ChemPubSoc Europe
DOI: 10.1002/chem.201405763
CHEMISTRY
A European Journal
Full Paper

Macrocycles |*Hot Paper*|

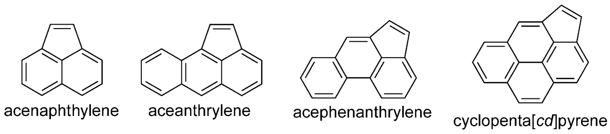
Palladium-Catalyzed Annulation of 9-Halophenanthrenes with Alkynes: Synthesis, Structural Analysis, and Properties of Acephenanthrylene-Based Derivatives**

En-Chih Liu, Min-Kuan Chen, Jen-Yi Li, and Yao-Ting Wu*[a]

Abstract: The palladium-catalyzed annulation of 9-bromo- and 9-chlorophenanthrenes with alkynes gave 4,5-disubstituted acephenanthrylenes in 58–95 % yield (9 examples). Asymmetric alkynes, such as 1-phenyl-1-propyne, 1-phenyl-1-hexyne, and 1-cyclopropyl-2-phenylethyne, regioselectively form (cyclo)alkyl-substituted products, following the regular rule that governs the carbopalladation of alkynes. This synthetic protocol can also be utilized in annulations with several π-extended bromoarenes, such as 7-bromo[5]helicene, 5-bromo[4]helicene, 9-bromoanthracene, 3-bromoperylene, and 3-bromofluoranthene, to give the corresponding annulated products in moderate to good yields (51–86 %; 6 examples). Similarly, bromocorannulene produced highly curved 1,2-disubstituted cyclopentacorannulenes. Reactions of 6,12-dibromochrysene and 4,7-dibromo[4]helicene with di(4-tolyl)ethyne provided the twofold annulated products in moderate yields. 4,5-Diphenylacephenanthrylene and 6,7-diphenylbenzo[*a*]acephenanthrylene thus generated were converted into phenanthro[9,10-*e*]acephenanthrylene and benzo[*a*]phenanthro[9,10-*e*]acephenanthrylene, respectively, by oxidative cyclodehydrogenation. The structures of 4,5-diphenylacephenanthrylene, 4,5-diphenyldibenzo[*a*,*l*]acephenanthrylene, 1,2-diarylcyclopentacorannulenes, and benzo[*a*]phenanthro[9,10-*e*]acephenanthrylene were verified by X-ray crystallography. The photophysical and electrochemical properties of the selected annulated products were investigated.

Introduction

The chemical and physical properties of cyclopentene-fused polycyclic aromatic hydrocarbons (PAHs), in which a five-membered ring cannot exhibit aromaticity associated with a Kekulé structure, differ from those of standard benzenoid PAHs.[1] Acenaphthylene is the simplest of this class of compounds, and it has been extensively studied.[2] In contrast, the chemistry of the two next higher-order benzo derivatives, aceanthrylene and acephenanthrylene, is largely unknown. This relative lack of investigations arises mainly from the poor availability of the compound. The main methods for the preparation of acephenanthrylene include high-temperature flash vacuum pyrolysis (FVP)[3] or solution-phase synthesis with Friedel–Crafts cyclization as a key step.[4] The required conditions for FVP considerably limit the range of functional groups, and cause thermal rearrangement of the molecular framework[3] owing to the low stability of acephenanthrylene.[5] The solution-phase synthesis requires many steps that involve commercially available starting materials.[5] A metal-catalyzed reaction for the formation of carbon–carbon bonds may provide an efficient means of overcoming these issues.[6] The formal [3+2] annulation of a haloarene with an alkyne is effective for enlarging existing aromatic systems in the synthesis of cyclopentene-fused PAHs. This synthetic strategy has been utilized in the preparation of acenaphthylenes,[7] aceanthrylenes,[8] cyclopenta[*cd*]pyrenes, and others.[9] However, established palladium-catalyzed protocols cannot be used to synthesize acephenanthrylene efficiently.[9]



According to Euler's rule[10] and the results of experimental investigations,[11] the cyclopentene annulation of corannulene, which is the elementary bowl-shaped fragment of fullerene, increases its curvature. Highly curved bowl-shaped polyarenes (so-called buckybowls) have a high inherent strain, so their preparation is challenging. This study presents a general protocol for synthesizing various planar, twisted, and bowl-shaped acephenanthrylene-based PAHs. The structures and properties of the prepared products were elucidated.

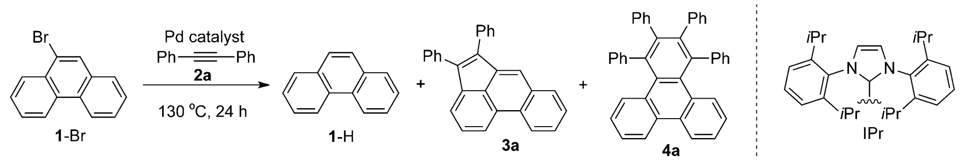
---

[a] *E.-C. Liu, M.-K. Chen, J.-Y. Li, Prof. Y.-T. Wu*
Department of Chemistry, National Cheng Kung University
No.1 Ta-Hsueh Road, 70101 Tainan (Taiwan)
E-mail: ytwuchem@mail.ncku.edu.tw

[**] *Metal-Catalyzed Reactions of Alkynes. Part XVII. For Part XVI see: Y.-C. Hsieh, H.-Y. Fang, Y.-T. Chen, R. Yang, C.-I. Yang, P.-T. Chou, M.-Y. Kuo, Y.-T. Wu, Angew. Chem. Int. Ed.* ***2015****, DOI: 10.1002/anie.201410316.*

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201405763.

