Palladium-Catalyzed Pentannulation of Polycyclic Aromatic Hydrocarbons

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Abstract: We present a new and versatile one-step synthesis of a series of small molecular chromophores based on cyclopentannulated polycyclic aromatic hydrocarbons (PAH). Easily available pyrene, anthracene, and perylene bromides serve as starting materials for the reactions. The formation of the five-membered ring is achieved by the straightforward palladium(0)-catalyzed carbannulation with various substituted acetylenes. This approach is applicable either to single or multiple annulation procedures leading to hitherto inaccessible PAH topologies. Ac-

Keywords: absorption • anthracene • cyclovoltammetry · perylene · pyrene

cording to the resulting products of the diverse reactions, a mechanistic explanation is proposed. UV/Vis absorption as well as cyclovoltammetric measurements were performed for characterization demonstrating the value of this annulation technique. Optical absorptions of up to 780 nm and absorption coefficients ranging from 8000 to $34\,000\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$ were detected.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) bearing cyclopentadienide moieties can be regarded as subunits of fullerenes or other nanospheres.^[1] There is a great interest in new and efficient syntheses of PAHs^[2] containing functional groups and structural motifs which control chemical and physical properties like stability, charge-carrier mobilities and spectroscopic behavior.^[3] Due to the remarkable optical^[4] and electronic^[5] properties of aromatic cyclopentadienides, they show characteristics of alternate PAHs, such as pentacene or hexa-peri-hexabenzocoronenes, that are already being used in organic field-effect transistors (OFETs),^[6] organic lightemitting diodes (OLEDs),^[7] and organic photovoltaics (OPVs).^[8] In contrast to PAH structures which obtain their properties from their sheer size and thus often need additional solubilizing groups,^[9] small pentannulated PAHs can be used without auxiliary substituents and easily purified.^[10] Surprisingly, only a few examples of cyclopentannulated PAHs can be found in the literature.^[11] Most of them contain derivatives of the well known indenopyrene $(1)^{[12]}$ or acenaphthylene (2) (see Scheme 1),^[10] like the formation of diphenylacenaphtylene using 1-iodonaphthalene and diphenylacetylene.^[13] It is noticeable at this point that palladiumcatalyzed reactions, such as Heck, [14] Negishi, [15] Suzuki-Miyaura^[16] and Sonogashira^[17] reactions play an important role, as they are known to be favorable for the formation of

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PAHs since a long time^[18] and further research on this is still in progress.^[19] Additionally the use of alkyne derivatives as substrates for palladium-catalyzed annulations became an essential part of the latter, as it enables a facile enlargement of existing aromatic systems.^[20]



Scheme 1. Examples for literature known cyclopentannulated PAH.

Herein, we present a straightforward pentannulation of easily available pyrene, anthracene, and perylene bromides with aryl or alkyl acetylenes under mild reaction conditions. It is shown that this procedure is applicable to either single or multiple annulation of PAHs. Additionally, it provides the possibility to use different acetylenes, which makes this approach a facile one-step synthesis of various PAHs including five-membered rings. As a further advantage it is shown that readily available palladium catalysts in combination with well understood phosphine ligands^[21] can be used.

Results and Discussion

Syntheses: The initial coupling reaction was carried out between 1-bromopyrene (3) and diphenylacetylene (a). When optimizing the reaction conditions, a mixture of toluene, acetonitrile, and triethylamine at reflux appears as most suitable in terms of yield and reaction time.^[22] Thus, the desired 3,4-diphenylcyclopenta[cd]pyrene (3a) could be ob-

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10

8a

6a–6b

tained in 82% yield using 1.2 equivalents of diphenylacetylene (a; throughout this article the acetylene derivatives are indicated as bold letters) in the presence of 10 mol% [Pd- $(dba)_2$] and 15 mol % P(otol)₃^[23] within 16 h. Applying 9-bromoanthracene (4) as a core structure together with diphenylacetylene (a), the reaction proceeded smoothly to produce the respective 1,2-diphenylaceanthrylene $(4a)^{[24]}$ in good yields, whereas the reaction based on 3-bromoperylene (5) gave lower yields probably due to the poor solubility of compound 5 (Scheme 2).



mopyrene.

