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Facile formation of acenaphtho[1,2-*a*]pyrene structures by thermal isomerization of bis(8-ethynyl-1-naphthyl)ethynes

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Abstract—The title 1,8-naphthylene–ethynylene compounds underwent thermal isomerization into acenaphtho[1,2-*a*]pyrene derivatives, and the structure of the new polycyclic aromatic system was established by X-ray analysis. The mechanism of the isomerization is explained in terms of sequential cyclization reactions via biradical intermediates followed by hydrogen migration.

In the chemistry of arylene–ethynylene oligomers and polymers, polycyclic aromatic hydrocarbon moieties such as naphthalene and helicenes are occasionally utilized as arene units to create novel types of π-conjugated compounds.[1–3] Recently, we reported the synthesis and structure of 1,8-anthrylene–ethynylene oligomers **1** (Fig. 1): the cyclic tetramer featured a diamond prism structure and a skeletal swing.[4] We attempted to realize a similar structural function with 1,8-naphthylene units, that is **2**, even though the target molecules seemed to be sterically unfavorable because of the close contacts between ethynylene units at the peri positions.[5] There are several examples of reactions between ethynyl groups[6] or other functional groups[7] at the peri positions to relief the severe steric congestion. Despite the expected difficulties, we were able to synthesize bis(8-ethynyl-1-naphthyl)ethynes derivatives, namely 1,8-naphthylene–ethynylene dimers, **3**–**5** by the Sonogashira coupling. During attempts to further elongate the oligomeric chain, for example toward the trimeric structure of **2**, we encountered facile isomerization of these compounds into acenaphtho[1,2-*a*]pyrene derivatives possessing a new ring parent system. We herein report the structural determination of the isomerized product, the mechanism of the isomerization by multiple cyclizations, and the spectroscopic properties of the polycyclic compound as a pyrene analogue.

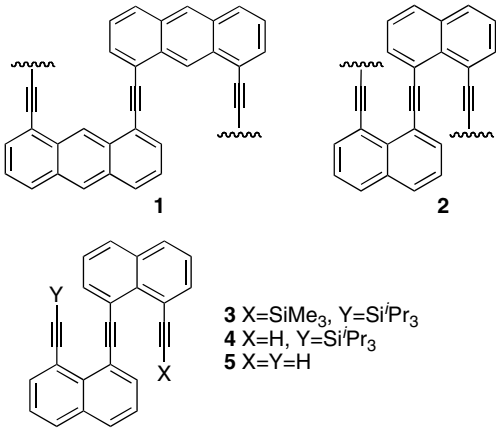

Figure 1. Arylene–ethynylene oligomers.

Building units **7**[6c] and **8**, which were prepared from 1,8-diiodonaphthalene **6**, were coupled by the Sonogashira reaction to give compound **3** with two different silyl groups at both ends (Scheme 1). Treatment of **3** with K_2CO_3 in methanol effectively removed the trimethylsilyl (TMS) group to give **4**, and that with tetrabutylammonium fluoride (TBAF) in THF effectively removed both silyl groups to give **5**. Even though we attempted to prepare trimers of **2** by the coupling between **4** and **7** or between **6** and **8**, the reactions were unsuccessful because of the severe steric congestion around the alkyne moieties.

To remove the TMS group in **3**, we first chose the reaction conditions of KF in refluxing ethanol. However, we

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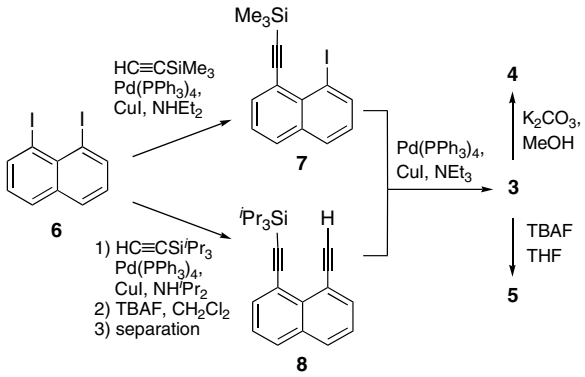


