Kiyoshi Sato*[a], Yuu Katayama[a], Takamichi Yamagishi[a], and Sadao Arai[b]

[a]Department of Applied Chemistry, Graduate School of Engineering, Tokyo Metropolitan University, 1-1 Minami-ohsawa, Hachioji, Tokyo 192-0397, Japan
[b]Department of Chemistry, Tokyo Medical University, 6-1-1 Shinjuku, Shinjuku-ku, Tokyo 160-8402, Japan

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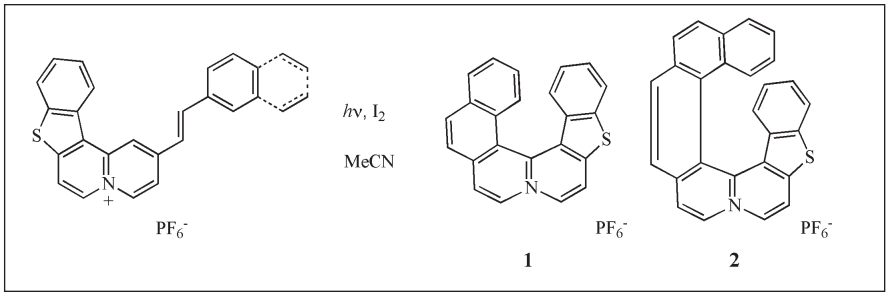

Synthesis of new azonia derivatives of thia[6]helicene (**1**) and thia[7]helicene (**2**) is described. The Knoevenagel condensation of 2-methylbenzothieno[3,2-*a*]quinolizinium salt (**8**) with appropriate arylaldehydes yielded 2-(arylvinyl)benzothieno[3,2-*a*]quinolizinium salts (**9** and **10**), respectively. Photocyclization of 2-styrylbenzothieno[3,2-*a*]quinolizinium salt (**8**) gave 7a-azonia-5-thia[6]helicene (**1**) in 63% yield. Similarly, 2-[2-(2-naphthyl)vinyl]benzothieno[3,2-*a*]quinolizinium salt (**10**) afforded 7a-azonia-5-thia[7]helicene (**2**) in 56% yield. The complete and unambiguous assignment of their ^{1}H- and ^{13}C-nmr spectra was performed by utilizing two-dimensional nmr spectroscopic methods.

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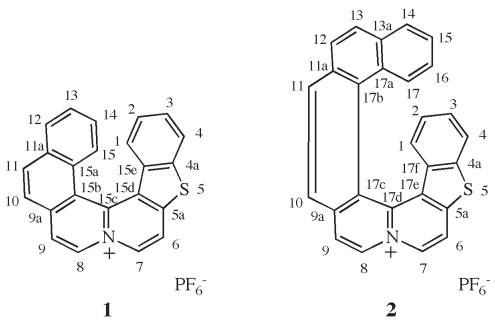
Introduction.

Helicences and heterohelicenes have received currently much interest because of their unique properties derived from the inherently helical structure for optoelectronic applications [1]. There are a number of studies on synthesis and properties of heterohelicenes that contain thiophene rings [2] or other heterocycles [3-5]. Previously, we have reported the first example for azonia derivatives of thia[5]helicenes [4e] and dithia[6]helicenes [4f], which include π-excessive thiophene rings and a π-deficient quinolizinium ring in one helicene framework. Those heterohelicenes are expected to have interesting properties, *e.g.* intra- and/or intermolecular charge transfer by through-bond and/or through-space interactions between π-electron systems of overlapping aromatic rings. In this paper we describe the synthesis of two hitherto unknown heterohelicenes, 7a-azonia-5-thia[6]helicene (**1**) and 7a-azonia-5-thia[7]helicene (**2**).