Table 1. Optimization of reaction conditions for the preparation of 4,5-diphenylacephenanthrylene **3a**.[a]



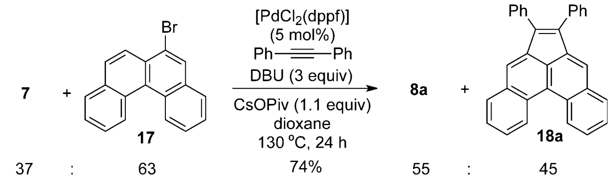
	Catalyst [mol %]	Solvent	Base	Additive ([equiv])	Conversion [%]	Ratio of **1**-H/**3a**/**4a**	Yield [%][b]
1	$[PdCl_2(PCy_3)_2]$ (10)	NMP	DBU	–	73	92:8:0	–
2	$Pd(OAc)_2$ (10)	NMP	DBU	IPr·HCl (0.2)	100	63:37:0	–
3	$Pd(OAc)_2$ (10)	NMP	DBU	P(*o*-tol)$_3$ (0.2)	100	12:88:0	–
4	$Pd(OAc)_2$ (10)	NMP	DBU	BINAP (0.1)	100	25:75:0	–
5	$Pd(OAc)_2$ (10)	NMP	DBU	dppm (0.1)	100	20:80:0	–
6	$Pd(OAc)_2$ (10)	NMP	DBU	dppe (0.1)	100	27:72:1	–
7	$[PdCl_2(PPh_3)_2]$ (10)	NMP	DBU	–	42	18:73:9	–
8	$[PdCl_2(PPh_3)_2]$ (10)	NMP	DBU	PPh_3 (0.2)	100	6:78:16	–
9	$[PdCl_2(dppf)]$ (10)	NMP	DBU	–	100	3:73:21	–
10	$[PdCl_2(dppf)]$ (10)	NMP	NEt_3	–	100	33:50:17	–
11	$[PdCl_2(dppf)]$ (10)	NMP	K_2CO_3	–	100	100:0:0	–
12	$[PdCl_2(dppf)]$ (10)	NMP	DBU	CsOPiv[c]	100	8:85:7	–
13	$[PdCl_2(dppf)]$ (10)	NMP	DBU	CsOPiv (1.1)	100	2:96:2	89
14	$[PdCl_2(dppf)]$ (10)	CH_3CN	DBU	CsOPiv (1.1)	100	62:38:0	–
15	$[PdCl_2(dppf)]$ (10)	DMF	DBU	CsOPiv (1.1)	100	5:95:0	–
16	$[PdCl_2(dppf)]$ (10)	dioxane	NEt_3	–	100	23:14:63	–
17	$[PdCl_2(dppf)]$ (5)	dioxane	DBU	CsOPiv (1.1)	100	2:98:0	85

[a] A mixture of 9-bromophenanthrene (**1**-Br, 0.25 mmol), alkyne **2a** (1.2 equiv), base (3.0 equiv), and a solvent (1 mL) in a sealed tube was heated for 24 h. The conversion of **1**-Br and the ratio of the compounds was determined by GC–MS. Cy = cyclohexyl, NMP = *N*-methylpyrrolidone, DBU = 1,5-diazabicyclo[5.4.0]undec-5-ene, BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, tol = tolyl, dppe = 1,2-bis(diphenylphosphino)ethane, dppm = 1,1-bis(diphenylphosphino)methane, dppf = 1,1′-bis(diphenylphosphino)ferrocene, Piv = pivaloyl. [b] Yields are given of products isolated after the reaction. [c] CsOPiv was prepared in situ by using Cs_2CO_3 (0.55 equiv) and PivOH (1.1 equiv).

Results and Discussion

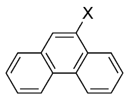
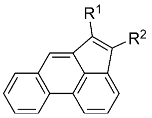
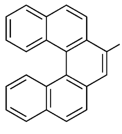
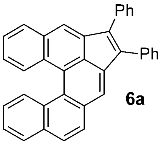
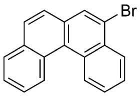
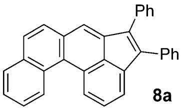
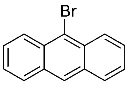
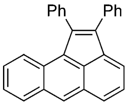
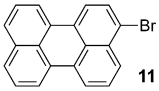
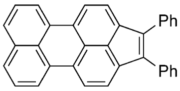
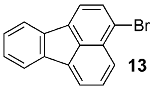
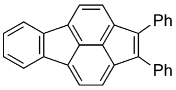
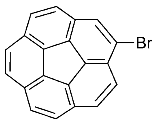
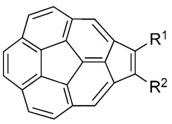
Heating 9-bromophenanthrene (**1**-Br) with diphenylacetylene (**2a**) and a palladium catalyst generated a mixture of debrominated phenanthrene **1**-H, 4,5-diphenylacephenanthrylene **3a**, and triphenylene **4a** (Table 1). The palladium catalyst, ligand, solvent, base and additive all have critical roles in this reaction. Catalyst $[PdCl_2(dppf)]$ was found to be superior to $[PdCl_2(PCy_3)_2]$, $[PdCl_2(PPh_3)_2]$, and the other catalytic systems presented in Table 1 in suppressing the formation of phenanthrene (**1**-H; Table 1, entries 1–9). DBU appeared to outperform other bases, such as K_2CO_3 and NEt_3, in the selective generation of **3a** (Table 1, entries 9–11). The additive CsOPiv strongly reduced the amount of **4a** (Table 1, entries 9 and 13–15), and provided a better result than a combination of Cs_2CO_3 and PivOH (Table 1, entry 12). The reaction was performed with acetonitrile, NMP, or DMF as the solvent, and the last two were observed to improve the debromination of the starting material (Table 1, entries 13–15). Under the optimal conditions, the desired product **3a** was obtained in 89% yield (Method A; Table 1, entry 13). Notably, the reaction conducted in dioxane with a lower catalyst loading (5 mol%) also gave a satisfactory result (Method B; Table 1, entry 17).

