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A new short-step synthesis of 8a-azonia[6]helicene (**1**) and the novel dithieno derivatives (**2** and **3**) is described. Double photocyclization of 2,8-distyrylquinolizinium salt (**8**) gave **1** in 35% yield. Similarly, 2,8-bis[2-(2-thienyl)vinyl]- and 2,8-bis[2-(3-thienyl)vinyl]-quinolizinium salts (**9** and **10**) afforded new azonia-[6]helicenes containing two thiophene rings at the ends of helix, that is 7a-azonia-3,12-dithia[6]helicene (**2**) and 7a-azonia-1,14-dithia[6]helicene (**3**), in 43 and 35% yields, respectively. The total assignment of their ^{1}H- and ^{13}C-nmr spectra was performed by utilizing two-dimensional and NOE nmr spectroscopic methods.

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Introduction.

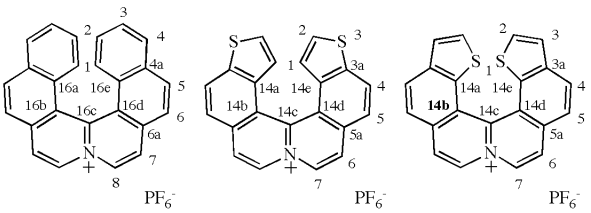
Helicences and heterohelicenes have received currently much interest because of their unique properties derived from the inherently helical structure for optoelectronic applications [1], and also attracted considerable attention in the field of self-assembly into helical aggregates [2].

There are a number of studies on synthesis and properties of heterohelicenes that contain thiophene rings [3] or other heterocycles [4,5]. The 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. Recently, we have reported the crystal structure of racemic 8a-azonia[6]helicene hexafluorophosphate (**1**•PF_6^-) containing quinolizinium ion [6]. The X-ray analysis revealed that the cationic heterohelicene **1** formed a well-defined homochiral columnar structure by an intermolecular face-to-face type π-π interaction with an attractive electronic interaction between the central π-accepting quinolizinium moiety and the terminal π-donative benzene rings of adjacent molecules.

These studies prompt us to synthesize heterohelicene comprising of two different heterocycles [7,8]. Previously, we have reported the first example for azonia derivatives of thia[5]helicenes [9], which include π-excessive thiophene rings and a π-deficient quinolizinium ring in one [5]helicene framework.

In this paper we describe the synthesis of two hitherto unknown hetero[6]helicenes, 7a-azonia-3,12-dithia[6]-helicene (**2**) and 7a-azonia-1,14-dithia[6]helicene (**3**), which are isoelectronic with 8a-azonia[6]helicene (**1**) but contain two thiophene rings at the ends of helix.

Scheme 1



1 **2** **3**

Results and Discussion.