Scheme 1

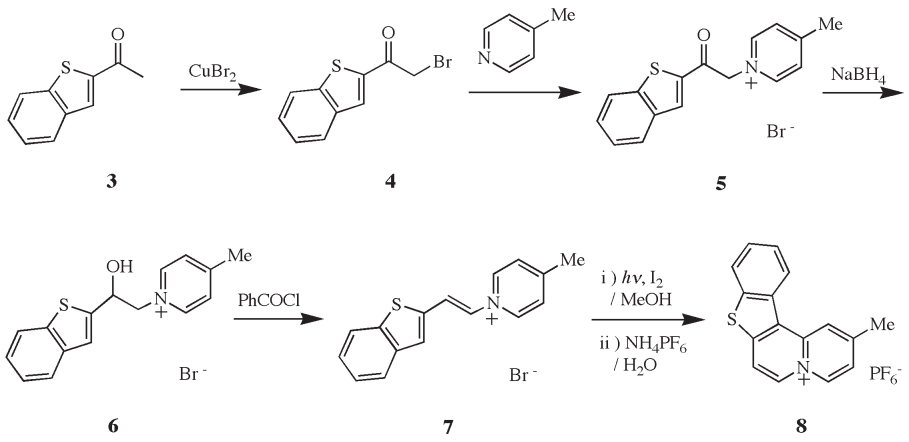


Results and Discussion.

2-Methylbenzothieno[3,2-*a*]quinolizinium hexafluorophosphate (**8**) was prepared by a method similar to our previous paper [4e] for the synthesis of the 9-methylthienoquinolizinium salts (Scheme 2). 2-(Bromoacetyl)-benzo[*b*]thiophene (**4**) was obtained by bromination of 2-acetylbenzo[*b*]thiophene (**3**) with $CuBr_2$ [6] (*ca.* 64% yield). The reaction of the crude 2-(bromoacetyl)benzo-[*b*]thiophene (**4**) and 4-methylpyridine gave pyridinium salt **5** (70% yield). The salt **5** was reduced with sodium borohydride in methanol to afford the alcohol **6** (86% yield). Dehydration of the alcohol **6** with benzoyl chloride gave 1-[2-(2-benzo[*b*]thienyl)vinyl]-4-methylpyridinium bromide (**7**) (84% yield). An aerated methanol solution of **7** was irradiated with a high-pressure mercury lamp through a Pyrex-filter in the presence of iodine to yield the cyclized product **8**. After counterion exchange with aqueous ammonium hexafluorophosphate the hexafluorophosphate salt **8** was obtained in 60% yield. The structure of **8** was confirmed by spectral data and elemental analysis.

The Knoevenagel condensation [7] of 2-methylbenzothieno[3,2-*a*]quinolizinium hexafluorophosphate (**8**) with benzaldehyde in the presence of piperidine gave 2-styrylbenzothieno[3,2-*a*]quinolizinium hexafluorophosphate (**9**) in 45% yield. Similarly 2-(2-naphthyl)vinylbenzothieno[3,2-*a*]quinolizinium hexafluorophosphate (**10**) was

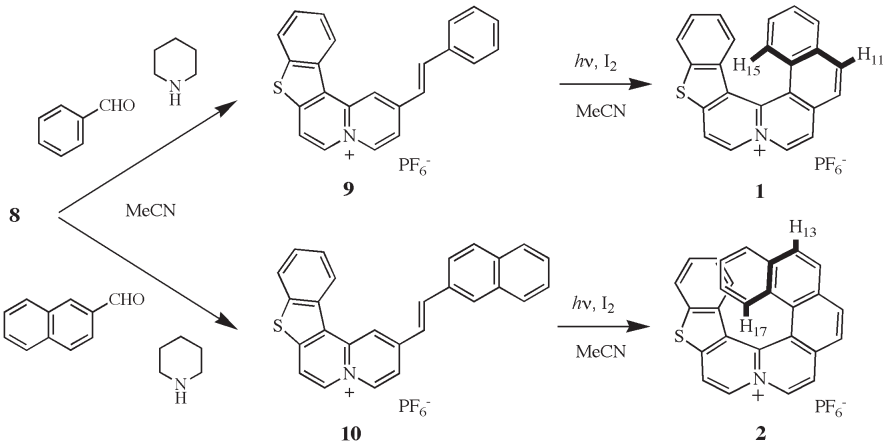
Scheme 2



obtained in 73% yield upon treatment of **8** with 2-naphthaldehyde (Scheme 3).

