THF/CH_2Cl_2, isoamyl nitrite, 50 °C. For chemical shifts (*), see Table 1.

Diels−Alder reaction of the acecyclone **1b** with maleimide and subsequent dehydrogenation with bromine gave the imidofluoranthene **9** in 78% yield. A Hofmann rearrangement on **9** yielded **10** in 62%. From diazotation of **10** with isoamyl nitrite at 50−60 °C, the corresponding aryne was generated in situ which added to **1b**. The primary adduct underwent decarbonylation during reaction to give the tetraphenyl-substituted fluoranthenofluoranthene **11** in 62% isolated yield. The moderate yield predominately results from loss during workup. The lack of intensive color in the TLC indicates that **1b** was completely converted.

The decision to introduce long flexible solubilizing side chains to **11** in addition to the phenyl groups was made to aid the future synthesis of even longer PAHs and polymeric structures and to increase their solubility. Scheme 4 shows the synthesis of the "dimeric" fluoranthenofluoranthene **15**. In the first step the new biscyclopentadienone **14** was synthesized by a 4-fold Knoevenagel reaction between the tetraketopyracene **12**[17] and the alkyl-substituted diphenylacetone **13**[18] in 45% yield. **13** was synthesized by an improved four-step sequence with 60% over all yield.[19]

Scheme 4^a



^{a} (a) EtOH, KOH, 50 °C, 45%; (b) THF/CH_2Cl_2, isoamyl nitrite 50 °C. For chemical shifts (*/**), see Table 1.

The reaction of **10** with **14** was carried out under conditions similar to those for the synthesis of **11** and yielded **15** in 56% isolated yield. **15** is a red amorphous solid with a bright red fluorescence in solution. Table 1 gives UV/vis data of compounds **8**, **11**, and **15**. The relatively small Stokes shifts indicate considerable rigidity of the structures. The electrooptical properties of **8**, **11**, and **15** are presently under investigation.

Chemical shifts for the inner protons of the terminal and that of the centered naphthalenic units for compounds **8**, **11**, and **15,** respectively, which are marked with asterisks in Schemes 2−4, are given in Table 1. An increase in phenyl substitution causes an increase in upfield shift. This is the result of the almost perpendicular orientation of the phenyl groups to the molecules' main planes, which brings the naphthalenic protons right into the phenyl groups upfield cones. The additional upfield shift of approximately 1 ppm going from diphenyl substitution to tetraphenyl substitution can be assigned to a bending of the phenyl groups toward the terminal naphthalenic units, which becomes evident from molecular mechanics simulations.[15] This is due to their

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[13] Crystal data for **8**: $C_{42}H_{24}$, $M = 528.61$, monoclinic, $P2(1)/n$, $a = 15.010(3)$, $b = 9.2219(16)$, and $c = 20.202(4)$ Å, $\alpha = 101.725°$, $V = 2738.2(8)$ Å^3, $Z = 4$, $D_c = 1.282$ g cm^{-1}. A total of 6279 observed reflections [$I > 26(I)$] and 379 variable parameters converged to $R = 0.0464$ and wR = 0.1302.

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[15] Hyperchem release 6.03, geometry optimization using implemented mm+ force field, AM1, and PM3 with Polak-Ribiere algorithm.

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[17] Clayton, M. D.; Marcinow, Z.; Rabideau, P. W. *J. Org. Chem.* **1996**, *61*, 6052.

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[19] See Supporting Information.

intramolecular *peri*-interactions in contrast to the abovementioned intermolecular interaction in the solid state of **8**. A further shift of 0.45 ppm is observed for the protons of the central naphthalenic unit of **15**. This shift is assigned to the influence of two phenyl groups flanking these protons.

In summary, we have presented the first two routes for the synthesis of 8,9-didehydrofluoranthene precursors and demonstrated their potential in the synthesis of novel extended CPAHs. The didehydrofluoranthenes either served as building blocks for the synthesis of a highly reactive isobenzofuran diene or were used directly as dienophile in Diels–Alder reactions with a acecyclone and a new biscyclopentadienone which allowed a convenient synthesis of a fully annulated 14 ring system. The synthesized CPAHs may be of interest both for their electrooptical properties, which are presently under investigation, and as a building block in the synthesis of larger fragments of C_{60}-fullerene to which they are structurally related. Future efforts in our laboratory will be directed at the synthesis of more extended CPAHs and polymeric structures.

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Supporting Information Available: Experimental procedures and characterization for all compounds, CIF file for compound **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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