

Sadao Arai\*, Masanori Ishikura, Kiyoshi Sato, and Takamichi Yamagishi

Department of Industrial Chemistry, Faculty of Engineering,  
Tokyo Metropolitan University, 1-1 Minami-ohsawa, Hachioji,  
Tokyo 192-03, Japan

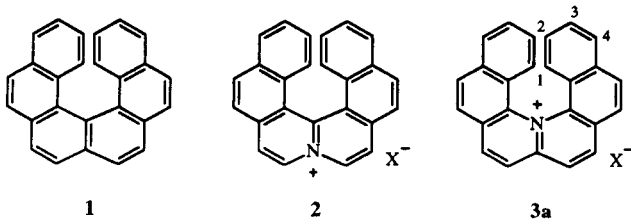
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The 16c-azonia[6]helicene salts, in which a carbon atom at the inner helix skeleton of [6]helicene is replaced by a quaternary nitrogen atom, have been synthesized by photo-induced intramolecular quaternization of 2-[2-(1-chloronaphthyl)vinyl]benzo[*h*]quinolines in acetonitrile.

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Helicenes, a well-known representative of non-planar polycyclic aromatic compounds, have attracted much attention because of their unique helical structure [1]. Since the first synthesis of [6]helicene (**1**) *via* a twelve step route by Newman in 1956 [2], a number of carbohelicenes have been synthesized mainly by photocyclodehydrogenation [1a,1b]. Although the heterohelicenes incorporating  $\pi$ -excessive thiophene, pyrrole, and furan rings have also been reported, only a few examples of heterohelicenes containing  $\pi$ -deficient heterocycles have been described. The 4-aza[6]helicene incorporating a pyridine ring was synthesized by Martin [3]. We have recently published the synthesis of 8a-azonia[6]helicene salt (**2**) incorporating a quinolizinium ring by photocyclodehydrogenation [4]. The azonia-helicene (**2**) has a bridgehead quaternary nitrogen atom at the middle helix skeleton [5].

As the extension of our azonia aromatic chemistry [6] we report here the synthesis of previously unknown 16c-azonia[6]helicene salts (**3**), which possess a quaternary nitrogen atom at the inner helix skeleton, by photo-induced intramolecular quaternization [7].



The reaction of benzo[*h*]quinoline and 1,10-phenanthroline with methyllithium in toluene followed by hydrolysis and rearomatization led to the 2-methyl derivatives **4a** and **4b**, respectively. The reaction of **4a** and **4b** with 1-chloro-2-naphthaldehyde in the presence of zinc chloride in boiling acetic anhydride afforded *trans*-olefins **5a** and **5b**, respectively. An acetonitrile solution of the olefin **5a** was irradiated with a high-pressure mercury lamp through a Pyrex-filter. The desired

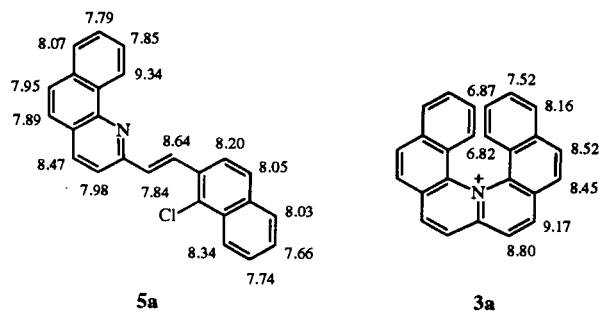
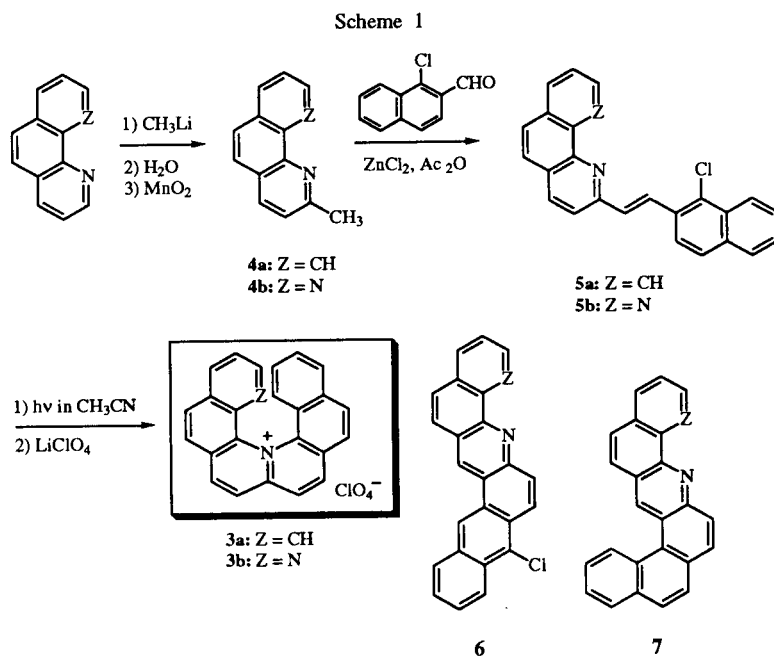