An acetonitrile solution of **9** was irradiated with a high-pressure mercury lamp through a Pyrex-filter in the presence of iodine as an oxidant [8] to yield only one of the two possible cyclization products (**1** and **11**) in 63% yield. Structural confirmation of the photo-product was established by spectral data and elemental analysis. The fab-ms spectrum of the product (m/z 336) showed a loss of two hydrogen atoms from **9** (m/z 338). The ^{1}H nmr spectrum of the photo-product exhibits ten doublets and four double doublets. The lack of singlets in the ^{1}H nmr spectrum excludes the possibility of the structure (**11**). Two doublets and four double doublets appeared at relatively upper-field (6.5-7.8 ppm), due to a shielding effect between the overlapped terminal aromatic rings, indicating that the product has a helical structure. One doublet at 7.67 ppm is assigned as H15 proton on the basis of its H-H COSY spectrum, which showed a characteristic long-range coupling ($^5J_{HH}$) with H11 proton (8.71 ppm). The other doublet at 6.57 ppm is assigned as H1. Thus, all terminal ring protons and H10 proton could be assigned through the cross coupling peaks in the COSY spectrum. The assignment of the remaining two set of doublet peaks of the quinolizinium moieties was rather ambiguous. The comparison with the chemical shifts of 5a-azonia-3-thia[5]-

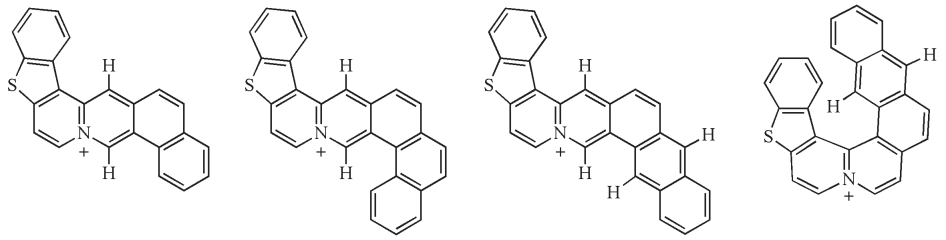
Scheme 3



helicene (**15** [4e], Figure 1) facilitates the assignment of H6/H7 and H8/H9 at 9.04/9.50 and 9.31/8.53 ppm, respectively. These data supported that the photo-product is 7a-azonia-5-thia[6]helicene (**1**).

Similarly, photocyclization of **10** afforded only one of the four possible cyclization products (**2** and **12**-**14**) in 56% yield. The ^{1}H nmr spectrum of the photo-product showed twelve doublets and four double doublets. These results strongly support that the photo-product is **2**,

Scheme 4



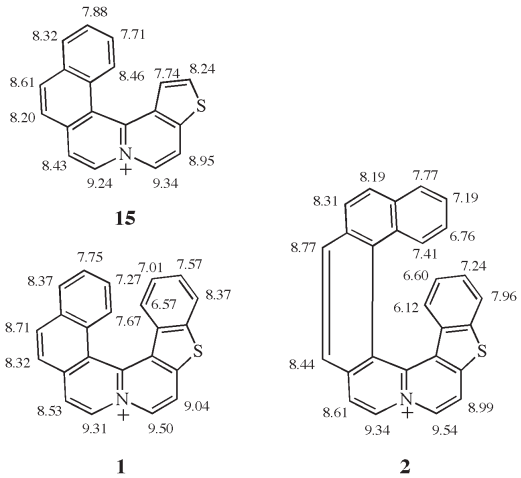
11 **12** **13** **14**

because the ^{1}H nmr spectra of the isomers (**12**-**14**) should show two or four singlets. The peaks assigned to the protons on the terminal benzene rings were observed at relatively higher field (6.1-7.9 ppm). The orientations of these peaks were established by the COSY spectrum and long-range coupling ($^5J_{HH}$) between H17 and H13. On the basis of the COSY spectrum and comparison with the [5]- and [6]-helicene systems, assignment can be made for all of the remaining protons.

