Zethrenes

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Synthesis, Structure, and Photophysical Properties of Dibenzo-[*de,mn*]naphthacenes**

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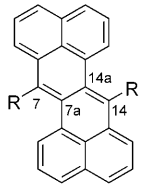
Dibenzo[*de*,*mn*]naphthacene (zethrene, **1a**, R = H) is a member of the benzenoid hydrocarbon family,[1] and has an interesting structure with respect to the formal definitions of aromaticity. The central two six-membered rings in zethrene (**1a**) cannot present aromaticity associated with the Kekulé structure. Based on Clar's aromatic sextet theory,[2] the π-electron sextets of the two periphery naphthalenes and the central butadiene moiety (i.e. C7, C7a, C14, and C14a) can be identified as "essential"[3] (benzene-like) and "fixed"[2] (localized) carbon–carbon double bonds, respectively.[4] Therefore, the π-electrons in the central two six-membered rings are localized and their index of local aromaticity[5] and induced π-electron currents[6] are much lower than those of a normal aromatic ring. However, no direct experimental evidence, such as an X-ray structure, is currently available to confirm the computational results. Although it can be viewed as weakly coupled double naphthalene units,[5c] zethrene and its derivatives exhibit interesting physical properties, which may have potential applications as organic materials, including electroluminescent devices[7] and organic transistors.[8] Theoretical investigations demonstrate that zethrene (**1a**) has singlet biradical character[9b] and is also a suitable building block for nonlinear optical materials[9] and near-infrared absorbing pigments.[10] These versatile physical properties have yet to be extensively explored because of the difficulty involved in synthesizing these molecules.



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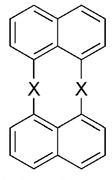
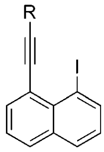


2 (X = CH=CH)
3 (X = C≡C)
4 (X = CH_2SCH_2)



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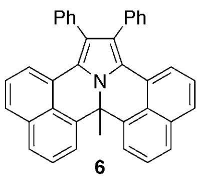
Zethrene (**1a**) was first prepared from chrysene through an inefficient route by Clar et al. in 1955.[11] Other synthetic approaches involving several steps have been also elucidated. Their key steps mainly involve either the transannular reaction of cyclodeca[1,2,3-*de*:6,7,8-*d*′*e*′]dinaphthalene (**2**)[12] and 7,8,15,16-tetradehydrocyclodeca[1,2,3-*de*:6,7,8-*d*′*e*′]dinaphthalene (**3**),[13] or the cyclization of 7*H*,9*H*,16*H*,18*H*-dinaphtho[1,8-*cd*:1′,8′-*ij*][1,7]dithiacyclododecane (**4**).[14] However, preparation of functionalized zethrenes using these protocols is inconvenient. Hence, the development of an efficient synthetic method is necessary. Numerous polyaromatic hydrocarbons can be accessed by metal-catalyzed annulation of haloarenes.[15] Accordingly, we observed that zethrenes **1** can be obtained from 1-ethynyl-8-iodonaphthalenes **5**[16] in the presence of Pd catalysts.

The synthesis of zethrene **1b** (R = Ph) from 1-iodo-8-(phenylethynyl)naphthalene (**5b**) was explored under several reaction conditions. The catalytic systems for the generation of dibenzo[*a*,*e*]pentalenes by the cyclodimerization of 1-ethynyl-2-halobenzenes[15f,g] are not efficient for producing **1b**. Therefore, reaction conditions for metal-catalyzed annelation[15a–e] or dimerization[17] of iodoarenes were utilized and it was determined that condition **F** is more effective than **A**–**E** (Table 1). Under condition **E**, **5b** gave an acetonitrile-mediated cycloadduct **6** as the major product (entry 5 in Table 1).[18] Fine-tuning condition **F** by varying the Pd catalyst, phosphine ligand, and solvent did not increase the yield of **1b** (entries 6–11 in Table 1). Under the best condition, the desired product **1b** was obtained in 73 %



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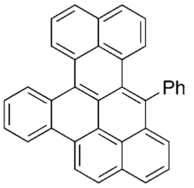

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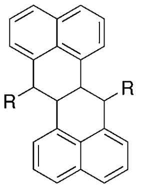

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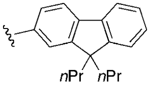
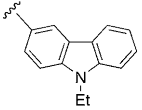
Table 1: Optimization of reaction conditions for preparation of **1b**.[a]

