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Tetradehydrodinaphtho[10]annulene and its transformation into zethrene: A hitherto unknown dehydroannulene and a forgotten aromatic hydrocarbon*

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Abstract: The synthesis and structural characterization of a hitherto unknown tetradehydrodinaphtho[10]annulene, which had eluded isolation since attempts initiated during the late 1960s, was achieved. Moreover, the dehydroannulene was transformed into stable derivatives of zethrene, which was first reported in 1955, but forgotten for a long time. These molecules are substituted at the 7,14-positions and open the door to the zethrene family for potential application as optoelectronic materials.

Keywords: alkynes; cross-coupling reactions; dehydroannulenes; polycyclic aromatic hydrocarbons; transannular cyclization.

INTRODUCTION

The last two decades have seen a renaissance of annulene chemistry thanks to development of Pd-catalyzed cross-coupling reactions between sp and sp^2 carbon centers [1]. This new synthetic method made it possible not only to prepare previously known annulenes much more efficiently than before but also to create new macrocycles which had not been achieved by means of traditional synthetic methods. As a result, a large number of tailor-made annulenes have been prepared to investigate their physical properties such as self-assembly, sensing, and optoelectronic properties [2].

Recently, we succeeded in the first synthesis of the long-sought tetradehydrodinaphtho[10]annulene (**1**), which had eluded isolation since attempts initiated during the late 1960s, utilizing Pd-catalyzed cross-coupling reaction as the pivotal step [3]. Moreover, **1** was readily transformed via transannular cyclization into 7,14-diiodozethrene (**2c**), which in turn was converted to bis(phenylethynyl) derivative **2d**. Zethrene (**2a**) itself is a light- and air-sensitive hydrocarbon first synthesized in 1955 [4], but it had not attracted particular interest for many years before theoretical predictions for second-order hyperpolarizability and singlet diradical character were reported recently. Herein, we present a short review on these classic molecules in *novel* aromatic chemistry, i.e., **1** and 7,14-disubstituted derivatives of **2a**, from renewed points of view.

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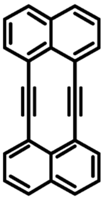
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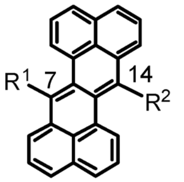
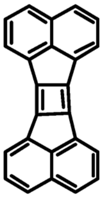


2a $R^1 = R^2 = H$
2b $R^1 = H, R^2 = I$
2c $R^1 = R^2 = I$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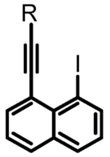
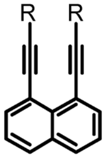
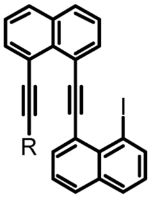


4a R = Cu
4b R = H
4c $R = SiMe_3$



5a R = Cu
5b R = H
5c $R = SiMe_3$

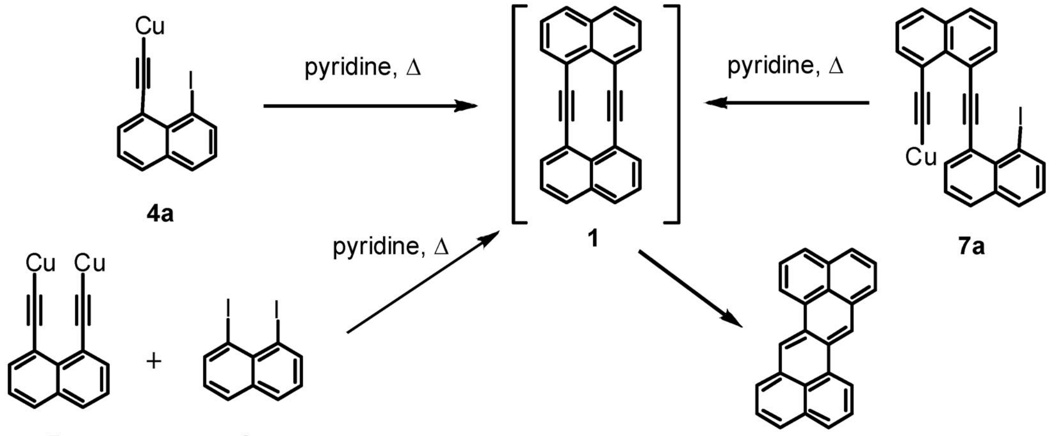


7a R = Cu
7b $R = SiMe_3$

TETRADEHYDRODINAPHTHO[10]ANNULENE

During the late 1960s, two leading groups in annulene chemistry, one led by Staab [5] and the other by Sondheimer [6], attempted the synthesis of tetradehydrodinaphtho[10]annulene (**1**), one of the target compounds in the field at the time. This compound attracted interest not only as a member of elusive dehydro[10]annulenes [7] but also in view of possible transformation to its valence isomer **3** having a cyclobutadiene core due to the presence of proximate triple bonds [5].