The reactivity of alkynes **2** in annulation was examined by using **1**-Br under conditions of Method A and/or B, and most products **3** were obtained in moderate to excellent yields (Table 2, entries 1–10). Generally, diarylacetylenes provided better results than (cyclo)alkyl-substituted alkynes. Asymmetric alkynes, such as 1-phenyl-1-propyne (**2f**), 1-phenyl-1-hexyne (**2g**), and 1-cyclopropyl-2-phenylethyne (**2h**), regioselectively formed **3f**, **3g**, and **3h**, respectively (Table 2, entries 8–10). Their structures were confirmed by using 2D NMR spectroscopy techniques (see the Supporting Information). The regioselectivity is consistent with the regular rule that governs the carbopalladation of alkynes.[12] Unlike in the other examples, compounds **2g** and **2h** can only be added to the reaction mixture by using a syringe pump over a period of 5 h to suppress the formation of the corresponding triphenylenes **4**. Rather than annulation, 1,2-bis(trimethylsilyl)ethyne (**2i**) underwent Sonogashira couplings to give di(9-phenanthyl)ethyne. When catalyst $[PdCl_2(dppf)]$ was replaced with $[PdCl_2(PCy_3)_2]$ (Method C), 9-chlorophenanthrene (**1**-Cl) could be applied in the annulation, but the products were obtained in slightly lower yields than those generated by Method B (Table 2, entries 2 and 5). The palladium-catalyzed annulations of several π-extended bromoarenes, including 7-bromo[5]helicene (**5**), 5-bromo[4]helicene (**7**), 9-bromoanthrene (**9**), 3-bromoperylene (**11**), and 3-bromofluoranthene (**13**), with **2a** produced the corresponding annulated products in moderate to good yields (45–86%; Table 2, entries 12–16, and Scheme 1). In the synthesis of naphth[1,2-*a*]acephenanthrylene **6a**, Method B is more efficient than Method A, and requires less catalyst loading (Table 2, entry 12). Regioisomeric bromo[4]helicenes **7** and **17** exhibited different reactivities in annulation. When a mixture of **7** and **17** (ratio 37:63) was heated with **2a** under the opti-



Scheme 1. Annulations of bromo[4]helicenes with diphenylethyne. The ratios were determined according to the ^1H NMR spectrum.

Table 2. Preparation of cyclopentene-fused PAHs.[a]

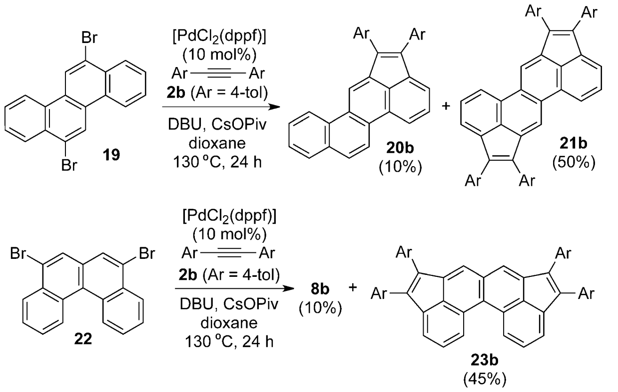
	Ar–X	Alkyne	Product	Method (Yield [%])
				
1	**1**-Br	**2a** ($R^1 = R^2 = Ph$)	**3a**	A (89), B (85, 82[b])
2	**1**-Cl	**2a**	**3a**	C (79)
3	**1**-Br	**2b** ($R^1 = R^2 = 4\text{-}CH_3\text{-}C_6H_4$)	**3b**	A (93)
4	**1**-Br	**2c** ($R^1 = R^2 = 4\text{-}OCH_3\text{-}C_6H_4$)	**3c**	A (81), B (63)
5	**1**-Cl	**2d** ($R^1 = R^2 = 3\text{-}CF_3\text{-}C_6H_4$)	**3d**	C (61)
6	**1**-Br	**2d** ($R^1 = R^2 = 3\text{-}CF_3\text{-}C_6H_4$)	**3d**	A (95)
7	**1**-Br	**2e** [$R^1 = R^2 = 3,5\text{-}C_6H_3(CH_3)_2$]	**3e**	A (70)
8	**1**-Br	**2f** (R^1 = Me, R^2 = Ph)	**3f**	A (89), B (53)
9	**1**-Br	**2g** (R^1 = *n*Bu, R^2 = Ph)	**3g**	A (73)[c]
10	**1**-Br	**2h** (R^1 = *c*Pr, R^2 = Ph)	**3h**	A (58)[c]
11	**1**-Br	**2i** ($R^1 = R^2 = SiMe_3$)	**3i**	A (0)[d]
12	 **5**	**2a** ($R^1 = R^2 = Ph$)	 **6a**	A (58), B (76)
13	 **7**	**2a** ($R^1 = R^2 = Ph$)	 **8a**	B (86)
14	 **9**	**2a** ($R^1 = R^2 = Ph$)	 **10a**	A (45), B (69)[e]
15	 **11**	**2a** ($R^1 = R^2 = Ph$)	 **12a**	A (51)
16	 **13**	**2a** ($R^1 = R^2 = Ph$)	 **14a**	B (51)[f]
				
17	**15**	**2b** ($R^1 = R^2 = 4\text{-}CH_3\text{-}C_6H_4$)	**16b**	B (32)[f]
18	**15**	**2e** [$R^1 = R^2 = 3,5\text{-}C_6H_3(CH_3)_2$]	**16e**	B (31)[f]
19	**15**	**2j** [$R^1 = R^2 = 3,5\text{-}C_6(i\text{Pr})_2H_3$]	**16j**	B (44)[f]

[a] Reaction conditions: Method A: [$PdCl_2$(dppf)] (10 mol %), bromoarene (0.25 mmol), alkyne (1.2 equiv), DBU (3 equiv), CsOPiv (1.1 equiv), NMP, 130 °C, 24 h. Method B: [$PdCl_2$(dppf)] (5 mol %), bromoarene (0.25 mmol), alkyne (1.2 equiv), DBU (3 equiv), CsOPiv (1.1 equiv), dioxane, 130 °C, 24 h. Method C: [$PdCl_2(PCy_3)_2$] (5 mol %), 9-chlorophenanthrene (**1**-Cl; 0.25 mmol), alkyne (1.2 equiv), DBU (3 equiv), CsOPiv (1.1 equiv), anisole, 150 °C, 36 h. [b] The reaction was conducted with 1.50 mmol of **1**-Br. [c] Alkyne (1.5 equiv) was slowly added within 5 h by using a syringe pump. [d] Di(9-phenanthyl)ethyne was obtained. [e] The reaction was conducted in dioxane in the absence of CsOPiv. [f] Reaction was conducted with 0.2 equivalents of CsOPiv.