Entry	Condition	Ligand ([mol%])	Solvent	Yield [%]
1	A	–	*p*-xylene	34, traces[b]
2	B	–	DMF	38
3	C	–	CH_3CN	32[c]
4	D	–	2-pentanone	< 37[d,e]
5	E	–	CH_3CN	3[f]
6	F	–	*o*-xylene	14
7	F	P(2-furyl)$_3$ (15)	*o*-xylene	73
8	F	P(2-furyl)$_3$ (15)	CH_3CN	26[c]
9	F	PPh_3 (15)	*o*-xylene	29
10	F	PCy_3 (15)	*o*-xylene	45
11	F	P(2-furyl)$_3$ (15)	*o*-xylene	< 37[e,g]

[a] Amounts of catalysts and additives relative to alkyne **5b** (0.5 mmol): Condition A: $Pd(OAc)_2$ (5 mol%), AgOAc (1 equiv), 110 °C, 36 h.[15a] B: $Pd(OAc)_2$ (5 mol%), K_2CO_3 (4 equiv), nBu_4NBr (2 equiv), 130 °C, 20 h.[15b] C: $Pd(OAc)_2$ (5 mol%), K_2CO_3 (2.4 equiv), 120 °C, 36 h.[18] D: $Pd(OAc)_2$ (5 mol%), $NaOAc{\cdot}H_2O$ (2 equiv), LiCl (0.5 equiv), 130 °C, 40 h.[15d] E: $[NiBr_2(dppe)]$ (5 mol%), Zn (3 equiv), 110 °C, 12 h.[15e] F: $Pd(OAc)_2$ (5 mol%), Ag_2CO_3 (1 equiv), 130 °C, 36 h.[15c] [b] AgOAc (2 equiv) was used. [c] A mixture of **1b** and **7** was obtained. [d] **5b** (63%) remained. [e] Yield according to NMR spectroscopy. [f] **6** (84%) was obtained. [g] $[Pd_2(dba)_3]$ (2.5 mol%; dba = *trans,trans*-dibenzylideneacetone) was used. **5b** (63%) remained.

Table 2: Preparation of compounds **1** from alkynes **5**.[a]

Entry	Alkyne	R	Product	Yield [%]
1	**5b**	Ph	**1b**	73
2	**5c**	4-FC_6H_4	**1c**	56[b]
3	**5d**	4-ClC_6H_4	**1d**	36[b]
4	**5e**	4-BrC_6H_4	**1e**	24[b]
5	**5f**	4-$CH_3C_6H_4$	**1f**	46,[c] 35[b]
6	**5g**	4-$CF_3C_6H_4$	**1g**	59[b]
7	**5h**	4-$OCH_3C_6H_4$	**1h**	22,[b] 61[d]
8	**5i**	4-$CO_2CH_3C_6H_4$	**1i**	40
9	**5j**	2,6-$Cl_2C_6H_3$	**1j**	26[d]
10	**5k**	3,5-$(CH_3)_2C_6H_3$	**1k**	34[b]
11	**5l**	2,4,6-$(CH_3)_3C_6H_2$	**1l**	24,[b] 26[d]
12	**5m**	3,4,5-$F_3C_6H_2$	**1m**	51[b]
13	**5n**		**1n**	44[d]
14	**5o**	9-anthracenyl	**1o**	14[d]
15	**5p**		**1p**	16
16	**5q**	$Si(CH_3)_3$	**1a**	20
17	**5r**	nC_4H_9	**1r**	20
18	**5s**, **5t**	tC_4H_9, $C{\equiv}CPh$	**1s**, **1t**	0

[a] Reaction was conducted with alkyne **5** (0.5 mmol) in *o*-xylene (condition F). [b] Ag_2CO_3 (1.5 equiv) was used. [c] **5f** (33%) was recovered. [d] $Pd(OAc)_2$ (10 mol%), Ag_2CO_3 (1.5 equiv), and P(2-furyl)$_3$ (30 mol%) were used.

yield (entry 7 in Table 1). Notably, reactions in acetonitrile under either condition **C** or **F** gave a mixture of **1b** and 11-phenylbenzo[*a*]naphtha[2,1,8-*cde*]perylene (**7**),[16,19] which was observed as the minor product and whose structure was verified by the X-ray crystal analysis. Compound **7** should be generated from **1b** by the cyclodehydrogenation.[20]