Figure 1.  $^1\text{H}$  NMR Chemical Shifts ( $\delta$  [ppm]) in  $\text{DMSO-}d_6$ .

new 16c-azonia[6]helicene perchlorate (**3a**) was obtained in 40% yield after anion exchange of the crude product with lithium perchlorate. The olefin **5b** in acetonitrile also underwent the photo-induced intramolecular quaternization to give 1-aza-16c-azonia[6]helicene salt (**3b**) in 32% yield. The formation of **6** by photocyclodehydrogenation and **7** by photocyclization with a loss of hydrogen chloride was ruled out by the spectral and analytical data. The helical structures of the compounds **3a** and **3b** were confirmed by  $^1\text{H}$  nmr spectra. The signals for protons 1-H, 2-H, and 3-H in the  $^1\text{H}$  nmr spectra of the azonia-helicene **3a** appeared at  $\delta$  6.82, 6.87, and 7.52, respectively. These signals shifted upfield as compared with the corresponding resonances in the olefin **5a** (Figure 1). These upfield shifts imply that the protons lie in the shielding region of the anisotropy effect originating from the overlapping rings. Similar observations were found in the  $^1\text{H}$  nmr spectra of the helicene **3b**.

The cyclic voltammetry of **3a** showed an irreversible cathodic peak at  $-0.97$  V vs.  $\text{Ag}/\text{AgNO}_3$  in acetonitrile. The reduction potential of **3a** is much more positive than that of **1** ( $-2.35$  V) [8]. This result indicates an increasing electron-accepting ability of **3a** incorporating  $\pi$ -deficient quinolizinium ring.

Further investigation including X-ray structure analysis is in due course.



## EXPERIMENTAL

Melting points were determined on a Yamato melting point apparatus MP-21 and are uncorrected. The uv spectra were obtained with a Hitachi 220A spectrophotometer.  $^1\text{H}$  nmr spectra were measured with JEOL-EX 270 (270 MHz) or EX400 (400 MHz) spectrometers using tetramethylsilane as internal standard. Chemical shifts were measured in ppm downfield from the internal standard. The fast-atom bombardment (FAB) mass spectra were recorded with a JEOL JMS-DX300 spectrometer with *m*-nitrobenzyl alcohol as matrix. The elemental analyses were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. An Eikosha 300W high-pressure mercury lamp was used as the irradiation source. Cyclic voltammetry experiments were performed using Hokuto Denko potentiostat HA-501 and function generator HB-104, and a Riken Denshi X-Y recorder Model F-35. Pt working and auxiliary electrodes and  $\text{Ag}^+/\text{AgNO}_3$  reference electrode were used. The supporting electrolyte was tetrabutylammonium perchlorate (0.1 M). 1-Chloro-2-naphthaldehyde was prepared from 2-methylnaphthalene according to a literature procedure: mp 103.7-105.2° (lit [9] 104.5-106°)