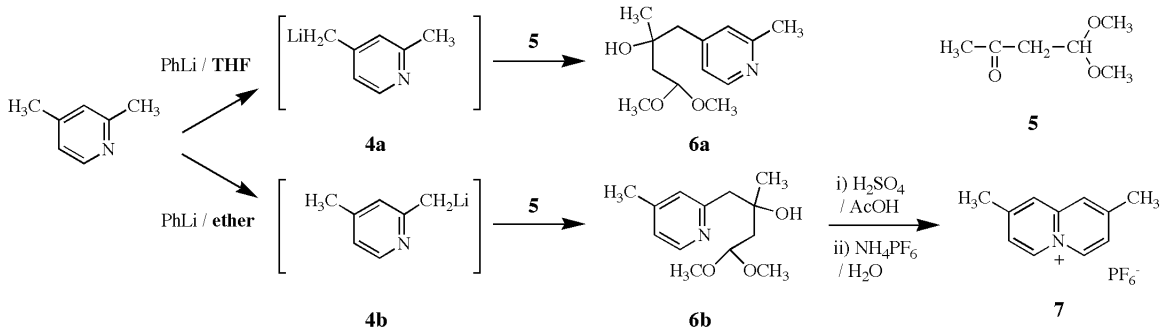
We have already succeeded in the first synthesis of 8a-azonia[6]helicene (**1**) by the photocyclization of 2-styryl-naphtho[1,2-*a*]quinolizinium [5a]. In order to synthesize the desired C_2 symmetric azoniadithia[6]helicenes (**2** and **3**), we devised a new synthetic strategy by using double photocyclization of 2,8-distyrylquinolizinium derivatives. In this new pathway, 2,8-dimethylquinolizinium cation (**7**) is a key intermediate, because the two methyl groups located at the *para* positions relative to the quaternary nitrogen atom of the quinolizinium cation would be react with arylcarbaldehydes to form arylvinylquinolizinium derivatives [10]. The synthesis of 2-methylquinolizinium from 2-picolyllithium has been reported [11]. To adapt this method for the preparation of 2,8-dimethylquinolizinium (**7**), however, it requires a selective lithiation of two reactive methyl groups of 2,4-lutidine: the 2-methyl group should be selectively lithiated in the presence of the 4-methyl group. Although several methods for the selective methylmetallation of 2,4-lutidine have been reported [12], we have discovered a simple solvent controlled selective methyllithiation method of 2,4-lutidine.

Treatment of 2,4-lutidine with phenyllithium in THF caused exclusive metallation of the 4-methyl group, which was identified by reaction with 4,4-dimethoxybutan-2-one (**5**) to form the corresponding alcohol **6a**, whose nmr spectrum indicated that one signal (at higher field, which was assigned to 4-position) of the two methyl groups of 2,4-lutidine moiety disappeared. In contrast, 2,4-lutidine reacted with phenyllithium in dry ether to give lithium derivatives at the 2 position, which was confirmed from the formation of hydroxy-acetal **6b** as a single adduct. In ^{1}H nmr spectrum of the product, the other methyl group (assigned to 2-position) of 2,4-lutidine moiety disappeared. No evidence of the reaction at the 4 position could be obtained under the above metallation conditions. The structure of the hydroxy-acetal **6b** was also identified by the subsequent acid-catalyzed dehydrative cyclization. The cyclization

product showed simple and highly symmetrical nmr spectrum, which is fully consistent with the structure of the dimethylquinolizinium salt (**7**).

azonia[6]helicene hexafluorophosphate (**1**) in 35% yield, whose spectral data are identical with the authentic sample [6].