Scheme 2. A) Overview about the palladium-catalyzed pentannulation reaction of pyrene-, anthracene-, and pervlenebromides with symmetric acetylene derivatives. B) Pentannulation reaction of 1-bromopyrene with diphenylacetylene.

We further investigated the twofold annulations of 9,10dibromoanthracene (6), 1,6-dibromopyrene (7), and 1,8-dibromopyrene (8). Applying 9,10-dibromoanthracene (6) in this annulation chemistry, one would expect to obtain two isomers as shown in Scheme 3. Remarkably, the formation of isomer 10 was not observed, which is in agreement with similar reports.^[25] Only the cyclopenta[*hi*]aceanthrylenes **6a** and **6b** were isolated in moderate yields.

In case of the twofold annulation of 1,6- and 1,8-dibromopyrene (7, 8), both starting materials were synthesized via

Scheme 3. Two-times pentannulation reactions of 9,10-dibromoanthracene, 1,6-dibromopyrene, and 1,8-dibrodirect bromination of pyrene according to the procedure of Yip et al.^[26] This reaction results in 1,6-dibromopyrene (7) and 1,8-dibromopyrene (8) in equal amounts and the separation of **7** and **8** is known to be difficult.^[27] When using the mixture for the pentannulation, the desired products 7a and 8a were also formed in a 1:1 ratio as expected, but in this case the purification of the isomers was considerably easier. While the dicyclopenta [cd, jk] pyrene (7a) precipitated right away from the cooled reaction mixture, the dicyclopenta-[cd, fg] pyrene (8a) could be obtained via column chromatography. The products were isolated in 54% yield. Finally the dicyclopenta[cd,lm]perylene 9a was synthesized from 3,9-dibromoperylene $(9)^{[28]}$ in 17% yield after recrystallization (Scheme 4). Due to its low solubility, 9a could also be received by direct precipitation from the cold reaction mixture. To determine a potential correlation between the product yield and the low solubility of compound 9a as well as its intermediates, an analogous annulation using 1,2-bis(4butylphenyl)acetylene (e) was performed. However, the solubilizing alkyl groups did not seem to have a positive effect (Table 1). Moreover the annulation of perylene in particular is weakened by the occurrence of side products derived from incomplete cyclization (11a) and addition of a third acetylene derivative (12e) (see Scheme 4). Whereas the first problem can be overcome by an increase of triethylamine to enhance the removal of HBr (see also Scheme 6), the second side reaction is caused by a higher concentration of the reactants.[29]

a-b

[Pd(dba)₂], P(o-tol)₃

toluene, CH₃CN, Et₃N

111°C

[Pd(dba)₂], P(o-tol)₃ toluene, CH3CN, Et3N

111°C

Β̈́r

8

6

Various aryl as well as alkyl substituted acetylenes (a,b,c,d, Scheme 2A) were used as annulation partners. Within this series the reaction with 4-octyne (b) was performed in order to study the influence of solubilizing groups attached to the respective cores. This time 3,4-dipropylcyclopenta[cd]pyrene (3b), 1,2-dipropylcyclopenta[cd]perylene (5b), and 1,2,6,7-tetrapropylcyclopenta[*hi*]aceanthrylene (6b) were obtained in slightly lower yields compared to their phenyl congeners, which is caused by the lowered ability to precipitate within the last purification step. The synthesis of thiophenyl- and pyridinyl-substituted pentannulated

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[a] Reaction conditions: Bromoaryl (1.0 mmol), acetylene (1.2 mmol), $[Pd(dba)_2]$ (10 mol%), $P(o-tol)_3$ (15 mol%), toluene (90 mL), CH_3CN (10 mL), Et_3N (5 mL), 111°C, 16 h. [b] Yield of the isolated product. [c] 2.4 mmol of the acetylene were used instead of 1.2 mmol, the amount of catalyst was doubled.

PAHs was carried out analogously. For this purpose, the dithiophenylacetylene (c) and the dipyridinylacetylene (d) were prepared in a two-step synthesis derived from the bromoaryl precursors and 2-methylbut-3-yn-2-ol according to the literature.^[30] The desired products 3c, 4c, and 5c could be obtained in moderate to good yields by reaction of 3-5with dithiophenylacetylene (c). This is comparable to the formation of the diphenyl derivatives 3a, 4a, and 5a. Annulation with dipyridinylacetylene (d) furnished the respective products 3d, 4d, and 5d in yields ranging from 8 to 40%, most probably because of the electron-withdrawing character of the pyridinyl groups. An analogous attempt using the more electron-demanding dicarboxyacetylene dimethylester was not successful. A summary of the annulation reactions leading to cyclopentannulated PAHs is given in Table 1.