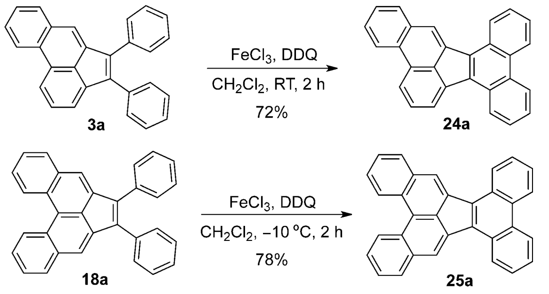
mal conditions (Method B), compounds **8a** and **18a** (ratio 55:45) were obtained in a total yield of 74 %; this reveals the higher reaction efficiency of **7** (Scheme 1). Compounds **8a** and **18a** cannot be separated by column chromatography. Both compounds were obtained in pure form by recrystallization of the mixture. The high reactivity of **7** is also verified by the high yield of **8a** (86 %; Table 2, entry 13). Unlike in the examples described above, 1,2-diaryl-substituted cyclopentacorannulenes **16b**, **16e**, and **16j** were acquired in yields of 31–44 %, which are much lower than those of the other examples in Table 2.[13] Presumably, the highly curved structure was responsible for the unsatisfactory results.[11] The bowl-to-bowl inversion barrier ($\Delta G^{\ddagger}_{inv}$) for the parent cyclopentacorannulene was theoretically predicted to be 27.7–30.9 kcal mol^{-1}).[14] In both the ^1H and ^{13}C NMR spectra, the signals for the two methyl and isopropyl groups in **16e** and **16j**, respectively, are identical, although they are diastereotopic. Annulated products **10a**, **12a**, and **14a**, which are not acephenanthrylene-based derivatives, were prepared from bromoarenes **9**, **11**, and **13**, respectively, in moderate yields (Table 2, entries 14–16). As reported in the literature, compounds **10a** and **12a** were generated in 76 and 30 % yields, respectively, by using a catalytic system that comprised $Pd(dba)_2$ (10 mol %; dba = dibenzylideneacetone) and P(*o*-tol)$_3$ (15 mol %) under highly dilute conditions (ca. 10^{-2} M) in toluene.[9] One advantage of our protocol is a reduction in the amounts of solvents used.

The synthetic method developed herein was also utilized in twofold annulations of dibromoarenes (Scheme 2). The reaction of 6,12-dibromochrysene (**19**) with di(4-tolyl)acetylene (**2b**) generated cyclopenta[*hi*]chrysene **20b** and dicyclopenta[*hi*,*qr*]chrysene **21b** in 10 and 50 % yields, respectively. Similarly, benzo[*l*]acephenanthrylene **8b** and **23b** were prepared by the annulation of dibromo[4]helicene **22** with **2b**. Notably, although both **21b** and **23b** contain four 4-tolyl groups, their solubility in common organic solvents is poor.

4,5-Diphenylacephenanthrylene (**3a**) was converted into phenanthro[9,10-*e*]acephenanthrylene (**24a**) in 72 % yield by oxidative cyclodehydrogenation (Scheme 3).[15] The low solubility of **24a** in common organic solvents was probably responsible for the low yield because some of the material was irreversibly lost during chromatography. It has been reported that the $AlCl_3$-mediated cyclodimerization of phenanthrene easily generates a mixture of **24a** and dibenzo[*fg*,*qr*]pentacene in



Scheme 2. Twofold annulations of dibromoarenes **21** and **23**.



Scheme 3. The Scholl reaction of **3a** and **18a**. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

a ratio of approximately 7:3, but the purification of the former requires many steps.[16] An attempt was made to close both the six- and the five-membered rings in **18a**, but only benzo[*a*]phenanthro[9,10-*e*]acephenanthrylene (**25a**) was obtained.

Single crystals of **3a**, **6a**, **16j**, and **25a** for X-ray crystallographic analysis were grown by the diffusion of MeOH into solutions of the compounds in CH_2Cl_2 at room temperature (Table 3 and Figure 1).[17] Unlike in the examples above, single crystals of **16b** were acquired by the diffusion of MeOH into a solution in benzene. Cyclopentene annulation caused the phenanthrene moiety in **3a** to be slightly more twisted than the parent phenanthrene,[18] as revealed by a comparison of the dihedral angles between rings A and C (4.5 vs. 2.4°). Although the shortest intermolecular carbon–carbon distance was determined to be 3.33 Å, π–π stacking in **3a** could be negligible.

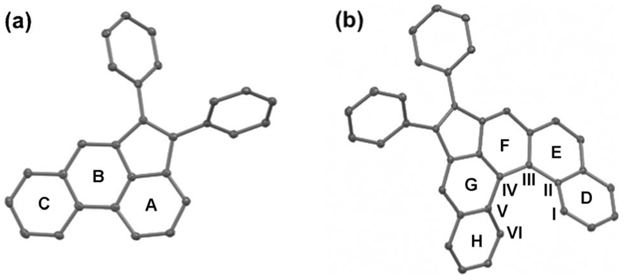


Figure 1. Molecular structures of **3a** (a) and **6a** (b). Only carbon atoms are shown for clarity, the thermal ellipsoids are set at the 30% probability level.

The helical structure of **6a** was analyzed by X-ray crystallography. The dihedral angle between the extremities (rings D and H) and the torsion angle measured for bay carbon atoms II–III–IV–V were determined to be 42.8 and 27.7°, respectively. The nonbonded contact between carbon atoms I and VI was found to be 2.96 Å. These structural data of the [5]helicene moiety described above are very similar to those of 3,12-disubstituted [5]helicenes **27** (Table 4).[19] Therefore, cyclopentene annulation does not significantly alter the structure of the [5]helicene fragment. Molecules of **6a** lack π–π stacking.