Both groups employed cross-coupling reactions of Cu(I) acetylides with iodoarenes both having naphthalene units in boiling pyridine either in an intermolecular manner, i.e., dimerization of **4a** or cross-coupling of **5a** and **6** [5], or intramolecularly from **7a** [6]. Instead of **1**, both groups isolated zethrene (**2a**, dibenzo[*de*,*mn*]naphthacene) [4] in variable amounts (22–52 % yields: Scheme 1) [8]. A formation mechanism was suggested, involving a diradical intermediate formed by spontaneous transannular cyclization of **1** [5b,6]. However, the mechanism has not been proved yet. We envisioned that, if the Pd-catalyzed cross-coupling reactions were conducted under mild conditions, **1** would "survive" the cyclization conditions and then would be isolated. Moreover, we expected that, once isolated, **1** would serve as a good precursor to zethrene derivatives [9]. In this section, we present the first successful synthesis of dehydroannulene **1** and its magnetic and structural properties.



Scheme 1 Attempted synthesis of tetradehydrodinaphtho[10]annulene (**1**) and unexpected formation of zethrene (**2a**).

Synthesis of tetradehydrodinaphtho[10]annulene

Though attempts to prepare **1** by coupling of 1,8-diethynylnaphthalene (**5b**) [5,6,10] and 1,8-diiodonaphthalene (**6**) or self-coupling of 1-ethynyl-8-iodonaphthalene (**4b**) [5] under the standard Sonogashira–Hagihara reaction conditions failed, the cross-coupling of **5c** and **6** with in situ deprotection by 1 equiv of aqueous NaOH [11] gave **1** in 22 % yield [3], together with a small amount (4 %) of monoiodozethrene **2b** [6]. When the reaction was undertaken without NaOH, the yield of **1** dropped to 6 % and mono-coupling product **7b** was obtained as the major product (33 %). Though the reason for the successful cyclization under the in situ desilylation protocol is not fully understood, the reaction times to the deprotection and Pd-catalyzed cross-coupling steps play a crucial role.

It should be pointed out that **1** is easily handled without visible decomposition at room temperature, in contrast to the parent tetradehydro[10]annulene whose half-life was reported to be 25 min at –90 °C [7e].

Magnetic and structural properties of tetradehydrodinaphtho[10]annulene

In the ^{1}H NMR spectrum, the aromatic protons of **1** resonate at 7.80 (dd), 7.71 (dd), and 7.45 (dd) ppm, whereas the corresponding signals of 1,8-diethynylnaphthalene (**5b**) appear at 7.85–7.80 (m) and 7.42 (dd) ppm, indicating that the annulene part of **1** exhibits negligible aromaticity in spite of the 10π perimeter. The structure optimization of **1** was carried out by density functional theory (DFT) method with the B3LYP/6-31G(d) basis-set, and the NICS value [12] was calculated by GIAO-HF/6-31G(d) [13] using Gaussian 03 [15]. The NICS value calculated at the center of the 10π system of **1** was +1.45, being consistent with its nonaromatic character based on the chemical shifts. Consequently, **1** is deduced to be nonaromatic in spite of the presence of 10π system due to the fused naphthalene rings which opt to sustain their aromaticity.

An X-ray crystallographic structure analysis of **1** (Fig. 1) showed that the bond lengths and bond angles of its [10]annulene framework agree well the calculated values. In accord with the ^{1}H NMR chemical shifts and the NICS value, the [10]annulene framework of **1** exhibits prominent bond length alternation. The acetylene units of **1** are almost linear with bending angles of less than 5° and the π-conjugated backbone is distinctly planar. The transannular interatomic distance between the sp carbons of **1** is 2.80 Å, which is slightly longer than that of dibenzocyclooctadienediyne (2.61 Å) [16] but shorter than that of a octadehydrodiacenaphtho[14]annulene derivative (2.97 Å) [17]. The observed short interatomic distance of **1** provides an indication for possible transannular C–C bond formation.

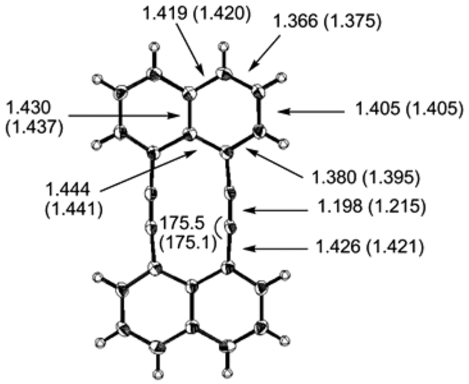
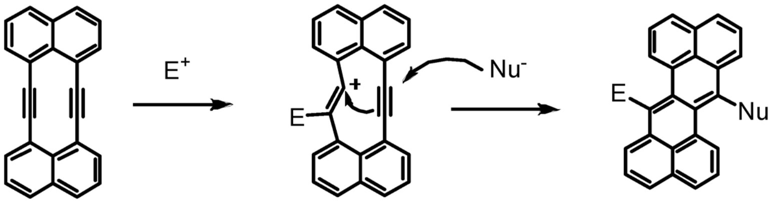


Fig. 1 ORTEP drawing of **1** with bond lengths (Å) and a bond angle (°) determined by X-ray analysis. Values calculated at the B3LYP/6-31G(d) level of theory are shown in parentheses.