### 2-Methylbenzo[*h*]quinoline (4a).

To benzo[*h*]quinoline (3.43 g, 19.1 mmol) in anhydrous toluene (100 ml), ethyl ether solution of methyl lithium (1.15 M ether solution, 50 ml) was added dropwise at 0°. The dark red mixture was stirred at 40° for 4 hours. After the mixture was hydrolyzed at 10° by the addition of water (100 ml), the organic phase was separated, then aqueous phase was extracted three times with dichloromethane (100 ml). To the combined organic phase manganese(IV) oxide (250 g) was added and the mixture was stirred at room temperature overnight. After filtration the organic layer was concentrated *in vacuo* to afford a residue, which was purified with column chromatography on silica-gel with benzene as eluent to give **4a** (1.23 g, 33%) as yellow vis-

cus oil;  $^1\text{H}$  nmr (270 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  2.79 (s, 3H,  $\text{CH}_3$ ), 7.24 (d,  $J = 8.2$  Hz, 1H, 3-H), 7.52 (d,  $J = 8.6$  Hz, 1H, 6-H), 7.60 (ddd,  $J = 7.6, 6.9,$  and  $1.3$  Hz, 1H, 9-H), 7.65 (d,  $J = 8.6$  Hz, 1H, 5-H), 7.67 (ddd,  $J = 8.3, 7.6,$  and  $1.6$  Hz, 1H, 8-H), 7.81 (dd,  $J = 8.3$  and  $1.3$  Hz, 1H, 7-H), 7.89 (d,  $J = 8.2$  Hz, 1H, 4-H), 9.33 (dd,  $J = 6.9$  and  $1.6$  Hz, 1H, 10-H); ms: FAB  $m/z$  194 ( $M+1$ ) $^+$ .

### 2-Methyl-1,10-phenanthroline (4b).

According to the above procedure 1,10-phenanthroline (5.10 g, 28.3 mmol) was methylated with methyl lithium (1.15 M ether solution, 100 ml). After work-up according to the above procedure followed by repeated purification with column chromatography brown viscous oil (3.41 g) was obtained. This material contained **4b** and 2,9-dimethyl-1,10-phenanthroline in a ratio 8:2, as determined by  $^1\text{H}$  nmr spectroscopy. Since the isolation of monomethyl product **4b** was difficult, this crude material was directly used for the subsequent reaction;  $^1\text{H}$  nmr (270 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  2.95 (s, 3H,  $\text{CH}_3$ ), 7.50 (d,  $J = 8.3$  Hz, 1H, 3-H), 7.59 (dd,  $J = 8.1$  and  $4.5$  Hz, 1H, 8-H), 7.70 (d,  $J = 8.9$  Hz, 1H, 6-H), 7.73 (d,  $J = 8.9$  Hz, 1H, 5-H), 8.11 (d,  $J = 8.3$  Hz, 1H, 4-H), 8.21 (d,  $J = 8.1$  Hz, 1H, 7-H), 9.20 (dd,  $J = 4.5$  and  $2.0$  Hz, 1H, 9-H); ms: FAB  $m/z$  194 ( $M+1$ ) $^+$ .

### *trans*-2-[2-(1-Chloro-2-naphthyl)vinyl]benzo[*h*]quinoline (5a).

Compound **4a** (1.94 g, 10.06 mmol) reacted with 1-chloro-2-naphthaldehyde (2.00 g, 10.49 mmol) in the presence of zinc chloride (68 mg, 0.50 mmol) in boiling acetic anhydride (20 ml) for 45 hours under a nitrogen atmosphere. After the solvent was removed, the residue was chromatographed on neutral alumina (benzene) to give the crude product, which was recrystallized from chloroform to afford the olefin **5a** as a yellow solid (0.99 g, 27%), mp 146.5-147.5°; uv (acetonitrile):  $\lambda$  max 240 (log  $\epsilon$  4.64), 256 (4.53), 289 (4.48), 323 (4.43), 373 (4.47), and 388 nm (4.28);  $^1\text{H}$  nmr (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  7.66 (dd,  $J = 8.8$  and  $7.6$  Hz, 1H, naphthyl 6-H), 7.74 (dd,  $J = 7.6$  and  $8.8$  Hz, 1H, naphthyl 8-H), 7.79 (dd,  $J = 7.8$  and  $6.8$  Hz, 1H, 8-H),