Table 4. Structural data of [5]helicene derivatives.

	6a	**27**-Cl	**27**-Ph
distance (I···VI) [Å]	2.96	2.93	2.90
torsion angle (II-III-IV-V) [°]	27.7	29.5	26.7
dihedral angle (rings D/H) [°]	42.8	49.9	42.8
ref.	this work	[19]	[19]

Table 3. Crystal structure data for **3a**, **6a**, **16b**, **16j**, and **25a**.

	3a	**6a**	**16b**	**16j**	**25a**
CCDC no.	1022047	1022048	1022049	1022050	1022051
formula	$C_{28}H_{18}$	$C_{36}H_{33}$	$C_{36}H_{22}{\cdot}C_6H_6$	$C_{46}H_{42}$	$C_{32}H_{18}$
M_r	354.42	454.54	532.64	594.79	402.46
T [K]	100(2)	100(2)	100(2)	100(2)	100(2)
crystal system	triclinic	orthorhombic	monoclinic	triclinic	orthorhombic
space group	$P\bar{1}$	*Pbca*	$P2_1/c$	$P\bar{1}$	*Pccn*
Z	2	8	8	2	4
a [Å]	7.2764(4)	15.9909(10)	19.9061(17)	10.4145(7)	3.8982(4)
b [Å]	10.6347(5)	16.5090(10)	16.3419(13)	11.8605(6)	18.1566(17)
c [Å]	12.1668(6)	17.9379(9)	17.9187(15)	13.8603(9)	26.409(2)
α [°]	83.123(2)	90	90	77.237(3)	90
β [°]	79.033(2)	90	105.902(2)	76.768(3	90
γ [°]	74.640(2)°	90	90	83.744(3)	90
V [Å^3]	644.72(14)	4735.5(5)	5605.9(8)	1622.33(17)	1869.2(3)
R factor [%]	4.82	4.12	5.62	4.71	3.67

In the solid state, two molecules of **16b** and two benzene solvent molecules form two asymmetric units. The two species of molecules **16b** have very similar structural data. The π-orbital axis vector (POAV) pyramidalization angle is a useful metric of buckybowl curvature: its values for planar benzene and C_{60} are 0 and 11.6°, respectively.[20] As presented in Table 5, the POAV pyramidalization angle is highest at the hub carbon atoms of a corannulene core, at which it is 11.2°. This value exceeds the corresponding value for corannulene (8.2°). The bowl depth of the corannulene fragment in **16b** was determined as 1.10 Å, which also exceeds that of corannulene (0.87 Å). Molecules of **16b** cannot form columnar stacks (Figure 2). The important interaction was the CH/π interaction, for which the distance between the center of a corannulenyl benzenoid and

Table 5. Structural data of cyclopentacorannulene derivatives.[a]

	Parent[b]	**16 b**	**16 j**
POAV [°] (atoms 1, 2, 3)	9.3, 10.0, 10.9	9.7, 10.2, 11.0 9.7, 10.3, 11.2	9.7, 10.3, 11.5
bowl depth [Å]	1.06 [1.08]	1.08, 1.10 [1.08]	1.11 [1.08]
bond length [Å]			
a	1.344 [1.361]	1.353, 1.360 [1.361]	1.352 [1.361]
b	1.374 [1.395]	1.392, 1.387 [1.397]	1.386 [1.396]
c	1.467 [1.487]	1.493, 1.493 [1.498]	1.491 [1.498]
d	1.388 [1.370]	1.381,1.382 [1.391]	1.379 [1.390]

[a] The values were obtained by averaging the symmetry-related data. The optimized structures at the B3LYP/cc-pVDZ level are shown in brackets. Bowl depths determined from the corannulene core. [b] Ref. [14b].

a hydrogen of benzene was 2.88 Å. This value is slightly shorter than the sum of the van der Waals radii of the corresponding atoms (2.90 Å).[21]

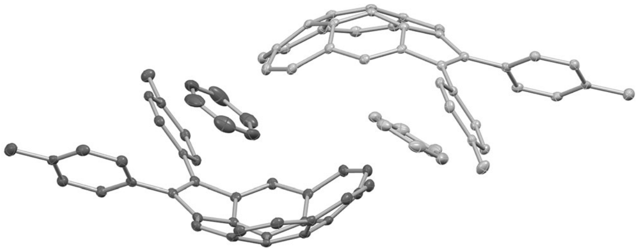
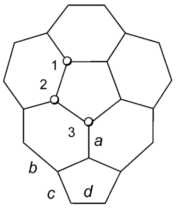


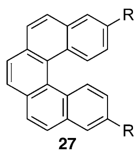
Figure 2. Crystal packing in **16 b**. Only carbon atoms are shown for clarity; the thermal ellipsoids are set at the 30 % probability level.

X-ray crystallography revealed that the maximum POAV angle and the bowl depth of the corannulene fragment in **16 j** were 11.5° and 1.11 Å, respectively. The former value is very close to that of C_{60}. All molecules of **16 j**, with concave faces, formed a "dimer" pair through CH/π interactions between isopropyl hydrogen and corannulene carbon atoms, and the short contact distances for these interactions were determined to be 2.84–2.89 Å (Figure 3). The distance between a methyl carbon atom and the center of the corannulenyl five-membered ring is 3.42 Å.

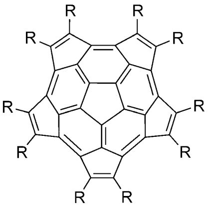
A significant difference between the parent[14b] and diaryl-substituted cyclopentacorannulenes **16** is in the molecular packing. Unlike **16 b**/**16 j**, all bowl molecules of the unsubstituted cyclopentacorannulene form quasi-bowl-in-bowl stacks, but crystals are apolar because half of the columns are oriented in opposite directions. Additionally, the curvature of the three cyclopentacorannulenes follows the order of **16 j** > **16 b** > parent compound, as verified by both the maximum POAV angle and bowl depth of the corannulenyl fragment. The lengths of some of the bonds in **16 b**/**16 j** significantly differed from those in the parent cyclopentacorannulene, as summarized in Table 5. To gain an insight into these structural differences, the optimized structures for three compounds were obtained by using DFT at the B3LYP/cc-pVDZ level. In contrast to the parent cyclopentacorannulene, the results for **16 b** and **16 j** agree more closely with crystallographic analysis. The significant structural derivation of the parent compound should be caused by the crystal packing and/or quasi-bowl-in-bowl stacks.