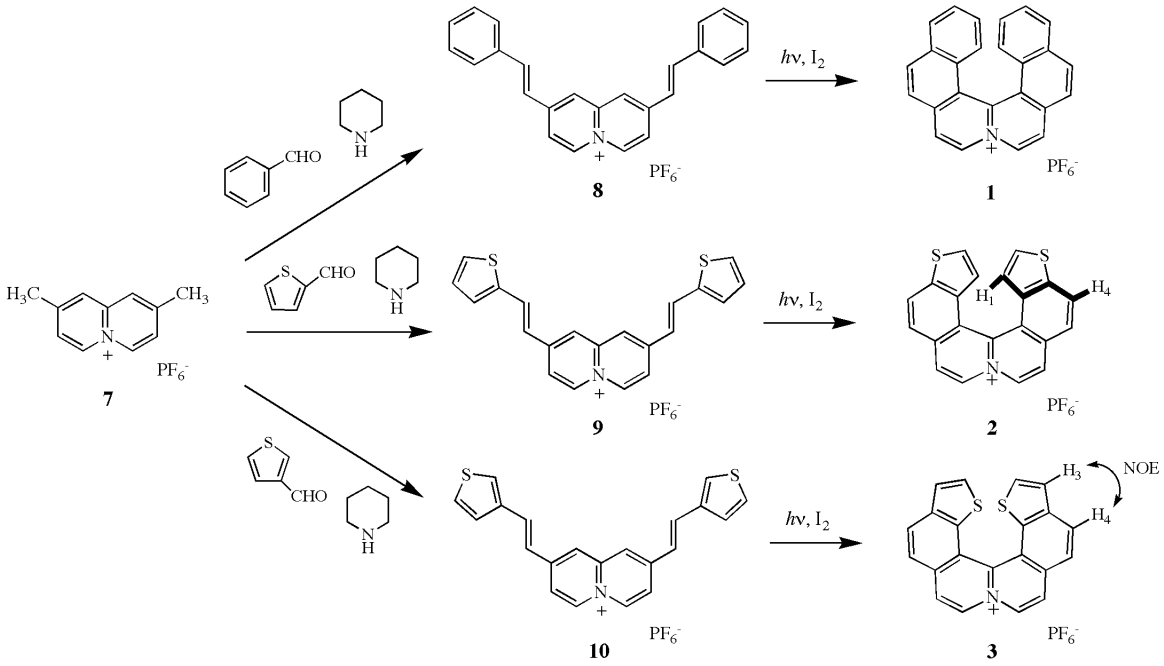
Scheme 2



The Knoevenagel condensation [10] of 2,8-dimethylquinolizinium hexafluorophosphate (**7**) with benzaldehyde in the presence of piperidine gave 2,8-distyrylquinolizinium hexafluorophosphate (**8**) in 82% yield. Similarly 2,8-bis[2-(2-thienyl)vinyl]quinolizinium hexafluorophosphate (**9**) and 2,8-bis[2-(3-thienyl)vinyl]quinolizinium hexafluorophosphate (**10**) were obtained in 98% and 98% yields upon treatment of **7** with the corresponding thiophenecarboxaldehydes, respectively (Scheme 3).

Irradiation of **9** in acetonitrile solution containing iodine gave a double cyclized product in 43% yield. Structural confirmation of the photo-product was established by spectral data and elemental analysis. The fab-ms spectrum of the product (m/z 342) showed a loss of four hydrogen atoms from **9** (m/z 346). The ^1H nmr spectrum of the photo-product exhibits three sets of doublets, indicating C_2 symmetrical structure. Two doublets with relatively small $^3J_{HH}$ (5.6 Hz) at δ 6.67 and 7.76 ppm correspond to

Scheme 3



An acetonitrile solution of **8** was irradiated with a high-pressure mercury lamp through a Pyrex-filter in the presence of iodine as an oxidant [13] to yield 8a-

a typical thiophenic α,β-coupling constant. The former resonance is assigned as H1/H14 on the basis of its H-H COSY spectrum, which showed a characteristic long-

range coupling ($^5J_{HH}$) between H1/H14 and H4/H11. Those data support that the photo-product is 7a-azonia-3,12-dithia[6]helicene hexafluorophosphate (**2**).

Photocyclization of **10** provided 7a-azonia-1,14-dithia[6]helicene hexafluorophosphate (**3**) in 35% yield as the only one of the ten possible isomers by ring closure between the 2-position of the 3-substituted thiophene rings and the 1/9-positions of the quinolizinium unit. The similar regio-selective cyclization was already reported in the photolysis of the precursors of azoniadithia[5]helicenes [9]. The spectral assignment of **3** was achieved in a similar way to that of **2**. The ^{1}H nmr spectrum of the product showed six doublets, of which two doublets have coupling constants similar to the thiophene moiety of **2**. These results strongly support that the photo-product is **3**, because the ^{1}H nmr spectra of the isomers will show two singlets corresponding to two α-protons of thiophene moiety or 1,4-protons of quinolizinium ring. Due to the absence of the long-range coupling in the COSY spectrum of **3**, assignment of the protons of the terminal thiophene moieties was rather ambiguous. In the NOE experiment, however, a correlation was observed between H(4)/H(11) and one of the protons of thiophene moiety appeared at 7.75 ppm, thus this signal was assigned to the protons at the 3,12-positions and the other (7.87 ppm) to H(2)/H(13) protons, respectively.