7.85 (dd,  $J = 7.8$  and  $7.8$ , 1H, 9-H), 7.84 (d,  $J = 16.1$  Hz, 1H, olefin-H), 7.89 (d,  $J = 8.8$  Hz, 1H, 5-H), 7.95 (d,  $J = 8.8$  Hz, 1H, 6-H), 7.98 (d,  $J = 8.3$  Hz, 1H, 3-H), 8.03 (d,  $J = 8.8$  Hz, 1H, naphthyl 5-H), 8.05 (d,  $J = 8.8$  Hz, 1H, naphthyl 4-H), 8.07 (d,  $J = 6.8$  Hz, 1H, 7-H), 8.20 (d,  $J = 8.8$  Hz, 1H, naphthyl 13-H), 8.34 (d,  $J = 8.8$  Hz, 1H, naphthyl 8-H), 8.47 (d,  $J = 8.3$  Hz, 1H, 4-H), 8.64 (d,  $J = 16.1$  Hz, 1H, olefin - H), 9.34 (d,  $J = 7.8$  Hz, 1H, 10-H); ms: FAB  $m/z$  366 and 368 (M+1)<sup>+</sup>, 330 (M-Cl)<sup>+</sup>.

*Anal.* Calcd. for C<sub>25</sub>H<sub>16</sub>NCl: C, 82.07; H, 4.41; N, 3.83. Found: C, 81.79; H, 4.22; N, 3.69.

*trans*-2-[2-(1-Chloro-2-naphthyl)vinyl]-1,10-phenanthroline (5b).

The crude product (2.02 g) from the reaction of 1,10-phenanthroline with methyllithium reacted with 1-chloro-2-naphthaldehyde (2.08 g, 10.9 mmoles) in boiling acetic anhydride (15 ml) for 2.5 hours under nitrogen atmosphere. After work-up according to the above procedure followed by repeated purification with silica-gel column chromatography (chloroform), crude olefin 4b (2.81 g) was obtained. Recrystallization from hexane-chloroform gave 5b as yellow solid (2.39 g, 39% from 1,10-phenanthroline), mp 236-237°; uv (acetonitrile):  $\lambda$  max 256 (log  $\epsilon$  4.40), 285 (4.40), 330 (4.42), 343 (4.42), and 363 nm (4.37); <sup>1</sup>H nmr (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  7.66 (dd,  $J = 8.8$  and  $7.7$  Hz, 1H, naphthyl 6-H), 7.75 (dd,  $J = 7.7$  and  $8.3$  Hz, 1H, naphthyl 7-H), 7.81 (dd,  $J = 4.4$  and  $8.1$  Hz, 1H, 8-H), 7.87 (d,  $J = 16.1$  Hz, 1H, olefin-H), 8.00 (d,  $J = 8.8$  Hz, 1H, 5-H), 8.00 (d,  $J = 8.8$  Hz, 1H, 6-H), 8.04 (d,  $J = 8.3$  Hz, 1H, naphthyl 4-H), 8.06 (d,  $J = 8.3$  Hz, 1H, naphthyl 5-H), 8.14 (d,  $J = 8.8$  Hz, 1H, 3-H), 8.22 (d,  $J = 8.3$  Hz, 1H, naphthyl 3-H), 8.34 (d,  $J = 8.3$  Hz, 1H, naphthyl 8-H), 8.53 (d,  $J = 8.1$  Hz, 1H, 7-H), 8.54 (d,  $J = 16.1$  Hz, 1H, olefin-H), 8.54 (d,  $J = 8.8$  Hz, 1H, 4-H), 9.18 (d,  $J = 4.4$  Hz, 1H, 9-H); ms: FAB  $m/z$  367 and 369 (M+1)<sup>+</sup>, 331 (M-Cl)<sup>+</sup>.

*Anal.* Calcd. for C<sub>24</sub>H<sub>15</sub>N<sub>2</sub>Cl: C, 78.58; H, 4.12; N, 7.64. Found: C, 78.85; H, 4.30; N, 7.81.

Typical Procedure for the Preparation of Compound 3 by Photocyclization of 5, e.g. 3a.

