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

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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.

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] 7,8,15,16-tetradehydrocyclodeca[1,2,3-de:6,7,8-d'e']diand naphthalene (3),^[13] or the cyclization of 7H,9H,16H,18H-**(4)**.^[14] dinaphtho[1,8-cd:1',8'-ij][1,7]dithiacyclododecane 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 $\mathbf{5}^{[16]}$ in the presence of Pd catalysts.

The synthesis of zethrene **1b** ($\mathbf{R} = \mathbf{Ph}$) 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 1ethynyl-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 acetonitrilemediated 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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Table 1: Optimization of reaction conditions for preparation of 1b.^[a]

Entry	Condition	Ligand ([mol%])	Solvent	Yield [%]
1	A	_	<i>p</i> -xylene	34, traces ^[b]
2	В	-	DMF	38
3	С	-	CH₃CN	32 ^[c]
4	D	-	2-pentanone	$< 37^{[d,e]}$
5	E	-	CH ₃ CN	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 ₃ CN	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%), K₂CO₃ (4 equiv), *n*Bu₄NBr (2 equiv), 130°C, 20 h.^[15b] C: Pd(OAc)₂ (5 mol%), K₂CO₃ (2.4 equiv), 120°C, 36 h.^[18] D: Pd(OAc)₂ (5 mol%), NaOAc·H₂O (2 equiv), LiCl (0.5 equiv), 130°C, 40 h.^[15d] E: [NiBr₂(dppe)] (5 mol%), Zn (3 equiv), 110°C, 12 h.^[15e] F: Pd(OAc)₂ (5 mol%), Ag₂CO₃ (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] [Pd₂(dba)₃] (2.5 mol%; dba = *trans,trans*-dibenzylideneacetone) was used. **5b** (63%) remained.

yield (entry 7 in Table 1). Notably, reactions in acetonitrile under either condition **C** or **F** gave a mixture of **1b** and 11phenylbenzo[*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 insitu 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

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

Entry	Alkyne	R	Product	Yield [%]
1	5 b	Ph	1b	73
2	5c	$4-FC_6H_4$	1c	56 ^[b]
3	5 d	4-ClC ₆ H₄	1d	36 ^[b]
4	5 e	$4-BrC_6H_4$	le	24 ^[b]
5	5 f	$4-CH_3C_6H_4$	1 f	46, ^[c] 35 ^[b]
6	5 g	$4-CF_3C_6H_4$	1g	59 ^[b]
7	5 h	4-OCH ₃ C ₆ H ₄	1 h	22, ^[b] 61 ^[d]
8	5 i	4-CO ₂ CH ₃ C ₆ H ₄	1i	40
9	5 j	2,6-Cl ₂ C ₆ H ₃	1j	26 ^[d]
10	5 k	3,5-(CH ₃) ₂ C ₆ H ₃	1 k	34 ^[b]
11	51	2,4,6-(CH ₃) ₃ C ₆ H ₂	11	24, ^[b] 26 ^[d]
12	5 m	3,4,5-F ₃ C ₆ H ₂	1 m	51 ^[b]
13	5 n	iz nPr nPr	ln	44 ^[d]
14	5 o	9-anthracenyl	10	14 ^[d]
15	5 p	""r" N Ét	٦p	16
16	5 q	Si(CH ₃) ₃	la	20
17	5 r	nC ₄ H ₉	1r	20
18	5 s, 5 t	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] **5 f** (33%) was recovered. [d] $Pd(OAc)_2$ (10 mol%), Ag_2CO_3 (1.5 equiv), and P(2-furyl)₃ (30 mol%) were used.

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 sixmembered 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 11 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

Table 3: Photophysical properties of zethrenes.[a]

Cpd	$\lambda_{\max(abs)}$ [nm] (ε [M ⁻¹ cm ⁻¹]	λ _{max(em)} [nm]	$\Phi_{ m PL}$
la	544 (42 900) ^[b]	571	0.34
1Ь	523 (29000)	569	0.38
1 h	526 (25 900)	578	0.34
1i	521 (43 600)	577	0.25
11	521 (35 500)	541	0.75
lm	514 (38000)	565	0.28
ln	526 (26800)	580	0.32
10	526 (27700)	552	0.60
1p	531 (27800)	593	0.31
lr	499 (37400)	525 ^[c]	_[c]
1t	576 (31 600)	610	0.07 ^[d]
	Cpd 1a 1b 1h 1i 11 1m 1n 1o 1p 1r 1t	$\begin{array}{c c} Cpd & \lambda_{\max(abs)} \ [nm] \\ (\varepsilon \ [M^{-1} \ cm^{-1}] \end{array} \\ \hline 1a & 544 \ (42 \ 900)^{[b]} \\ 1b & 523 \ (29 \ 000) \\ 1h & 526 \ (25 \ 900) \\ 1i & 521 \ (43 \ 600) \\ 1i & 521 \ (35 \ 500) \\ 1m & 514 \ (38 \ 000) \\ 1n & 526 \ (26 \ 800) \\ 1o & 526 \ (27 \ 700) \\ 1p & 531 \ (27 \ 800) \\ 1r & 499 \ (37 \ 400) \\ 1t & 576 \ (31 \ 600) \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

[a] All samples were measured in CH₂Cl₂ at 25 °C. Rhodamine B in EtOH (Φ_{PL} =0.70; λ_{ex} =500 nm)^[25] was used as the standard for the determination of quantum yields. [b] In benzene, λ_{abs} =550 nm.^[11] [c] Excitation at 480 nm. [d] Ref. [13d].

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. In conclusion, this investigation developed a simple method for synthesizing zethrenes. The central two sixmembered 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(2furyl)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/CH2Cl2 (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 CH₂Cl₂/MeOH at 4°C. ¹H NMR (300 MHZ, CDCl₃): $\delta = 6.98-7.04$ (brs, 4H), 7.27-7.32 (m, 8H), 7.40 ppm (brs, 10H). ¹H NMR (300 mHz, C₆D₆): $\delta = 7.02$ (t, ³J = 7.8 Hz, 2 H), 7.14 (t, ³J = 7.7 Hz, 2H), 7.21 (brs, 4H), 7.25 (brs, 6H), 7.26 (d, ${}^{3}J = 7.7$ Hz, 2H), 7.42–7.49 ppm (m, 6H). ¹³С NMR (75.5 мнz, C₆D₆, 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 C₃₆H₂₂: 454.1722; found: 454.1728.

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