Scheme 1. Synthesis of bis(8-ethynyl-1-naphthyl)ethyne derivatives **3**–**5**.

obtained only a small amount of the desired compound **4**, plus an unexpected compound (**9**) in 57% yield as yellow crystals. This compound was also easily obtained by heating **4** in ethanol in 56% yield (Scheme 2). There were no alkynic carbon signals but 26 aromatic carbon signals in the ^{13}C NMR spectrum of **9**.[8] ^{1}H NMR measurement indicated the presence of a triisopropylsilyl (TIPS) group and 13 aromatic protons. The coupling constants between aromatic proton signals showed that there was no significant bond alternation in the newly formed aromatic system. When the isomerization experiment was performed with **4** where terminal alkyne was partially deuterated (ca. 65%), one of the aromatic protons at δ 8.95 was also deuterated at a comparable rate in the product.

The structure of **9** was finally established by X-ray analysis (Fig. 2).[9] The molecule has an acenaphtho[1,2-*a*]pyrene skeleton[10] with a TIPS group at the 6-position (the numbering indicated in Scheme 2). There are significant out-of-plane deformations around the aromatic carbon attaching to the TIPS group: some torsion angles are off by more than 15° from the ideal planar structure. The TIPS group is bent away from the aromatic plane to relieve excess steric interactions with the surrounding aromatic area, and the angle made by the C–Si bond relative to the averaged aromatic plane is 33°. The TIPS group in **9** was easily cleaved by treatment with trifluoroacetic acid to give **10**,[11] which was also obtained by thermal isomerization of **5** (Scheme 2).

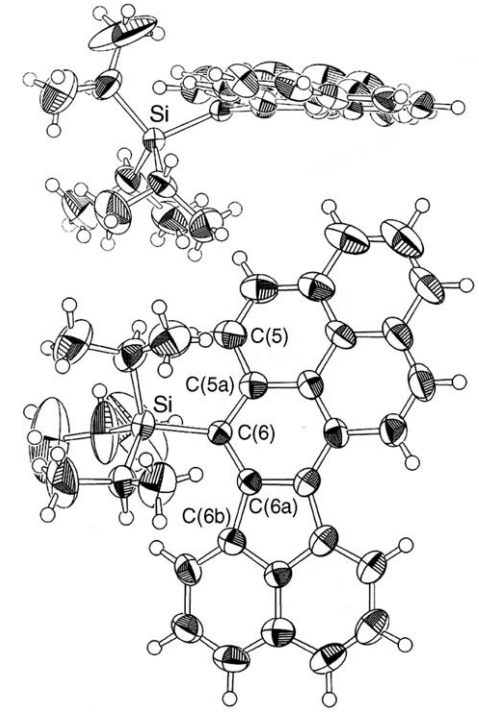
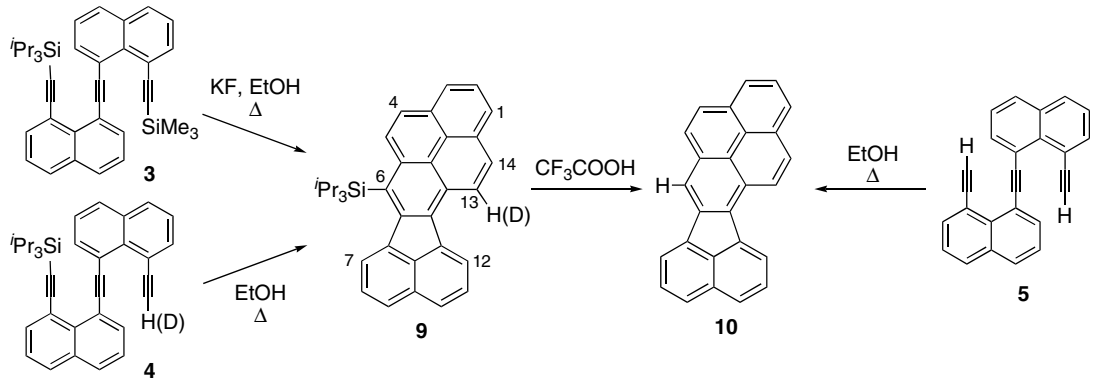
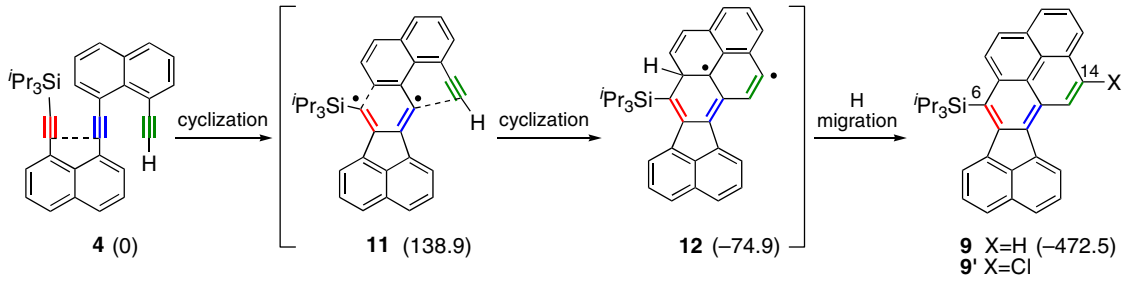