Once all the proton resonance in **1** and **2** had been established, ^{13}C nmr signals of the tertiary carbons can be dealt with in a straightforward manner by direct C-H correlation through HETCOR experiments. Assignments of the bridgehead quaternary carbons were made on basis of long-range HETCOR method.

The ^{1}H nmr chemical shifts of the azoniathia-[5]-, [6]-, and [7]-helicenes are shown in Figure 1, which clearly shows that upper field shift of the terminal ring protons of the novel [6]- and [7]-heterohelicenes reflects the degree of the overlapping of the benzene rings.

In conclusion, the novel azoniathia[6] and [7]helicenes (**1** and **2**) have been synthesized by photocyclization and their ^{1}H- and ^{13}C-nmr spectra were assigned by two-dimensional nmr methods. Further studies on the synthesis of higher fused heterohelicenes containing both quinolizinium and thiophene rings are now under way.



15 **1** **2**

Figure 1. ^{1}H Nmr Chemical Shifts (δ [ppm]) in DMSO-d_6.

EXPERIMENTAL

General.

All melting points were determined on a Yamato melting point apparatus MP-21, and are uncorrected. The ^{1}H and ^{13}C nmr spectra were obtained using a JEOL JNM-EX270 (270MHz and 67.5MHz) spectrometer, respectively. Chemical shifts are reported in ppm based on the resonance of DMSO-d_6 as 2.50 ppm for ^{1}H nmr and as 39.5 ppm for ^{13}C nmr, respectively. The uv and visible spectra were obtained with a JASCO V-550 spectrophotometer. The fast-atom bombardment mass spectra (fab-ms) were recorded with a JEOL LX1000 spectrometer with *m*-nitrobenzyl alcohol as a matrix. Microanalyses were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. 2-Acetylbenzo[*b*]thiophene was purchased from Tokyo Kasei Kogyo Co., Ltd.

The systematic names and numberings of the new heterohelicenes are based on the nomenclature suggested by Newman [1a].

1-[2-(2-Benzo[*b*]thienyl)-2-oxoethyl]-4-methylpyridinium Bromide (**5**).

To an acetonitrile solution (40 ml) of 2-(bromoacetyl)benzo-[*b*]thiophene 15.5 g (60 mmoles), which were obtained by bromination of 2-acetylbenzo[*b*]thiophene with copper(II) bromide [6] and used without purification, 4-methylpyridine (70 mmoles) was added. The mixture was refluxed for 2 hours. The resulting solid was filtered, washed with acetone, and recrystallized from ethanol to afford 1-[2-(2-benzo[*b*]thienyl)-2-oxoethyl]-4-methylpyridinium bromide (**5**) as pale brown prisms (70%), mp 234-235.5 °C dec.; ^{1}H nmr (DMSO-d_6): δ 2.68 (s, 3H, CH_3), 6.48 (s, 2H, CH_2), 7.55 (dd, J = 6.9 and 7.9 Hz, 1H, 5-H), 7.62 (dd, J = 7.3 and 7.9 Hz, 1H, 6-H), 8.10 (d, J = 6.6 Hz, 2H, pyridyl-3',5'), 8.15 (d, J = 7.3 Hz, 1H, 7-H), 8.17 (d, J = 6.9 Hz, 1H, 4-H), 8.64 (s, 1H, 3-H), 8.90 (d, J = 6.6 Hz, 2H, pyridyl-2',6'); ^{13}C nmr (DMSO-d_6): δ 21.7, 64.8, 123.2, 125.6, 126.5, 127.9, 128.3, 132.2, 138.5, 138.6, 141.4, 145.0, 159.9, 185.2; fab-ms: m/z 268 $(M-Br)^+$.