Similar to a single pentannulation of 9-bromoanthracene (4), 9-bromophenanthrene (13) was tested. Surprisingly, the expected acephenanthrylene 13a was observed only in trace amounts, instead triphenylene $14^{[31]}$ was obtained as main product derived from hexannulation of 13 (Scheme 5). Doubling the amount of acetylene applied, the yield of 14 could be improved to 20%. The fact that an attachment of a second alkyne can occur in a single annulation reaction leads to the following mechanistic explanation.

Based upon a mechanism for the hexannulation of biphenyl compounds already described by Larock,^[32] it is proposed that the reaction starts with an insertion of the alkyne into the aryl-palladium(II) species, resulting in an open vinylic palladium intermediate (B). Subsequently two processes can take place: i) a ring closure by electrophilic attack (C), forming the desired cyclopentadienide derivative after reductive elimination of Pd⁰ (D); or ii) a second alkyne inserts (E) followed by ring closure to yield the respective hexannulated product (F+G). (Scheme 6)

Photophysical characterization: The described compounds are soluble in common organic solvents such as dichloromethane or chloroform. Whereas the annulations of the different core structures significantly affect the shape of the absorption spectra, only little effects were observed upon varying the substituents (Table 2). A discussion can therefore be restricted to the di- and tetraphenyl derivatives.

All three cyclopentapyrene compounds (3a, 7a, and 8a) show sharp bands in the region of shorter wavelengths up to 450 nm with high absorption coefficients ranging from $22000 \text{ M}^{-1} \text{ cm}^{-1}$ (3a, $\lambda = 380 \text{ nm}$, and 7a, $\lambda = 419 \text{ nm}$) to $34300 \text{ M}^{-1} \text{ cm}^{-1}$ (8a, $\lambda = 430 \text{ nm}$). In the long wavelength region of the spectrum of the single annulated pyrene 3a a weak broad band appears between 420 and 600 nm being responsible for the red color (Figure 1). The spectrum of 7a shows a similar but much stronger band located at 450 to 560 nm, whereas the mirror-symmetric 8a exhibits only minimal absorption beyond 450 nm. Upon going from unsubstituted over alkyl- to aryl-substituted analogues of 3a, 7a, and 8a the additional phenyl groups appear to have a crucial effect on the absorption spectrum, as compounds 3a, 7a, and 8a show a larger bathochromic shift and a higher in-



Scheme 4. Two-times pentannulation reaction of 3,9-dibromoperylene.



Scheme 5. Hexannulation reaction of 9-bromophenanthrene with diphenylacetylene.

tensity of the broad bands compared both to the alkyl substituted **3b** and to the unsubstituted parent compounds.^[4c] Pyrene **8a** plays a special role, since two of its phenyl groups are twisted out of the plane by about 80° due to the steric hindrance and thus do not conjugate with the pyrene core.^[33]

The spectra of the anthracene derivatives 4a and 6a also possess sharp peaks from 300 to 450 nm, and 490 nm respectively, followed by a broad band located between 450 and 650 nm for the red colored 4a and even between 500 and



Scheme 6. Proposed mechanism of the palladium-catalyzed pentannulation and hexannulation reaction.

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R R R 12e 780 nm for **6a**, leading to a bright green appearance of the tetraphenylcyclopenta[*hi*]aceanthrylene (Figure 2). The observed absorption coefficients are $7800 \text{ M}^{-1} \text{ cm}^{-1}$ (**4a**, $\lambda = 375 \text{ nm}$) and $20400 \text{ M}^{-1} \text{ cm}^{-1}$ (**6a**, $\lambda = 393 \text{ nm}$) (Table 2). Surprisingly the unsubstituted cy-

clopenta[hi]aceanthrylene is re-

Table 2. Absorption maxima (λ_{max}) and absorption coefficients (ε) of all compounds derived from palladium-catalyzed pentannulation.