The reactivity of several alkynes **5** for the preparation of zethrenes **1** was investigated under the optimized conditions described above (condition **F**). Most of them are less reactive than **5b** (Table 2). It was necessary to increase the amount of silver carbonate and/or Pd catalysts (10 mol%) to ensure complete consumption of the starting material. Aryl-substituted reactants are more appropriate than alkyl and phenylethynyl analogues in this reaction. The steric congestion and the electronic properties of the substituents strongly affect the yield. The electron-deficient aryl substituent increased the reaction efficiency relative to the electron-rich moiety (entries 2–8, Table 2). As expected, bulky groups, such as mesityl, 9-anthracenyl, and 2,6-dichlorophenyl, gave unsatisfactory results, and *tert*-butyl-substituted alkyne **5s** did not undergo the cyclodimerization (entries 9, 11, 14, and 18, Table 2). 1-Iodo-8-(trimethylsilylethynyl)naphthalene (**5q**) formed zethrene (**1a**) in low yield through the in situ desilylation of 7,14-bis(trimethylsilyl)zethrene (entry 16, Table 2).[21] Cycloadducts **1** cannot be obtained in good yields for two possible reasons: 1) The structure is significantly out-of-plane and 2) zethrenes are unstable and they significantly decompose in solution after a few days.[16,22] Additionally, 5-bromo-6-(phenylethynyl)acenaphthene did not give the corresponding cycloadduct. The crossed cycloaddition between **5b** and 1,2-diphenylacetylene was inefficient and only **1b** was obtained.

X-ray-quality crystals of **1a**, **1b**, **1l**, and **1r** were obtained by slow evaporation of the CH_2Cl_2/MeOH solvent mixture at 4 °C.[16,19] To the best of our knowledge, these are the first examples of crystal structures of this compound class. Zethrene (**1a**) is planar, whereas 7,14-disubstituted zethrenes **1b**, **1l**, and **1r** deviate significantly from planarity (approximately 45°)[16] because they contain two substructures of 4-substituted phenanthrene (Figure 1).[23] The central two six-membered rings in both planar and twisted zethrenes **1** exhibit remarkable bond alternation with a range of 0.070–0.116 Å,[16,24] and, accordingly, they lack aromaticity.

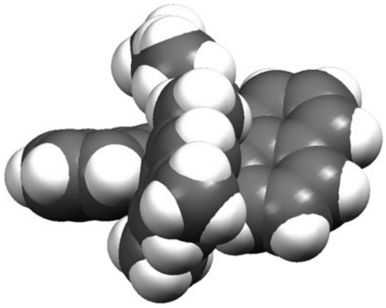
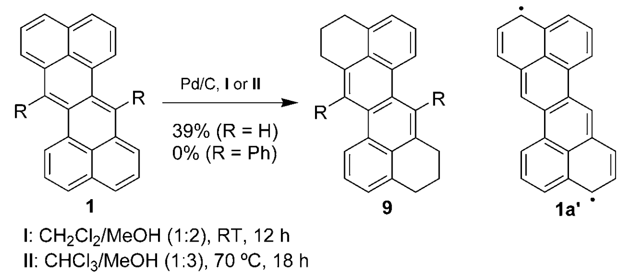


Figure 1. Molecular structure of **1l** as a space-filling model.

The character of two fixed double bonds in **1** was examined by Pd-catalyzed hydrogenation under ambient pressure (condition **I**, Scheme 1), and tetrahydrozethrenes **8** are the expected products. However, compound **1a** generated a complex mixture, and hexahydrozethrene was identified to be the major product based on GC–MS analysis. After careful purification of the product, the structure was determined to



Scheme 1. Palladium-catalyzed hydrogenation of zethrenes **1**.

be 4,5,6,11,12,13-hexahydrozethrene (**9a**, R = H), which was verified by X-ray crystal analysis.[19] In addition, **9a** was predicated to be the final hydrogenation product of zethrene (**1a**) almost 60 years ago.[4b] Although the mechanism of the formation of **9a** is not clear, Coulson et al. suggested that **9a** is formed via **8a** (R = H) through hydrogenation and hydrogen shift.[4b] Alternatively, the singlet biradical property of zethrene (**1a**), as shown by the structure **1a′**,[9b] also provides the possibility to generate **9a** by hydrogenation. In contrast, when compound **1b** was conducted under conditions either **I** or **II**, it remained unchanged. This is perhaps caused by the crowdedness in central butadiene moiety and the twisted structure, which could decrease the biradical property.