Anal. Calcd. for $C_{16}H_{14}NOSBr$: C, 55.18; H, 4.05; N, 4.02. Found: C, 54.87; H, 3.73; N, 3.97.

1-[2-(2-Benzo[*b*]thienyl)-2-hydroxyethyl]-4-methylpyridinium Bromide (**6**).

To a solution of 13.6 g (39 mmoles) of the pyridinium salt **5** in methanol (550 ml), a solution of 0.47 g (12 mmoles) of sodium borohydride in water (20 ml) was added portionwise at room temperature. The reaction mixture was stirred at room temperature for 15 hours. After hydrolysis with HBr (48 %), the solvent was removed under reduced pressure, and the residue was recrystallized from methanol to give 1-[2-(2-benzo[*b*]thienyl)-2-hydroxyethyl]-4-methylpyridinium bromide (**6**) as white prisms (86%), mp 210-211 °C dec.; ^{1}H nmr (DMSO-d_6): δ 2.62 (s, 3H, CH_3), 4.74 (dd, J = 8.6 and 13.2 Hz, 1H, CH_2), 5.03 (dd, J = 3.2 and 13.0 Hz, 1H, CH_2), 5.47 (m, 1H, CH), 6.65 (broad s, 1H, OH), 7.34 (dd, J = 7.8 and 8.0 Hz, 1H, 6-H), 7.39 (dd, J = 7.8 and 8.0 Hz, 1H, 5-H), 7.45 (s, 1H, 3-H), 7.84 (d, J = 7.8 Hz, 1H, 7-H), 7.97 (d, J = 7.8 Hz, 1H, 4-H), 8.00 (d, J = 6.7 Hz, 2H, pyridyl-3',5'), 8.91 (d, J = 6.7 Hz, 2H, pyridyl-2',6'); ^{13}C nmr (DMSO-d_6): δ 21.5, 65.2, 67.8, 120.7, 122.4, 123.5, 124.2, 124.3, 127.6, 138.4, 139.1, 144.3, 145.4, 159.1; fab-ms: m/z 270 $(M–Br)^+$.

Anal. Calcd. for $C_{16}H_{16}NOSBr$: C, 54.86; H, 4.60; N, 4.00. Found: C, 54.71; H, 4.50; N, 3.88.

(*E*)-1-[2-(2-Benzo[*b*]thienyl)vinyl]-4-methylpyridinium Bromide (**7**).

A solution of the alcohol **6** (4.00 g, 11.4 mmoles) in benzoyl chloride (10 ml) was heated at 160 °C for 1 hour. After the reaction mixture was cooled to room temperature, the excess benzoyl chloride was removed under reduced pressure. The residue was recrystallized from ethanol to yield (*E*)-1-[2-(2-benzo[*b*]thienyl)-vinyl]-4-methylpyridinium salt (**7**) as yellow micro needles (84%), mp 234-236 °C dec.; ^{1}H nmr (DMSO-d_6): δ 2.67 (s, 3H, CH_3), 7.42 (dd, J = 7.2 and 8.3 Hz, 1H, 6-H), 7.45 (dd, J = 7.1 and 8.3 Hz, 1H, 5-H), 7.77 (s, 1H, 3-H), 7.93 (d, J = 7.1 Hz, 1H, 4-H), 8.03 (d, J = 7.2 Hz, 1H, 7-H), 8.09 (d, J = 6.7 Hz, 2H, pyridyl-3',5') 8.11 (d, J = 14.2 Hz, 1H, CH=CH), 8.17 (d, J = 14.2 Hz, 1H, CH=CH), 9.26 (d, J = 6.7 Hz, 2H, pyridyl-2',6'); ^{13}C nmr (DMSO-d_6): δ 21.7, 122.5, 122.6, 124.3, 125.0, 126.1, 128.0, 128.2, 130.0, 136.2, 138.9, 139.0, 140.5, 160.0; fab-ms: m/z 252 $(M–Br)^+$.