All ^{13}C nmr assignments of **1**, **2**, and **3** were performed on the basis of hetero-nuclear two-dimensional (C-H COSY) nmr techniques [14].

In conclusion, we have synthesized two novel hetero-[6]helicenes containing both of quinolizinium and thiophene rings in a new short-step method. The complete assignments of the ^{1}H and ^{13}C spectra of the hetero[6]-helicenes **1-3** have been accomplished by concerted usage of H-H COSY, C-H COSY, and NOE nmr techniques. Further studies on the synthesis of higher fused heterohelicenes are now under way.

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 (270 MHz and 67.5 MHz) 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 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.

3-Hydroxy-3-methyl-4-[4-(2-methylpyridyl)]butanal Dimethyl Acetal (**6a**).

2-Methyl-4-pyridylmethyl lithium (**4a**) was prepared from phenyl lithium (1.90 g; 22.7 mmoles (22.0 ml of 1.0 mol/l cyclohexane-ether solution)), 2,4-lutidine (2.32 g; 21.6 moles), and absolute THF (10 ml). A solution of 4,4-dimethoxybutan-2-one (5) (2.99 g; 22.6 moles) in dry THF (3 ml) was added dropwise with stirring to the lithium solution at 0 °C. The reaction mixture was then stirred at r.t. for 1 hr, and poured onto a mixture of ice and water (50 g). The organic phase was separated, the aqueous layer extracted with Et_2O (2 x 100 ml) and the combined organic extracts dried with magnesium sulfate, and concentrated *in vacuo* to give pale yellow oil: 3.26 g (63%). ^{1}H nmr ($CDCl_3$): δ 1.19 (s, 3H, CH_3), 1.74 and 1.83 (dd, 2H, J = 14.2 and 6.3 Hz, CH_2), 2.53 (s, 3H, Py-CH_3), 2.69 and 2.75 (d, J = 13.4 Hz, 2H, Py-CH_2), 3.34 (s, 3H, OCH_3), 3.37 (s, 3H, OCH_3), 4.69 (t, 1H, J = 6.3 Hz, $CH(OMe)_2$), 7.00 (d, 1H, J = 5.1 Hz, Py-5), 7.06 (s, 1H, Py-3), 8.38 (d, 1H, J = 5.1 Hz, Py-6); ^{13}C nmr ($CDCl_3$): δ 24.0, 27.1, 42.5, 48.1, 52.7, 53.2, 70.5, 102.4, 123.1, 125.5, 147.0, 148.2, 157.6; ms m/z 240 $(M+H)^+$, 208 $(M-OCH_3)^+$, 150 $(M-(OCH_3)_2CHCH_2)^+$, 107 $(M-(OCH_3)_2CHCH_2CCH_3OH)^+$. This product contained a small amount of 2,4-lutidine.

3-Hydroxy-3-methyl-4-[2-(4-methylpyridyl)]butanal Dimethyl Acetal (**6b**).