7,14-DISUBSTITUTED ZETHRENE DERIVATIVES

As mentioned above, the incidental formation of zethrene (**2a**) in attempts to synthesize dehydroannulene **1** suggests that **1** would be readily transformed into 7,14-disubstituted derivatives of **2a**. Such transformation can be achieved by either electrophilic [18], nucleophilic [19], or reductive [20] pathway. For example, attack of an electrophile to the triple bond, transannular bond formation, and capture of the vinylic cation intermediate by a nucleophile would give a zethrene derivative as shown in Scheme 2. According to this, we envisioned that **1** would serve as a good precursor to 7,14-disubstituted derivatives of **2a**. Here we describe a brief overview of zethrene (**2a**) and the synthesis of its 7,14-disubstituted derivatives from **1** [9].



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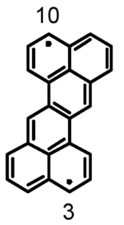
Scheme 2 Electrophile-induced transannular cyclization of tetradehydrodinaphtho[10]annulene (**1**) leading to zethrene derivatives.

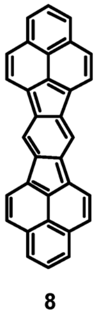
Zethrene: A forgotten aromatic hydrocarbon

In 1955, Clar and co-workers found that a small amount of deep red-colored hydrocarbon, which was readily susceptible to photooxidation under ambient conditions, was found in the products obtained by either catalytic dehydrogenation of acenaphthene to acenaphthylene, thermolysis of acenaphthene, or treatment of acenaphthylene [or bi(acenaphthylidene)] with NaCl and $AlCl_3$ at 110 °C [4]. Alternatively, an authentic sample of this hydrocarbon, which was identified as zethrene (**2a**), was synthesized from 2,8-dicyanochrysene via a classic method based on Friedel–Crafts reaction, albeit in low overall yield [4]. In addition, Clar pointed out characteristic properties of **2a** associated with its Kekulé structure consisting of naphthalene and fixed butadiene substructures [4].

In view of the structural similarity of **2a** to acene-type organic semiconductors, tetracene and pentacene, together with the fact that **2a** contains two phenalenyl units in the molecular backbone, **2a** and its stable derivatives are expected to exhibit properties relevant to potential application to optoelectronic materials. However, these molecules did not seem to attract special interest for many years, except for several patents [21] before theoretical predictions for significant proton affinity, second-order hyperpolarizability, and singlet diradical character of **2a** appeared recently. In 2006, Maksić et al. reported theoretical prediction based on semiempirical AM1 calculations of the absolute proton affinity (APA) and second-order hyperpolarizability (γ) for a large number of aromatic hydrocarbons and found that zethrene and its longitudinal homologues would exhibit large APA as well as γ values [22]. This was followed by a paper of Nakano and co-workers based on a hybrid DFT method which not only confirmed the results of Maksić et al. regarding the large γ values of **2a** but also revealed significant singlet diradical character at 3,10-positions of **2a** as expressed by structure **2a'** [23]. They had already found the relationship between the singlet diradical character and second hyperpolarizability for a number of conjugated systems including those possessing two phenalenyl units such as **8/8'** with different connectivity from that of **2a** [24,25]. These results suggest that stable derivatives of **2a**, not only those having substituents that stabilize the highly sensitive molecule **2a** but also those substituted at strategic positions with donor/acceptor groups, would be good candidates for nonlinear optical materials.



2a'



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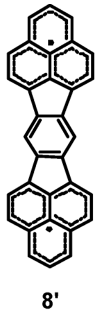
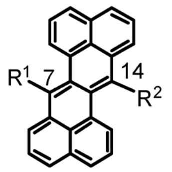


8'



2c $R^1 = R^2 = I$
2d $R^1 = R^2 =$ ≡—Ph

To compare the molecular orbital energies of **2a** with those of pentacene, DFT calculations at the B3LYP/6-31G(d) level of theory were performed. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of **2a** lie at –4.56 and –2.34 eV, respectively, whereas those of pentacene at –4.60 and –2.39 eV, respectively; **2a** and pentacene have the same calculated HOMO–LUMO gap [26]. The greater density probabilities of the HOMO and LUMO of **2a** are located in the 7,14-positions similarly to the 6,13-positions in pentacene.