Anal. Calcd. for $C_{16}H_{14}NSBr$: C, 57.84; H, 4.25; N, 4.22. Found: C, 57.82; H, 4.07; N, 4.11.

2-Methylbenzothieno[3,2-*a*]quinolizinium Hexafluorophosphate (**8**).

A methanol solution (1000 ml) of **7** (1.58 g, 4.76 mmoles) and iodine (90 mg) in a Pyrex vessel was irradiated for 6 hours with a 450 W high-pressure mercury lamp (Ushio UM-452) at room temperature. After the reaction was complete, the solution was concentrated and the residue was dissolved in hot water (450 ml). An insoluble brown solid was filtered off and a saturated aqueous solution of ammonium hexafluorophosphate was added to the filtrate. The precipitates were collected by filtration, washed with cold water, and recrystallized from acetonitrile-ethanol to afford **8** as yellow needles (60%), mp 273-274 °C dec.; ^{1}H nmr (DMSO-d_6): δ 2.87 (s, 3H, CH_3), 7.81 (dd, J = 7.5 and 7.7 Hz, 1H, 11-H), 7.84 (dd, J = 7.5 and 7.9 Hz, 1H, 10-H), 8.06 (d, J = 6.8 Hz, 1H, 3-H), 8.44 (d, J = 7.9 Hz, 1H, 9-H), 8.75 (d, J = 7.1 Hz, 1H, 7-H), 9.15 (d, J = 7.7 Hz, 1H, 12-H), 9.20 (s, 1H, 1-H), 9.22 (d, J = 7.1 Hz, 1H, 6-H), 9.38 (d, J = 6.8 Hz, 1H, 4-H); ^{13}C nmr (DMSO-d_6): δ 21.6, 117.6, 121.0, 124.1, 124.1, 125.0, 125.2, 126.7, 128.0, 132.2, 133.0, 137.7, 138.8, 140.0, 146.4, 152.0; fab-ms: m/z 250 $(M–PF_6)^+$.

Anal. Calcd. for $C_{16}H_{12}NSPF_6$: C, 48.61; H, 3.06; N, 3.54. Found: C, 48.44; H, 2.74; N, 3.49.

General Procedure for the Preparations of the (*E*)-2-(Arylvinyl)benzothieno[*a*]quinolizinium Hexafluorophosphates (**9** and **10**).

To a refluxing acetonitrile solution (5 ml) of **8** (0.25 mmoles) and arylaldehyde (1 mmoles) was added piperidine (0.5 mmoles). The mixture was refluxed for 2 hours. After the mixture was allowed to cool to room temperature, ethyl acetate (50 ml) and diethyl ether (150 ml) were added. The resulting precipitates were collected by filtration, washed with ethyl acetate, and dried *in vacuo* to give (*E*)-2-(2-arylvinyl)benzothieno[*a*]quinolizinium salts (**9** and **10**). The analytical samples were obtained by recrystallization from acetonitrile-ethanol.

(*E*)-2-Styrylbenzothieno[3,2-*a*]quinolizinium Hexafluorophosphate (**9**).

This compound was obtained as yellow prisms (45%), mp 257.5-258.5 °C dec.; ^{1}H nmr (DMSO-d_6): δ 7.47 (t, J = 7.2 Hz, 1H, phenyl-4'), 7.55 (dd, J = 6.9 and 7.2 Hz, 2H, phenyl-3',5'), 7.82 (d, J = 6.9 Hz, 2H, phenyl-2',6'), 7.84-7.90 (m, 2H, 10- and 11-H), 8.04 (s, 2H, CH=CH), 8.46 (d, J = 7.3 Hz, 1H, 9-H), 8.56 (d, J = 7.1 Hz, 1H, 3-H), 8.73 (d, J = 7.1 Hz, 1H, 7-H), 9.18 (d, J = 7.1 Hz, 1H, 12-H), 9.19 (d, J = 7.1 Hz, 1H, 6-H), 9.24 (s, 1H, 1-H), 9.42 (d, J = 7.1 Hz, 1H, 4-H); ^{13}C nmr (DMSO-d_6): δ 117.6, 117.6, 119.6, 124.1, 124.6, 125.1, 125.6, 126.7, 127.7, 128.1, 128.9, 129.9, 132.3, 133.2, 135.5, 138.0, 138.8, 139.3, 139.9, 146.7, 146.9; fab-ms: m/z 338 $(M–PF_6)^+$.