The photophysical properties of zethrenes are strongly influenced by the conformation and substituents (Table 3). The twisted backbone would cause the absorption and emission band to shift hypsochromically, and this prediction is verified by comparing compounds **1a** and **1r**. In contrast to its diaryl and dialkyl analogues, 7,14-bis(phenylethynyl)zethrene (**1t**) displays significantly red-shifted absorption and emission bands, and the more-extended π system should be responsible for this phenomenon (entries 2–10 in Table 3). In the subclass of the diaryl-substituted zethrenes, the effects of aryl moieties should not be important because the X-ray structures demonstrate that two aryl rings are twisted from the zethrene core (entries 2–9 in Table 3). Accordingly, their photophysical properties are very similar.

Table 3: Photophysical properties of zethrenes.[a]

Entry	Cpd	$\lambda_{\max(\mathrm{abs})}$ [nm] (ε [$\mathrm{M^{-1}\,cm^{-1}}$])	$\lambda_{\max(\mathrm{em})}$ [nm]	Φ_{PL}
1	**1a**	544 (42 900)[b]	571	0.34
2	**1b**	523 (29 000)	569	0.38
3	**1h**	526 (25 900)	578	0.34
4	**1i**	521 (43 600)	577	0.25
5	**1l**	521 (35 500)	541	0.75
6	**1m**	514 (38 000)	565	0.28
7	**1n**	526 (26 800)	580	0.32
8	**1o**	526 (27 700)	552	0.60
9	**1p**	531 (27 800)	593	0.31
10	**1r**	499 (37 400)	525[c]	–[c]
11	**1t**	576 (31 600)	610	0.07[d]

[a] All samples were measured in CH_2Cl_2 at 25 °C. Rhodamine B in EtOH ($\Phi_{\mathrm{PL}} = 0.70$; $\lambda_{\mathrm{ex}} = 500$ nm)[25] was used as the standard for the determination of quantum yields. [b] In benzene, $\lambda_{\mathrm{abs}} = 550$ nm.[11] [c] Excitation at 480 nm. [d] Ref. [13d].

In conclusion, this investigation developed a simple method for synthesizing zethrenes. The central two six-membered rings of zethrenes are confirmed to lack aromaticity. Further studies of their physical properties and their applications as organic materials are in progress.

Experimental Section

Preparation of **1b**: A mixture of alkyne **5b** (177 mg, 0.50 mmol), P(2-furyl)$_3$ (18.0 mg, 77.6 μmol), Ag_2CO_3 (138 mg, 0.50 mmol), $Pd(OAc)_2$ (5.60 mg, 25.0 μmol), and *o*-xylene (5 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 36 h. The mixture was cooled to room temperature and filtered over celite, and the solvent of the filtrate was removed under reduced pressure. The residue was subjected to chromatography on silica gel; eluting with hexane/CH_2Cl_2 (4:1) afforded **1b** (83.0 mg, 73 %) as red solids. A suitable crystal of **1b** [m.p. 331–332 °C (dec.)] for the X-ray diffraction analysis was grown from degassed CH_2Cl_2/MeOH at 4 °C. ^1H NMR (300 MHZ, $CDCl_3$): $\delta = 6.98$–7.04 (brs, 4H), 7.27–7.32 (m, 8H), 7.40 ppm (brs, 10H). ^1H NMR (300 MHZ, C_6D_6): $\delta = 7.02$ (t, $^3J = 7.8$ Hz, 2H), 7.14 (t, $^3J = 7.7$ Hz, 2H), 7.21 (brs, 4H), 7.25 (brs, 6H), 7.26 (d, $^3J = 7.7$ Hz, 2H), 7.42–7.49 ppm (m, 6H). ^{13}C NMR (75.5 MHZ, C_6D_6, plus DEPT): $\delta =$ 124.8 (CH), 125.6 (CH), 126.4 (CH), 127.1 (CH), 127.3 (CH), 127.9 (CH), 129.5 (CH), 129.9 (CH), 130.0 (C_{quat}), 131.7 (C_{quat}), 132.0 (CH), 132.7 (C_{quat}), 133.3 (C_{quat}), 135.0 (C_{quat}), 137.4 (C_{quat}), 140.7 ppm (C_{quat}). EI MS (70 eV), *m/z* (%): 454 (100) [M^+], 422 (34), 328 (29), 57 (39). HRMS (EI) calcd for $C_{36}H_{22}$: 454.1722; found: 454.1728.