16c-Azonia[6]helicene Perchlorate (3a).

A solution of the *trans*-5a (50 mg, 0.14 mmoles) in acetonitrile (1000 ml) in a Pyrex reaction vessel was irradiated with a 300 W high-pressure mercury lamp. The reaction mixture was magnetically stirred at room temperature and the progress of the photocyclization was monitored by uv spectroscopy. After the peak at 459 nm reached a maximum, the solvent was evaporated. This procedure was repeated twice. The combined residue was dissolved in water and an insoluble solid was filtered. To the filtrate an aqueous lithium perchlorate solution was added and the resulting yellow solid was filtered, washed with cold water, recrystallized from ethanol-acetonitrile to give 3a (47 mg, 40%), mp 322-325° dec; uv (acetonitrile):  $\lambda$  max 253 (log  $\epsilon$  4.62), 318 (4.30), 340 (4.21), and 459 nm (3.89); <sup>1</sup>H nmr (270 MHz, DMSO-d<sub>6</sub>):  $\delta$  6.82 (dd,  $J = 8.2$  and  $1.3$  Hz, 1H, 1-H), 6.87 (ddd,  $J = 8.2$ , 6.7, and  $1.3$  Hz, 1H, 2-H), 7.52 (ddd,  $J = 8.2$ , 6.7, and  $1.3$  Hz, 1H, 3-H), 8.16 (dd,  $J = 8.2$  and  $1.3$  Hz, 1H, 4-H), 8.45 (d,  $J = 8.7$  Hz, 1H, 6-H), 8.52 (d,  $J = 8.7$  Hz, 1H, 5-H), 8.80

(d,  $J = 8.6$  Hz, 1H, 8-H), 9.17 (d,  $J = 8.6$  Hz, 1H, 7-H); ms: FAB  $m/z$  330 (M-ClO<sub>4</sub>)<sup>+</sup>.

*Anal.* Calcd. for C<sub>25</sub>H<sub>16</sub>NClO<sub>4</sub>: C, 69.85; H, 3.75; N, 3.26. Found: C, 69.75; H, 3.62; N, 3.41.

1-Aza-16c-azonia[6]helicene Perchlorate (3b).

This compound was obtained in 32% yield as yellow solid, mp 304-306° dec; uv (acetonitrile):  $\lambda$  max 256 (log  $\epsilon$  4.64), 311 (4.29), and 453 nm (3.80); <sup>1</sup>H nmr (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  6.85 (dd,  $J = 8.3$  and  $7.3$  Hz, 1H, 15-H), 7.06 (d,  $J = 8.3$  Hz, 1H, 16-H), 7.51 (dd,  $J = 7.8$  and  $7.3$  Hz, 1H, 14-H), 7.51 (dd,  $J = 8.3$  and  $3.9$  Hz, 1H, 3-H), 7.95 (dd,  $J = 3.9$  and  $1.5$  Hz, 1H, 2-H), 8.15 (d,  $J = 7.8$  Hz, 1H, 13-H), 8.35 (d,  $J = 8.8$  Hz, 1H, 11-H), 8.45 (d,  $J = 8.8$  Hz, 1H, 12-H), 8.53 (d,  $J = 8.3$  Hz, 1H, 5-H), 8.57 (d,  $J = 8.3$  Hz, 1H, 6-H), 8.59 (dd,  $J = 8.3$  and  $1.5$  Hz, 1H, 4-H), 8.79 (d,  $J = 9.3$  Hz, 1H, 9-H), 8.86 (d,  $J = 8.3$  Hz, 1H, 8-H), 9.18 (d,  $J = 8.3$  Hz, 1H, 7-H), and 9.21 (d,  $J = 9.3$  Hz, 1H, 10-H); ms: FAB  $m/z$  331 (M-ClO<sub>4</sub>)<sup>+</sup>.

*Anal.* Calcd. for C<sub>24</sub>H<sub>15</sub>N<sub>2</sub>ClO<sub>4</sub>: C, 66.91; H, 3.51; N, 6.50. Found: C, 66.65; H, 3.39; N, 6.45.

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