Figure 2. Two views of ORTEP drawing of **9**. Selected torsion angles (°): C(5)–C(5a)–C(6)–C(6a) 164.4(4), C(5a)–C(6)–C(6a)–C(6b) 162.0(4), Si–C(6)–C(5a)–C(5) −28.1(5), Si–C(6)–C(6a)–C(6b) 31.0(6).

A plausible mechanism of the formation of the acenaphtho[1,2-*a*]pyrene structure is shown in Scheme 3, where the biradical intermediates play important role in cyclization. It is known that two parallel oriented alkyne moieties tend to isomerize to 1,4-divinyl biradicals in 1,8-diethynylnaphthalenes[6] and related compounds.[12,13] This type of cyclization leads compound **4** to biradical **11**, which was further cyclized at two reaction sites to give biradical **12**. Although we could not determine whether the formation of three C–C bonds takes place by a concerted mechanism or by a stepwise mechanism from available information, the calculations at the B3LYP/3-21G* level indicate that biradical **12** is much more stable than the starting material **4** and biradical **11**. The following hydrogen migration results in the thermodynamically stable final product **9**. When **4** was heated in CCl_4, the main product was not **9** but the



Scheme 2. Thermal isomerization of **3**–**5** into acenaphtho[1,2-*a*]pyrene derivatives.



Scheme 3. A plausible mechanism for isomerization of **4** into acenaphtho[1,2-*a*]pyrene **9**. Values in parentheses are relative energies (in kJ/mol) calculated at the B3LYP/3-21G* level.

14-chlorinated product **9′**. This result is attributed to the abstraction of a chloro atom by biradical intermediate **12**, and supporting evidence of the proposed mechanism. The overall reaction is similar to the formation of a benzopyrene derivative from 1,8-diethynylnaphthalene and benzyne reported by Cobas et al.[6c]

One remaining question is the direction of the cyclization: if the cyclization of **4** were to proceed from the substituent-free ethyne, the isomerization would give 13-TIPS-acenaphtho[1,2-*a*]pyrene. We consider that this selectivity is attributed to the steric effect of the TIPS group, which significantly interacts with the nearby naphthyl group in **4**. Therefore, the initial cyclization to form a five-membered ring occurs at the naphthalene moiety with the TIPS-ethynyl group rather than the terminal ethynyl group to relieve excess steric strains. Further studies are expected to relieve the details of the reaction mechanism including the intermediates and selectivity.