16



27



28

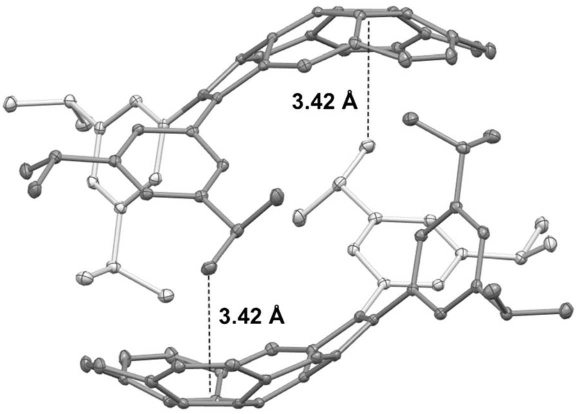


Figure 3. Crystal packing in **16 j**. Only carbon atoms are shown for clarity; the thermal ellipsoids are set at 30 % probability.

Compound **25 a** is not planar, as confirmed by X-ray analysis (Figure 4). The dihedral angle between the extremities (rings I and L) and the torsion angle measured for bay carbon atoms VII-VIII-IX-X were determined to be 23.8 and 26.3°, respectively. The nonbonded contact between carbon atoms VII and X was found to be 2.96 Å. The π–π stacks were observed in crystals of **25 a**. The molecules in each stack are slightly slipped from the stacking axis. Therefore, the separation between two neighboring molecules is 3.90 Å, but the shortest distance between any two closed carbon atoms is 3.44 Å.

The photoabsorption properties of selected compounds in CH_2Cl_2 (10 μM) at room temperature were studied (Table 6 and the Supporting Information), and they were found to be strongly influenced by the aromatic π system in the backbone. The cyclopentene annulation redshifts λ_{max}. For example, phen-

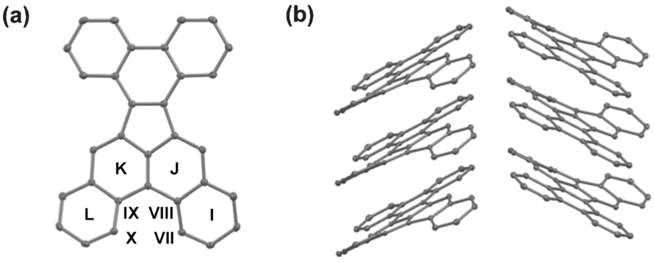


Figure 4. Illustration of the molecular structure (a) and crystal packing (b) in **25 a**. Only carbon atoms are shown for clarity; the thermal ellipsoids are set at the 30 % probability level.

Table 6. Physical properties of the cyclopentene-annulated products.[a]

	Compound	λ_{abs} [nm]	$E_{1/2}^{ox}$ [V]	$E_{1/2}^{red}$ [V]
1	**3a**	357, 376, 411 (sh)	1.11	–
2	**6a**	360, 402, 426	1.03	–
3	**8a**	377, 396, 450 (sh)	1.08	–
4	**14a**	390, 410	0.93, 1.27	−1.54
5	**16j**	349, 477 (sh)	0.90	–
6	**18a**	388, 409	1.06	–
7	**20b**	369, 381, 439 (sh)	0.95	–
8	**21b**	388, 410, 476 (sh)	0.94	–
9	**23b**	338, 354, 421 (sh)	0.94	–
10	**24a**	344, 379, 397, 464 (sh)	1.15	–

[a] Photophysical properties were measured at a concentration of about 10^{-5} M in CH_2Cl_2, and absorption bands over $\lambda = 340$ nm are listed. Redox properties were investigated with compounds (concentration ca. 10^{-3} M) in background electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in CH_2Cl_2. $E_{1/2}^{ox}$ and $E_{1/2}^{red}$ are half-wave potentials of the oxidative and reductive waves, respectively, with potentials versus the ferrocene (Fc/Fc^+) couple.

anthrene does not exhibit any significant absorption bands at wavelengths of greater than $\lambda = 300$ nm,[22] whereas **3a** exhibits strong absorptions at $\lambda = 376$ and 411 nm (Table 6, entry 1). Results concerning corannulene/cyclopentacorannulene **16j** ($\lambda = 320$[23] vs. 349 nm) and monoannulated **20b**/bisannulated **21b** ($\lambda = 439$ vs. 477 nm) also support this conclusion (Table 6, entries 5, 7, and 8). In contrast to **3a**, the oxidative cyclodehydrogenation product **24a** has a bathochromic shift of λ_{max} (Table 6, entries 1 and 10).

The redox properties of selected annulated products were characterized by cyclic voltammetry, and the results are shown in Table 6. The oxidation waves of all compounds are observed, but only **14a** exhibits a reversible reduction signal (Table 6, entry 4). All oxidation signals are irreversible,[24] which indicates the low thermodynamic stability of these cationic species. Compounds **24a** (1.15 V vs. Fc/Fc^+) and **16j** (0.90 V) have the highest and lowest oxidation potentials, respectively (Table 6, entries 5 and 10). The oxidation potential of the annulated products is not very sensitive to the aromatic π system in the backbone, as revealed by the following three examples. The members of each pair of compounds, annulated [4]- and [5]helicenes **8a**/**6a** (1.08 vs. 1.03 V), mono- and bisannulated chrysenes **20b**/**21b** (0.95 vs. 0.94 V), and **3a** and its cyclization product **24a** (1.11 vs. 1.15 V), have very similar oxidation potentials (Table 6, entries 1–3, 7, 8, and 10). The oxidation potentials for isomers **8a**/**18a** and **21b**/**23b** are (almost) identical (Table 6, entries 3, 6, 8, and 9).