In addition, as predicted by Clar based on the Kekulé structure considerations, the theoretical bond distances of **2a** predicted that the molecule exhibits a central butadiene moiety flanked by two naphthalene rings as shown in Fig. 2. Namely, the central butadiene unit exhibit significant bond length alternation (1.368 and 1.468 Å), whereas the bond lengths of the naphthalene units are normal.

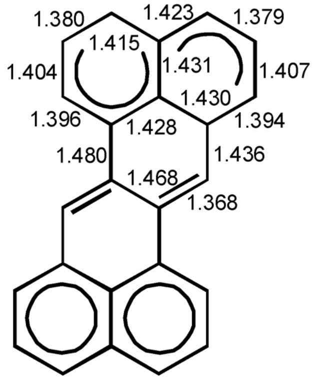


Fig. 2 Theoretical bond lengths (Å) of zethrene (**2a**) optimized by DFT calculations. The lower half of the molecule is symmetrical with respect to the upper half because of the C_{2v} symmetry of the molecular structure.

Synthesis and properties of 7,14-disubstituted zethrene derivatives

As we had expected, treatment of a solution of **1** in $CHCl_3$ with I_2 at room temperature afforded 7,14-diiodozethrene (**2c**) in 65 % isolated yield as a sole product. Diiodo compound **2c** would serve in turn as a good precursor to 7,14-disubstituted derivatives of **2a** by using transition-metal-catalyzed cross-coupling reactions. For example, reaction of **2c** with phenylacetylene under the standard Sonogashira–Hagihara reaction conditions gave 7,14-bis(phenylethynyl)zethrene (**2d**) in 65 % yield. The zethrene derivatives **2c,d** display significantly enhanced stability than **2a** which is very sensitive toward oxidation in the presence of light and air [27].

To evaluate the electrochemical properties of **2d**, cyclic voltammetry measurement was undertaken. Zethrene **2d** showed reversible first oxidation and reduction waves at ${}^{ox}E_1 = 0.29$ and ${}^{red}E_1 =$

–1.64 V vs. ferrocene/ferrocenium (Fc/Fc$^+$), respectively. In addition, irreversible second oxidation and reduction waves were observed at $^{ox}E_2$ = 0.79 V and $^{red}E_2$ = –2.03 V vs. Fc/Fc$^+$, respectively. The first oxidation and reduction potentials of **2d** are comparable to those of pentacene (^{ox}E = 0.3 V, ^{red}E = –1.87 V, vs. Fc/Fc$^+$ in $C_6H_4Cl_2$) [28] and its bis(triisopropylsilyl)ethynyl derivative ($^{ox}E_1$ = 0.38 V, $^{red}E_1$ = –1.72 V, $^{red}E_2$ = –2.23 V, vs. Fc/Fc$^+$ in THF) [29]. These results are in accord with the theoretically predicted frontier molecular orbital energies of **2a** and pentacene calculated by DFT method at the B3LYP/6-31G(d) level of theory, suggesting that derivatives of **2a** may serve as a good organic semiconductor.

CONCLUSIONS

After 50 years, since the attempts to synthesize tetradehydrodinaphtho[10]annulene (**1**) were initiated, synthesis was achieved thanks to the new synthetic methodologies. Based on the theoretical (DFT calculations and NICS) and experimental (NMR spectrum and X-ray analysis) methods, **1** is proven to be nonaromatic in spite of the presence of 10π system in the middle, due to the fused naphthalene ring which opts to sustain their aromaticity. The most interesting feature of **1** is that it is readily transformed via transannular bond formation into diiodozethrene (**2c**) by treatment with I_2. Moreover, **2c** would serve as a pivotal intermediate for stable 7,14-disubstituted zethrene derivatives as exemplified by its conversion to bis(phenylethynyl) derivative **2d**. The syntheses of zethrene derivatives as well as higher homologues of zethrene are currently undertaken in our laboratories.

While the optimized structure of **2a** (Fig. 2) by DFT calculations is perfectly planar, 7,14-disubstituted derivatives are anticipated to twist because of the steric interaction between the substituent and the proximate cata position of the naphthalene ring. 7,14-Disubstituted zethrenes would, therefore, constitute a class of significantly twisted aromatic compounds, which are one of the long-standing challenges in structural organic chemistry [30]. Moreover, recent theoretical studies revealed that zethrene (**2a**) would exhibit interesting properties such as optical nonlinearity and singlet diradical character. Molecular structures and these properties of zethrene derivatives derived from **2c** as well as zetherene homologues will be clarified in due course, opening the door to the zethrene family, which was a forgotten class of aromatic hydrocarbons, for potential application as optoelectronic materials.

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