Anal. Calcd. for $C_{23}H_{16}NSPF_6$: C, 57.15; H, 3.34; N, 2.90. Found: C, 57.21; H, 3.25; N, 2.94.

(*E*)-2-[2-(2-Naphthyl)vinyl]benzothieno[3,2-*a*]quinolizinium Hexafluorophosphate (**10**).

This compound was obtained as orange needles (73%), mp 307-307.5 °C dec.; ^{1}H nmr (DMSO-d_6): δ 7.59-7.62 (m, 2H, Napht-6',7'), 7.85 (dd, J = 7.1 and 7.7 Hz, 1H, 11-H), 7.91 (dd, J = 7.4 and 7.7 Hz, 1H, 10-H), 7.96-8.09 (m, 4H, Napht-3', 4', 5', and 8'), 8.16 (d, J = 16.3 Hz, 1H, CH=CH), 8.23 (d, J = 16.3 Hz, 1H, CH=CH), 8.24 (s, 1H, Napht-1'), 8.48 (d, J = 7.4 Hz, 1H, 9-H), 8.60 (d, J = 7.0 Hz, 1H, 3-H), 8.74 (d, J = 7.1 Hz, 1H, 7-H), 9.21 (d, J = 7.1 Hz, 2H, 6- and 12-H), 9.28 (s, 1H, 1-H), 9.44 (d, J = 7.0 Hz, 1H, 4-H); ^{13}C nmr (DMSO-d_6): δ 117.5, 117.6, 119.5, 123.4, 124.2, 125.0, 125.1, 125.6, 126.8, 126.8, 127.1, 127.6, 128.1, 128.2, 128.5, 129.0, 132.4, 132.8, 133.1, 133.2, 133.4, 138.0, 138.8, 139.3, 139.9, 146.6, 146.9; fab-ms: m/z 388 $(M–PF_6)^+$.

Anal. Calcd. for $C_{27}H_{18}NSPF_6$: C, 60.79; H, 3.40; N, 2.63. Found: C, 60.98; H, 3.47; N, 2.76.

General Procedure for Photocyclization of **9** and **10**.

An acetonitrile solution (1000 ml) of **9** or **10** (0.1 mmoles) and iodine (0.1 mmoles) in a Pyrex vessel was irradiated for 3-4 hours with a 450 W high-pressure mercury lamp at room temperature. The reaction was monitored by the uv/visible spectra. When the spectra of the *E*- and *Z*-forms of **9** or **10** had disappeared, irradiation was stopped and the solution was concentrated under reduced pressure. The residue was recrystallized from acetonitrile-ethanol.

7a-Azonia-5-thia[6]helicene Hexafluorophosphate (**1**).

This compound was obtained as yellow micro needles after 3 hours irradiation, yield 63% from **9**, mp 274-275 °C (dec.); ^{1}H nmr (DMSO-d_6): δ 6.57 (d, J = 8.4 Hz, 1H, 1-H), 7.01 (dd, J = 6.9 and 8.4 Hz, 1H, 2-H), 7.27 (dd, J = 6.5 and 8.1 Hz, 1H, 14-H),