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Compound	λ_{\max} [nm]	$\varepsilon (\lambda_{\max}) [M^{-1} cm^{-1}]$
3a	380/400	21 000/17 100
3b	340/356/376	14100/16900/12400
3c	384/405	22700/19900
3 d	382/401	22000/19000
4a	375/417/439	7800/6400/5100
4c	376/417/440	7900/7300/5800
4d	374/420/443	9400/7400/6300
5a	480/507	30 000/28 500
5b	456/484	34100/24900
5c	480/507	29000/27700
5 d	488/513	15900/15600
6a	393/441/468	20400/11800/10800
6 b	382/424/450	15800/5900/5000
7a	398/419	20500/22000
8a	406/430	31 500/34 300
9a	462/493/530	10800/20800/26700

ported to be dark-brown and does not show absorption beyond 500 nm.^[34] The alkyl-substituted analogue **6b** reveals a decrease of the absorption between 500 and 780 nm of ap-

proximately 50%. This again proves that the phenyl groups enlarge the conjugation of the core, compared to alkyl- or non-substituted analogues and thus affect the spectral properties of the compounds.

The analogous annulation of pervlene leads to a bathochromic shift of about 70 nm (5a) and 93 nm (9a) compared with the parent compound (Figure 3). This results in a red color with a λ_{max} of 507 nm (5a) and 530 nm (9a) and absorption coefficients of 30000 and $26700 \,\mathrm{m}^{-1} \mathrm{cm}^{-1}$. As already stated in the case of the pyrene derivative 8a, both mirror-symmetric perylenes do not show any broad bands in the region of longer wavelengths.

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Figure 1. Absorption spectra of cyclopenta[cd]pyrene **3a** (solid line), dicyclopenta[cd.jk]pyrene **7a** (dotted line), and dicyclopenta[cd.jg]pyrene **8a** (dashed line) (solvent: chloroform).



Figure 2. Absorption spectra of aceanthrylene 4a (solid line), and cyclopenta[hi]aceanthrylene 6a (dashed line) (solvent: chloroform).

Simple semiempirical quantum mechanical calculations (Gaussian 03W, AM1)^[35] of the electronic structure of the phenyl-substituted pentannulated compounds give an explanation for the difference in the shape of the respective spectra. As an example the frontier orbitals of cyclopenta-[hi]aceanthrylene **6a** and dicyclopenta [cd,lm]perylene **9a** are depicted (Figure 4). The anthracene derivative exhibits a significant difference in the shape of the respective orbitals. The HOMO of **6a** shows a strong influence of two phenyl substituents resulting in a linear extension of this orbital, whereas the LUMO is mostly centered in the core of the molecule. The difference between the orbitals leads to an intramolecular charge transfer, yielding the broad band in the absorption spectrum (Figure 2). In contrast, the calculations of the perylene **9a** indicate only little changes between the



Figure 3. Absorption spectra of cyclopenta[cd]perylene **5a** (solid line), and dicyclopenta[cd,lm]perylene **9a** (dashed line) (solvent: chloroform).

HOMO and LUMO, which are both located on the core and resemble the orbitals of the parent perylene.^[36] Thus the absorption spectrum of **9a** consists of sharp peaks only. Similar correlations between the shapes of the orbitals and the optical absorption were obtained for the other pentannulated structures, which are listed in the Supporting Information. It appears that all presented mirror-symmetric molecules only show sharp peaks in their absorption spectra, due to the similarity between their HOMOs and LUMOs (no charge transfer), whereas non-symmetric annulation induces a strong difference in the shape of the respective orbitals and thus a broadening of the absorption bands.

Cyclic voltammetry: In order to determine the respective orbital energies, cyclovoltammetric measurements were performed in dichloromethane.^[37] The results are compiled in Table 3. Almost all PAHs show at least one reversible reduction reaction. Some of them even exhibit partially reversible oxidation behavior, even though they are reported to be mostly irreversible for unsubstituted pentannulated PAH, such as aceanthrylene, cyclopenta[cd]pyrene, or cyclopenta[cd] pervlene.^[5] In the case of the anthracene derivatives 4a and 6a, it can be seen from the data, that the LUMO as well as the HOMO energies are lowered by introducing a second five-membered ring. In contrast to that, the pyrene compounds 3a, 7a, and 8a do not show any noticeable change in the HOMO-LUMO energies. The same is true for the resulting HOMO-LUMO gaps. Whereas the ΔE values of 3a, 7a and 8a do not vary much, the difference of the orbital energies is much larger when going from anthracene 4a to 6a, leading to a narrowing of the HOMO-LUMO gap. This conforms to the bathochromic shift comparing the absorption spectra of 4a and 6a (see Table 3 and Figure 2). Similar results are obtained for the perylene derivatives **5a** and **9a**. In this case the second pentannulation also leads to a strong decrease of the energy levels and at the same time results in a convergence of the orbital ener-