4-Methyl-2-pyridylmethyl lithium (**4b**) was prepared from phenyl lithium (1.90 g; 22.7 mmoles (22.0 ml of 1.0 mol/l cyclohexane-ether solution)), 2,4-lutidine (2.32 g; 21.6 mmoles), and absolute ether (18 ml). A solution of 4,4-dimethoxybutan-2-one (5) (2.99 g; 22.6 mmol) in dry ether (6 ml) was added dropwise with stirring to the lithium solution at 0 °C. The reaction mixture was then stirred at r.t. for 1 hr, and poured onto a mixture of ice and water (50 g). The organic phase was separated, the aqueous layer extracted with Et_2O (2 x 100 ml) and the combined organic extracts dried with magnesium sulfate, and concentrated *in vacuo* to result in red oil: 3.65 g (70%). ^{1}H nmr ($CDCl_3$): δ 1.20 (s, 3H, CH_3), 1.74 and 1.83 (dd, 2H, J = 14.3 and 5.2 Hz, CH_2), 2.33 (s, 3H, Py-CH_3), 2.86 and 2.96 (d, 2H, J = 14.3 Hz, Py-CH_2), 3.31 (s, 3H, OCH_3), 3.34 (s, 3H, OCH_3), 4.71 (t, 1H, J = 5.2 Hz, $CH(OMe)_2$), 6.92 (d, 1H, J = 4.8 Hz, Py-5), 6.99 (s, 1H, Py-3), 8.34 (d, 1H, J = 4.8 Hz, Py-6); ^{13}C nmr ($CDCl_3$): δ 20.9, 27.5, 44.0, 47.7, 52.6, 52.7, 71.0, 102.4, 122.3, 125.5, 147.9, 148.7, 159.1; ms m/z 240 $(M+H)^+$, 208 $(M-OCH_3)^+$, 190 $(M-OCH_3-H_2O)^+$, 158 $(M-OCH_3-H_2O-CH_3OH)^+$, 150 $(M-(OCH_3)_2CHCH_2)^+$, 107 $(M-(OCH_3)_2CHCH_2CCH_3\ OH)^+$. This compound contained a small amount of 2,4-lutidine but it was used for the next step without further purification.

2,8-Dimethylquinolizinium Hexafluorophosphate (**7**).

A solution of the hydroxy-acetal **6b** (4.0 g; 16.7 mmoles) in acetic anhydride (10 ml) and sulfuric acid (5 drops) was heated for 1 hr at 150 °C with occasional shaking. The reaction mixture was then cooled to r.t., then poured onto water (10 ml). Insoluble material was filtered off, then ammonium hexafluorophosphate (3.0 g; 18.7 mmoles) was added into the filtrate. Resulting precipitate was collected and purified by recrystallization from acetonitrile-ethanol; yield: 1.67 g (33%); colorless plates, mp 153–154°; ^{1}H nmr (DMSO-d_6): δ 2.63 (s, 6 H, 2-Me), 7.88 (dd, 2 H, $J_{3,4}$ = 6.9 Hz, $J_{1,3}$ = 2.0 Hz, 3-H), 8.20 (s, 2 H, 1-H), 9.12 (d, 2 H, $J_{3,4}$ = 6.9 Hz, 4-H,); ^{13}C nmr (DMSO-d_6): δ 21.1, 124.4, 124.7, 135.5, 141.9, 149.0; ms m/z 158 $(M-PF_6)^+$.

Anal. Calcd for $C_{11}H_{12}NPF_6$: C, 43.58; H, 3.98; N, 4.62. Found: C, 43.56; H, 3.84; N, 4.49.

General Procedure for the Preparation of the (*E,E*)-2,8-Bis(arylvinyl)quinolizinium Hexafluorophosphates (**8-10**).

To a refluxing acetonitrile solution (6 ml) of 2,8-dimethylquinolizinium hexafluorophosphate (**7**) (1.1 mmoles) and arylaldehyde (8.8 mmoles) was added piperidine (2.0 mmoles). The mixture was refluxed for 2 hours. After cooling of the mixture to room temp., diethyl ether (150 ml) was added. The resulting precipitate was filtered, washed with ether, and dried *in vacuo* to give (*E,E*)-2,8-bis(arylvinyl)quinolizinium hexafluorophosphate (**8-10**). Analytically pure sample was obtained by recrystallization from acetonitrile-ethanol.

(*E,E*)-2,8-Distyrylquinolizinium Hexafluorophosphate (**8**).

This compound was obtained as yellow needles (82%), mp 264-265° (dec.); ^{1}H nmr (DMSO-d_6): δ 7.44 (t, J = 7.3 Hz, 2H, phenyl-4), 7.50 (dd, J = 6.9 and 7.3 Hz, 4H, phenyl-3,5), 7.57 (d, J = 16.5 Hz, 2H, CH=CH), 7.77 (d, J = 6.9 Hz, 4H, phenyl-2,6), 7.91 (d, J = 16.5 Hz, 2H, CH=CH), 8.31 (d, J = 7.1 Hz, 2H, 3,7-H), 8.39 (s, 2H, 1,9-H), 9.14 (d, J = 7.1 Hz, 2H, 4,6-H); ms: m/z 334 $(M-PF_6)^+$.