7.57 (dd, J = 6.9 and 7.5 Hz, 1H, 3-H), 7.67 (d, J = 8.1 Hz, 1H, 15-H), 7.75 (dd, J = 6.5 and 7.7 Hz, 1H, 13-H), 8.32 (d, J = 8.6 Hz, 1H, 10-H), 8.37 (d, J = 7.5 Hz, 1H, 4-H), 8.37 (d, J = 7.7 Hz, 1H, 12-H), 8.53 (d, J = 6.9 Hz, 1H, 9-H), 8.71 (d, J = 8.6 Hz, 1H, 11-H), 9.04 (d, J = 7.1 Hz, 1H, 6-H), 9.31 (d, J = 6.9 Hz, 1H, 8-H), 9.50 (d, J = 7.1 Hz, 1H, 7-H); ^{13}C nmr (DMSO-d_6): δ 118.3 (6-C), 120.3 (15b-C), 120.8 (9-C), 123.5 (10-C), 123.6 (4-C), 124.2 (2-C), 125.2 (1-C), 126.7 (15-C), 127.8 (14-C), 127.8 (15a-C), 128.2 (3-C), 128.5 (15d-C), 128.5 (13-C), 129.0 (12-C), 132.0 (11a-C), 132.0 (15e-C), 132.7 (8-C), 133.6 (7-C), 135.1 (9a-C), 136.1 (11-C), 137.2 (15c-C), 139.1 (4a-C), 150.0 (5a-C); fab-ms: m/z 336 $(M-PF_6)^+$.

Anal. Calcd. for $C_{23}H_{14}NSPF_6$: C, 57.38; H, 2.93; N, 2.91. Found: C, 57.50; H, 2.91; N, 2.78.

7a-Azonia-5-thia[7]helicene Hexafluorophosphate (**2**).

This compound was obtained as yellow micro needles after 4 hours irradiation, yield 56% from **10**, mp >300 °C; ^{1}H nmr (DMSO-d_6): δ 6.12 (d, J = 8.4 Hz, 1H, 1-H), 6.60 (dd, J = 7.1 and 8.4 Hz, 1H, 2-H), 6.76 (dd, J = 6.8 and 8.4 Hz, 1H, 16-H), 7.19 (dd, J = 6.8 and 7.7 Hz, 1H, 15-H), 7.24 (dd, J = 7.1 and 7.9 Hz, 1H, 3-H), 7.41 (d, J = 8.4 Hz, 1H, 17-H), 7.77 (d, J = 7.7 Hz, 1H, 14-H), 7.96 (d, J = 7.9 Hz, 1H, 4-H), 8.19 (d, J = 8.6 Hz, 1H, 13-H), 8.31 (d, J = 8.6 Hz, 1H, 12-H), 8.44 (d, J = 8.2 Hz, 1H, 10-H), 8.61 (d, J = 6.8 Hz, 1H, 9-H), 8.77 (d, J = 8.2 Hz, 1H, 11-H), 8.99 (d, J = 6.9 Hz, 1H, 6-H), 9.34 (d, J = 6.8 Hz, 1H, 8-H), 9.54 (d, J = 6.9 Hz, 1H, 7-H); ^{13}C nmr (DMSO-d_6): δ 117.5 (17c-C), 118.2 (6-C), 120.6 (9-C), 121.3 (1-C), 122.7 (4-C), 123.6 (2-C), 124.5 (17-C), 124.7 (10-C), 124.9 (16-C), 125.9 (12-C), 127.5 (17b-C), 127.6 (15-C), 127.8 (3-C), 127.8 (14-C), 127.9 (17a-C), 128.5 (17e-C), 130.0 (13-C), 132.0 (11a-C), 132.1 (17f-C), 132.4 (13a-C), 132.7 (8-C), 133.7 (7-C), 134.7 (9a-C), 135.5 (11-C), 138.4 (4a-C), 139.1 (17d-C), 148.8 (5a-C); fab-ms: m/z 386 $(M-PF_6)^+$.

Anal. Calcd. for $C_{27}H_{16}NSPF_6$: C, 61.02; H, 3.03; N, 2.64. Found: C, 61.00; H, 2.99; N, 2.66.

Acknowledgment.

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