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Figure 4. Molecular orbitals of cyclopenta[hi]aceanthrylene 6a and dicyclopenta[cd,lm]perylene 9a. HOMO=highest occupied molecular orbital, LUMO=lowest unoccupied molecular orbital (Gaussian 03W, AM1).

Table 3. HOMO-LUMO calculations according CV measurements.

Compound	$E_{\rm HOMO} [{\rm eV}]$	$E_{\rm LUMO} [{\rm eV}]$	$\Delta E [eV]$	λ_{\max} [nm]	$\varepsilon (\lambda_{max}) [M^{-1} cm^{-1}]$
3a	-5.57	-3.59	1.98	380/400	21 000/17 100
4a	-5.12	-3.10	2.02	375/417/439	7800/6400/5100
5a	-5.48	-3.24	2.24	480/507	30 000/28 500
6a	-5.42	-3.55	1.87	393/441/468	20 400/11 800/10 800
7a	-5.57	-3.61	1.96	398/419	20700/22500
8a	-5.46	-3.56	1.90	406/430	31 500/34 300
9a	-5.57	-3.83	1.74	462/493/530	10800/20800/26700

gies, which is again accompanied by a bathochromic shift in the absorption spectrum.

Conclusion

In summary, the palladium-catalyzed pentannulation of arylbromides with aryl and alkyl acetylenes appears as a powerful method for the preparation of functionalized pentannulated PAHs, since novel cyclopentadienide moieties can be achieved in a feasible one-step reaction. The successful application of mono- and dibromo derivatives of pyrene, anthracene, and pervlene as well as the use of 4-octyne, diphenyl-, dithiophenyl-, and dipyridinylacetylene as coupling partners demonstrates the versatility of this reaction. Further, one can envision the use of this pentannulated PAHs in organic photovoltaics, as the performed UV/Vis absorption measurements show that the synthesized compounds exhibit colors going from yellow (8a) over red (3a, 4a, and 5a) up to green in the case of the cyclopenta[hi]aceanthrylene 6a. Thus they provide easily accessible dyes covering a large spectral range together with high absorption coefficients. The cyclovoltammetric measurements are in good agreement with the spectroscopic data. Furthermore they reveal illustrative redox behavior similar to literature known PAH.^[5] The compounds derived from palladium-catalyzed pentannulations possess good solubility in common organic solvents, even without additional solubilizing groups, enabling an easy solution processing for organic electronic devices.

Experimental Section

General methods: See Supporting Information.

Cyclic voltammetry: Cyclic voltammetry for spectroelectrochemistry experiments was carried out with an EG&G Princeton Applied Research potentiostat, model 273. The working electrode consisted of an inlaid platinum disk (1.5 mm diameter) that was polished on a felt pad with 0.05 μ m alumina and sonicated in milli-Q water for 5 min before each experiment. A platinum wire was used as the counter electrode and an Ag wire was used as the reference electrode internally calibrated with ferrocene/ferrocenium (Fc/Fc⁺) in the measurement. The CV measurements were carried out in a solution of Bu₄NPF₆ (0.1 M) in dry CH₂Cl₂ with a scan rate of 50 mV s⁻¹ at room temperature under argon. Redox potentials were determined via the onset method.

Representative synthetic procedure: A stirred solution of 3 (1.0 mmol)

and \mathbf{a} (1.2 mmol) in toluene (90 mL),
acetonitrile (10 mL), and triethyla-
mine (5 mL) was purged with argon
for 20 min. Subsequently, [Pd(dba) ₂]
$(10 \text{ mol }\%)$ and $P(o-tol)_3$ $(15 \text{ mol }\%)$
were added. The resulting solution
was evacuated and purged with argon
two times and then refluxed for 16 h.
After cooling to room temperature,
the solvents were evaporated in
vacuo and the crude product was pu-
rified by column chromatography
(silica gel, petroleum ether/dichloro-
methane 4:1) to give product 3a in
82 % yield.

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