Anal. Calcd. for $C_{25}H_{20}NPF_6$: C, 62.64; H, 4.21; N, 2.92. Found: C, 62.88; H, 4.03; N, 2.89.

(*E,E*)-2,8-Bis[2-(2-thienyl)vinyl]quinolizinium Hexafluorophosphate (**9**).

This compound was obtained as yellow needles (98%), mp 239-240° (dec.); ^{1}H nmr (DMSO-d_6): δ 7.76 (dd, J = 3.3 and 5.0 Hz, 2H, thienyl-5), 7.25 (d, J = 16.2 Hz, 2H, CH=CH), 7.50 (d, J = 3.3 Hz, 2H, thienyl-3), 7.76 (d, J = 5.0 Hz, 2H, thienyl-5), 8.10 (d, J = 16.2 Hz, 2H, CH=CH), 8.24 (d, J = 7.3 Hz, 2H, 3,7-H), 8.30 (s, 2H, 1,9-H), 9.06 (d, J = 7.3 Hz, 2H, 4,6-H); ms: m/z 346 $(M-PF_6)^+$.

Anal. Calcd. for $C_{21}H_{16}NS_2PF_6$: C, 51.32; H, 3.28; N, 2.85. Found: C, 51.13; H, 3.09; N, 2.91.

(*E,E*)-2,8-Bis[2-(3-thienyl)vinyl]quinolizinium Hexafluorophosphate (**10**).

This compound was obtained as yellow needles (98%), mp 236-237° (dec.); ^{1}H nmr (DMSO-d_6): δ 7.38 (d, J = 16.2 Hz, 2H, CH=CH), 7.63 (d, J = 5.1 Hz, 2H, thienyl-4), 7.71 (dd, J = 2.8 and 5.1 Hz, 2H, thienyl-5), 7.91 (d, J = 2.8 Hz, 2H, thienyl-2), 7.91 (d, J = 16.2 Hz, 2H, CH=CH), 8.22 (d, J = 7.3 Hz, 2H, 3,7-H), 8.30 (s, 2H, 1,9-H), 9.09 (d, J = 7.3 Hz, 2H, 4,6-H); ms: m/z 346 $(M-PF_6)^+$.

Anal. Calcd. for $C_{21}H_{16}NS_2PF_6$: C, 51.32; H, 3.28; N, 2.85. Found: C, 51.21; H, 3.42; N, 2.95.

General Procedure for Photocyclization of **8-10**.

An acetonitrile solution (1000 ml) of **8-10** (0.2 mmoles) and iodine (0.2 mmoles) in a Pyrex vessel was irradiated for 10-17 hours with a 450W high-pressure mercury lamp at room temperature. The reaction was monitored by uv and visible spectra. When the spectra of the *Z,Z* form of **8-10** had disappeared, irradiation was stopped and the solution was concentrated under reduced pressure The residue was recrystallized from acetonitrile-ethanol.

8a-Azonia[6]helicene Hexafluorophosphate (**1**).