Conclusion

We developed a simple method for synthesizing acephenanthrylene-based derivatives, including 1,2-disubstituted cyclopentacorannulenes, by the palladium-catalyzed annulation of 9-halophenanthrenes with alkynes. The diaryl-substituted acephenanthrylenes thus generated were converted into condensed arenes by oxidative cyclodehydrogenation. Because the bowl-to-bowl inversion barriers to cyclopentacorannulene derivatives have not been determined experimentally, the preparation and chiral resolution of suitable compounds are underway to study the inversion dynamics. In light of the good reactivity of **1**-Cl in annulation, this synthetic protocol opens up a possible route to construct the highly curved buckybowl **28** ($C_{30}R_{10}$)[25] from 1,3,5,7,9-pentachlorocorannulene.

Experimental Section

General procedures for the Pd-catalyzed annulation of a haloarene with an alkyne

Method A: A mixture of bromoarene (0.25 mmol), alkyne (0.30 mmol), $[PdCl_2(dppf)]\cdot CH_2Cl_2$ (20.4 mg, 25.0 µmol, 10 mmol%), DBU (114 mg, 0.75 mmol), CsOPiv (65.5 mg, 0.28 mmol), and NMP (1 mL) in a thick-walled Pyrex tube was purged with nitrogen for 5 min. The sealed tube was kept in an oil bath at 130 °C for 24 h. After cooling to room temperature, the suspension was filtered through a 3 cm thick layer of Celite. The Celite was rinsed well with CH_2Cl_2 (40 mL). The solution was washed with 2 N HCl (3× 10 mL), and dried over $MgSO_4$. The solvent of the filtrate was removed under reduced pressure, and the residue was subjected to chromatography on silica gel.

Method B: Similar to Method A, but the reaction was conducted with 1,4-dioxane (1 mL) and less $[PdCl_2(dppf)]\cdot CH_2Cl_2$ (10.2 mg, 12.5 µmol, 5 mmol%).

Method C: Similar to Method A, but the reaction was conducted with chloroarene (0.25 mmol), $[PdCl_2(PCy_3)_2]$ (9.2 mg, 25.0 µmol, 10 mmol%) and anisole (1 mL) at 150 °C for 36 h.

Acknowledgements

This work was supported by the Ministry of Science and Technology of Taiwan (NSC 101-2628M-006-002-MY3). We also thank Prof. Sue-Lein Wang and Pei-Lin Chen (National Tsing-Hua University, Taiwan) for the X-ray structure analyses.

Keywords: alkynes · annulation · macrocycles · palladium · synthesis design

[1] R. G. Harvey, *Polycyclic Aromatic Hydrocarbons*, Wiley, New York, **1997**.
[2] More than 10000 articles concerning acenaphthylene, based on a search performed by using SciFinder, have been published, whereas there have only been a few studies on aceanthrylene (122) and acephenanthrylene (330); for a review article of annulated PAHs, see: W.-C. Lin, Y.-T. Wu, in *Science of Synthesis, Vol. 45b* (Eds.: J. Siegel, Y. Tobe), Thieme, Stuttgart, **2010**, pp. 1017.
[3] a) M. Sarobe, L. W. Jenneskens, J. Wesseling, J. D. Snoeijer, J. W. Zwikker, *Liebigs Ann./Recueil* **1997**, 1207; b) M. Sarobe, L. W. Jenneskens, A. Kleij, M. Petroutsa, *Tetrahedron Lett.* **1997**, *38*, 7255; c) R. F. C. Brown, F. W. Eastwood, N. R. Wong, *Tetrahedron Lett.* **1993**, *34*, 3607.
[4] a) Y.-S. Chung, H. Kruk, O. M. Barizo, M. Katz, E. Lee-Ruff, *J. Org. Chem.* **1987**, *52*, 1284; b) S. Amin, G. Balanikas, K. Huie, N. Hussain, J. E. Geddie, S. S. Hecht, *J. Org. Chem.* **1985**, *50*, 4642; c) L. T. Scott, G. Reinhardt, N. H. Roelofs, *J. Org. Chem.* **1985**, *50*, 5886.
[5] J. Cioslowski, P. Piskorz, D. Moncrieff, *J. Org. Chem.* **1998**, *63*, 4051.
[6] For reviews on metal-catalyzed reactions for C–C bond formation, see: a) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147; b) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem. Int. Ed.* **2009**, *48*, 5094;

Angew. Chem. **2009**, *121*, 5196; c) L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem. Int. Ed.* **2009**, *48*, 9792; *Angew. Chem.* **2009**, *121*, 9976; d) C.-J. Li, *Acc. Chem. Res.* **2009**, *42*, 335; e) L. Yin, J. Liebscher, *Chem. Rev.* **2007**, *107*, 133; f) M. Wagner, *Angew. Chem. Int. Ed.* **2006**, *45*, 5916; *Angew. Chem.* **2006**, *118*, 6060; g) J.-P. Corbet, G. Mignani, *Chem. Rev.* **2006**, *106*, 2651; h) R. C. Larock, *Top. Organomet. Chem.* **2005**, *14*, 147; i) J. Tsuji, *Palladium Reagents and Catalysts*, 2nd ed., Wiley, Chichester, **2004**; j) *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: A. de Meijere, F. Diederich), 2nd ed., Wiley-VCH, Weinheim, **2004**; k) *Transition Metals For Organic Synthesis* (Eds.: M. Beller, C. Bolm), 2nd ed., Wiley-VCH, Weinheim, **2004**; l) *Handbook of Organopalladium Chemistry for Organic Synthesis* (Eds.: E. Negishi, A. de Meijere), Wiley, New York, **2002**.