The electronic spectra of the acenaphtho[1,2-*a*]pyrenes were measured to evaluate their spectroscopic properties as pyrene derivatives (Table 1). Compounds **9** and **10** gave strong absorption bands around 340 nm, which are typical of the parent pyrene. The new bands appeared at 430–480 nm for the acenaphtho[1,2-*a*]pyrene derivatives, and are attributable to the condensation of extra aromatic rings. The TIPS group on the acenaphtho[1,2-*a*]pyrene core results in the bathochromic shift of up to ca. 10 nm for each absorption band. Emission bands of **9** and **10** were observed at 484 and 466 nm as structured shapes, and their fluorescence quantum yields (Φ_f) are smaller than that of pyrene. Although pyrene is known to form an excimer in solution as revealed by fluorescence measurements at high concentration,[14] no excimer bands were observed for **9** and **10**.

Table 1. UV–vis and fluorescence spectra of **9**, **10**, and pyrene in cyclohexane

Compound	UV–vis[a]	FL[b]	
	λ_{max} (nm)	λ_{max} (nm)	Φ_f[c]
9	347, 448, 478	484, 517	0.23
10	339, 434, 463	466, 498, 534	0.47
Pyrene[d]	336	369	0.65

[a] Wavelengths of representative absorptions at >330 nm.
[b] Excited at 393 nm.
[c] Fluorescence quantum yield determined relative to 9,10-diphenylanthracene.
[d] Ref. 14.

In summary, we obtained the acenaphtho[1,2-*a*]pyrene derivatives by thermal isomerization of the 1,8-naphthylene–ethynylene structure. The driving force for the isomerization is attributable to the three parallel oriented ethyne units within van der Waals radii and the energy advantage due to aromatization, both of which facilitated the sequential cyclizations. Because silyl groups attaching to aryl groups can be transformed into various functional groups, compound **9** is a candidate for the key compound to synthesizing higher polycyclic aromatic compounds.

Acknowledgements

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Supplementary data

Detail procedures of synthesis and isomerization are available in Supporting data. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.08.011.

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8. Compound **9**: mp 300–302 °C; ^{1}H NMR ($CDCl_3$): δ 1.17 (d, 18H, $J = 7.4$ Hz), 2.23 (septet, 3H, $J = 7.4$ Hz), 7.64 (t, 1H, $J = 7.3$ Hz), 7.71 (t, 1H, $J = 7.3$ Hz), 7.84 (d, 1H, $J = 7.3$ Hz), 7.85 (d, 1H, $J = 8.8$ Hz), 7.91 (t, 1H, $J = 9.5$ Hz), 8.00 (d, 1H, $J = 8.8$ Hz), 8.10 (d, 1H, $J = 8.8$ Hz), 8.12 (d, 1H, $J = 8.8$ Hz), 8.14 (d, 1H, $J = 8.8$ Hz), 8.35 (d, 1H, $J = 6.8$ Hz), 8.49 (d, 1H, $J = 8.8$ Hz), 8.56 (d, 1H, $J = 7.3$ Hz), 8.95 (d, 1H, $J = 8.8$ Hz); ^{13}C NMR ($CDCl_3$): δ 15.1, 20.5, 123.2, 123.6, 124.3, 124.5, 125.2, 125.3, 125.36, 125.41, 125.6, 126.3, 126.8, 127.9, 128.0, 129.0, 130.0, 130.2, 130.9, 131.0, 131.2, 132.4, 133.4, 137.7, 138.1, 139.4, 145.7 (one aromatic signal is missing due to overlapping); HRMS (FAB) for $C_{35}H_{34}Si$ $[M]^+$ calcd 482.2430, found 482.2391.
9. Crystallographic data for **9**: $C_{35}H_{34}Si$, FW 482.74, orthorhombic, *Pbca* (#61), $a = 18.4834(4)$, $b = 7.9341(2)$, $c = 35.937(1)$ Å, $V = 5270.1(2)$ Å^3, $Z = 8$, $D_c = 1.22$ g cm^{-3}, $R1 = 0.076$, $wR2 = 0.122$. Crystallographic data (excluding structure factors) for the structure, have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 612652. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).
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