This compound was obtained as yellow micro needles after 10 hours irradiation, yield 35% from **8**, mp 302-303° (dec.); ^{1}H nmr (DMSO-d_6): δ 6.90 (dd, J = 6.9 and 8.6 Hz, 2H, H-2 and H-15), 7.25 (d, J = 8.6 Hz, 2H, H-1 and H-16), 7.52 (dd, J = 6.9 and 7.9 Hz, 2H, H-3 and H-14), 8.14 (d, J = 7.9 Hz, 2H, H-4 and H-13), 8.31 (d, J = 8.6 Hz, 2H, H-6 and H-11), 8.62 (d, J = 8.6 Hz, 2H, H-5 and H-12), 8.66 (d, J = 6.6 Hz, 2H, H-7 and H-10), 9.40 (d, J = 6.6 Hz, 2H, H-8 and H-9); ^{13}C nmr (DMSO-d_6): δ 122.3 (C-7 and C-10), 123.4 (C-16b and C-16d), 123.7 (C-6 and C-11), 125.6 (C-1 and C-16), 127.1 (C-2 and C-15), 127.9 (C-16a and C-16e), 128.5 (C-3 and C-14), 128.8 (C-4 and C-13), 132.5 (C-4a and C-12a), 133.2 (C-8 and C-9), 135.2 (C-6a and C-10a), 136.6 (C-5 and C-12), 140.1 (C16c); ms: m/z 330 $(M-PF_6)^+$.

Anal. Calcd. for $C_{25}H_{16}NPF_6$: C, 63.17; H, 3.39; N, 2.95. Found: C, 63.21; H, 3.42; N, 2.82.

7a-Azonia-3,12-dithia[6]helicene Hexafluorophosphate (**2**).

This compound was obtained as yellow micro needles after 17 hours irradiation, yield 43% from **9**, mp 225-226° (dec.); ^{1}H nmr (DMSO-d_6): δ 6.67 (dd, J = 1.0 and 5.6 Hz, 2H, H-1 and H-14), 7.76 (d, J = 5.6 Hz, 2H, H-2 and H-13), 8.34 (d, J = 8.6 Hz, 2H, H-5 and H-10), 8.68 (d, J = 6.1 Hz, 2H, H-6 and H-9), 8.91 (dd, J = 1.0 and 8.6 Hz, 2H, H-4 and H-11), 9.23 (d, J = 6.1 Hz, 2H, H-7 and H-8); ^{13}C nmr (DMSO-d_6): δ 121.1 (C14b and C14d), 122.2 (C-5 and C-10), 122.6 (C-6 and C-9), 124.2 (C-1 and C-14), 130.2 (C-2 and C-13), 130.4 (C-4 and C-11), 131.0 (C-7 and C-8), 133.5 (C-5a and C-9a), 135.5 (C-14a and C-14e), 141.0 (C-3a and C-11a), 141.1 (C-14c); ms: m/z 342 $(M-PF_6)^+$.

Anal. Calcd. for $C_{21}H_{12}NS_2PF_6$: C, 51.75; H, 2.48; N, 2.87. Found: C, 51.71; H, 2.12; N, 3.07.

7a-Azonia-1,14-dithia[6]helicene Hexafluorophosphate (**3**).

This compound was obtained as yellow micro needles after 10 hours irradiation, yield 35% from **10**, mp 270-271° (dec.); ^{1}H nmr (DMSO-d_6): δ 7.75 (d, J = 5.4 Hz, 2H, H-3 and H-12), 7.87 (d, J = 5.4 Hz, 2H, H-2 and H-13), 8.41 (d, J = 8.6 Hz, 2H, H-5 and H-10), 8.72 (d, J = 6.6 Hz, 2H, H-6 and H-9), 8.74 (d, J = 8.6 Hz, 2H, H-4 and H-11), 9.26 (d, J = 6.6 Hz, 2H, H-7 and H-8); ^{13}C nmr (DMSO-d_6): δ 120.4 (C-14b and C-14d), 123.0 (C-6 and C-9), 123.6 (C-5 and C-10), 124.2 (C-3 and C-12), 129.9 (C-2 and C-13), 130.8 (C-7 and C-8), 131.4 (C-4 and C-11), 133.5 (C-5a and C-9a), 137.5 (C-14a and C-14e), 139.1 (C-14c), 141.9 (C-3a and C-11a); ms: m/z 342 $(M-PF_6)^+$.

Anal. Calcd. for $C_{21}H_{12}NS_2PF_6$: C, 51.75; H, 2.48; N, 2.87. Found: C, 51.93; H, 2.32; N, 2.86.

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