[7] For palladium-catalyzed reactions, see: a) R. Grigg, P. Kennewell, A. Teasdale, V. Sridharan, *Tetrahedron Lett.* **1993**, *34*, 153; b) G. Dyker, *J. Org. Chem.* **1993**, *58*, 234; for the platinum-mediated reaction, see: c) R. A. Begum, N. Chanda, T. V. V. Ramakrishna, P. R. Sharp, *J. Am. Chem. Soc.* **2005**, *127*, 13494; for nickel-mediated conditions, see: d) J. S. Brown, P. R. Sharp, *Organometallics* **2003**, *22*, 3604.

[8] a) H. Dang, M. Levitus, M. A. Garcia-Garibay, *J. Am. Chem. Soc.* **2002**, *124*, 136; b) H. Dang, M. A. Garcia-Garibay, *J. Am. Chem. Soc.* **2001**, *123*, 355.

[9] C. L. Eversloh, Y. Avlasevich, C. Li, K. Müllen, *Chem. Eur. J.* **2011**, *17*, 12756.

[10] A. Beck, M. N. Bleicher, D. W. Crowe, *Excursions into Mathematics*, Worth, New York, **1969**.

[11] For reviews on bowl-shaped polyarenes (buckybowls), see: a) Y.-T. Wu, J. Siegel, *Top. Curr. Chem.* **2014**, *349*, 63; b) Y.-T. Wu, T.-C. Wu, M.-K. Chen, H.-J. Hsin, *Pure Appl. Chem.* **2014**, *86*, 539; c) B. M. Schmidt, D. Lentz, *Chem. Lett.* **2014**, *43*, 171; d) *Fragments of Fullerenes and Carbon Nanotubes: Designed Synthesis Unusual Reactions, and Coordination Chemistry* (Eds.: M. A. Petrukhina, L. T. Scott), Wiley, Hoboken, **2011**; e) S. Higashibayashi, H. Sakurai, *Chem. Lett.* **2011**, *40*, 122; f) T. Amaya, T. Hirao, *Chem. Commun.* **2011**, *47*, 10524; g) V. M. Tsefrikas, L. T. Scott, *Chem. Rev.* **2006**, *106*, 4868; h) Y.-T. Wu, J. S. Siegel, *Chem. Rev.* **2006**, *106*, 4843; i) A. Sygula, P. W. Rabideau, in *Carbon-Rich Compounds: From Molecules to Materials* (Eds.: M. M. Haley, R. R. Tykwinski), Willey-VCH, Weinheim, **2006**, p. 529.

[12] For a review on the regioselectivity of alkyne insertion (carbopalladation of alkynes), see ref. [6l], p. 1335.

[13] A proper name cyclopenta[*bc*]corannulene for **16** has been elucidated previously; for details, see: ref. [11d], p. 257. For other synthetic approaches to the parent cyclopentacorannulene, see: a) A. H. Abdourazak, A. Sygula, P. W. Rabideau, *J. Am. Chem. Soc.* **1993**, *115*, 3010; b) T. J. Seiders, E. L. Elliott, G. H. Grube, J. S. Siegel, *J. Am. Chem. Soc.* **1999**, *121*, 7804.

[14] a) T. J. Seiders, K. K. Baldridge, G. H. Grube, J. S. Siegel, *J. Am. Chem. Soc.* **2001**, *123*, 517; b) A. Sygula, P. W. Rabideau, *J. Chem. Soc. Chem. Commun.* **1994**, 1497.

[15] L. Zhai, R. Shukla, R. Rathore, *Org. Lett.* **2009**, *11*, 3474.

[16] H.-G. Franck, H. Buffleb, *Liebigs Ann. Chem.* **1967**, *701*, 53.

[17] CCDC-1022047 (**3a**), 1022048 (**6a**), 1022049 (**16b**), 1022050 (**16j**), 1022051 (**25a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[18] M. I. Kay, Y. Okaya, D. E. Cox, *Acta Crystallogr. Sect. B* **1971**, *27*, 26.

[19] O. Songis, J. Míšek, M. B. Schmid, A. Kollárovič, I. G. Stará, D. Šaman, I. Císařová, I. Starý, *J. Org. Chem.* **2010**, *75*, 6889.

[20] a) R. C. Haddon, L. T. Scott, *Pure Appl. Chem.* **1986**, *58*, 137; b) R. C. Haddon, *Acc. Chem. Res.* **1988**, *21*, 243; c) R. C. Haddon, *J. Am. Chem. Soc.* **1990**, *112*, 3385; d) R. C. Haddon, *Science* **1993**, *261*, 1545.

[21] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, **1960**.

[22] Y. Nakamura, T. Mita, J. Nishimura, *Tetrahedron Lett.* **1996**, *37*, 3877.

[23] Y.-T. Wu, D. Bandera, R. Maag, A. Linden, K. K. Baldridge, J. S. Siegel, *J. Am. Chem. Soc.* **2008**, *130*, 10729.

[24] Although some oxidation signals of the studied compounds seem reversible, their peak cathodic currents (i_{pc}) and anodic currents (i_{pc}) are not identical.

[25] K. K. Baldridge, J. S. Siegel, *Theoret. Chem. Acc.* **1997**, *97*, 67.

Received: October 21, 2014

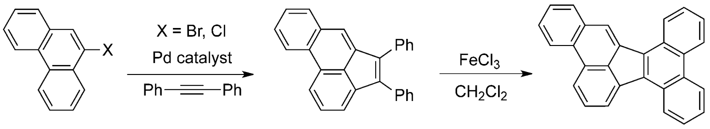
FULL PAPER

Macrocycles

*E.-C. Liu, M.-K. Chen, J.-Y. Li, Y.-T. Wu**

■■–■■

Palladium-Catalyzed Annulation of 9-Halophenanthrenes with Alkynes: Synthesis, Structural Analysis, and Properties of Acephenanthrylene-Based Derivatives



Put a ring on it: The palladium-catalyzed annulation of 9-halophenanthrenes with alkynes produced 4,5-disubstituted acephenanthrylenes (see scheme). The annulated diphenyl-substituted acephenanthrylene derivatives were converted into phenanthro[9,10-*e*]acephenanthrylenes by oxidative cyclodehydrogenation. The photophysical and electrochemical properties of selected compounds were investigated.