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[18] The structure of **6** was verified by X-ray crystal analysis (T.-C. Wu, Y.-T. Wu, unpublished results).

[19] X-ray crystallographic data for **1a** (CCDC 762793), **1b** (CCDC 762790), **1l** (CCDC 762792), **1r** (CCDC 762794), **7** (CCDC 762791), and **9a** (CCDC 771823) 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.

[20] In the presence of Pd catalysts and silver salts, hexaphenylbenzene undergoes the partial cyclodehydrogenation to generate 1,2,3,4-tetraphenyltriphenylene; see: a) Y.-T. Wu, K.-H. Huang, C.-C. Shin, T.-C. Wu, *Chem. Eur. J.* **2008**, *14*, 6697. A cycloadduct generated via **1b** through the full cyclodehydrogenation was not observed. Reviews for Lewis acid-mediated cyclodehydrogenation of polycyclic aromatic hydrocarbons: b) M. D. Watson, A. Fechtenkötter, K. Müllen, *Chem. Rev.* **2001**, *101*, 1267; c) J. Wu, W. Pisula, K. Müllen, *Chem. Rev.* **2007**, *107*, 718.

[21] Y.-H. Kung, Y.-S. Cheng, C.-C. Tai, W.-S. Liu, C.-C. Shin, C.-C. Ma, Y.-C. Tsai, T.-C. Wu, M.-Y. Kuo, Y.-T. Wu, *Chem. Eur. J.* **2010**, *16*, 5909.

[22] It was reported that zethrene (**1a**) is air- and light-sensitive (Ref. [11]). When compound **1b** was irradiated with a sunlight lamp (250 W) at room temperature under aerobic conditions overnight (approximately 12 h), **1b** was completely decomposed. An orange-yellow compound ($C_{36}H_{22}O_2$) was isolated in 92 % yield. Unfortunately, the accurate structure cannot be determined on the basis of ^{1}H and ^{13}C NMR and MS spectra. Crystallization of this compound was not successful because it slowly decomposed.

[23] Phenanthrene with small displacements from exact planarity: a) M. I. Kay, Y. Okaya, D. E. Cox, *Acta Crystallogr. Sect. B* **1971**, *27*, 26. Some 4,5-disubstituted phenanthrenes deviate significantly from planarity: b) R. Cosmo, T. W. Hambley, S. Sternhell, *J. Org. Chem.* **1987**, *52*, 3119; c) F. Imashiro, A. Saika, Z. Taira, *J. Org. Chem.* **1987**, *52*, 5727; d) R. N. Armstrong, H. L. Ammon, J. N. Darnow, *J. Am. Chem. Soc.* **1987**, *109*, 2077. 6,8,15,17-Tetraphenyl-1.18,4.5,9.10,13.14-tetrabenzoheptacene, which contains phenanthrene substructures, is a twisted acene: e) H. M. Duong, M. Bendikov, D. Steiger, Q. Zhang, G. Sonmez, J. Yamada, F. Wudl, *Org. Lett.* **2003**, *5*, 4433. A recent review for twisted acenes: f) R. A. Pascal, Jr., *Chem. Rev.* **2006**, *106*, 4809.

[24] Bond alternation (or localization) in aromatic systems is also a method to distinguish between benzene and cyclohexatriene. For example, the bond alternation in tris(bicyclo-[2.1.1]hexeno)benzene is estimated to be 0.089 Å, see: a) N. L. Frank, K. K. Baldridge, J. S. Siegel, *J. Am. Chem. Soc.* **1995**, *117*, 2102; b) H.-B. Bürgi, K. K. Baldridge, K. Hardcastle, N. L. Frank, P. Gantzel, J. S. Siegel, J. Ziller, *Angew. Chem.* **1995**, *107*, 1575; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1454. Epoxidation and cyclopropanation of tris(bicyclo[2.1.1]hexeno)benzene give triexpoxide and tercyclopropane, respectively, see: c) A. Matsuura, K. Komatsu, *J. Am. Chem. Soc.* **2001**, *123*, 1768.

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