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Received March 2, 2000**This paper is dedicated to the memory of Professor Raymond N. Castle**

The Knoevenagel condensation of the 9-methyl derivatives of thieno[3,2-*a*]- and thieno[2,3-*a*]-quinolizinium salts (**2b** and **3b**) with appropriate arylaldehydes yielded 9-(arylviny)thieno[3,2-*a*]- and 9-(arylviny)thieno[2,3-*a*]quinolizinium salts (**4a-c** and **5a-c**), respectively, which underwent photocyclization to give a series of novel hetero[5]helicenes (**6a,b** and **7a-d**) containing quinolizinium and thiophene rings.

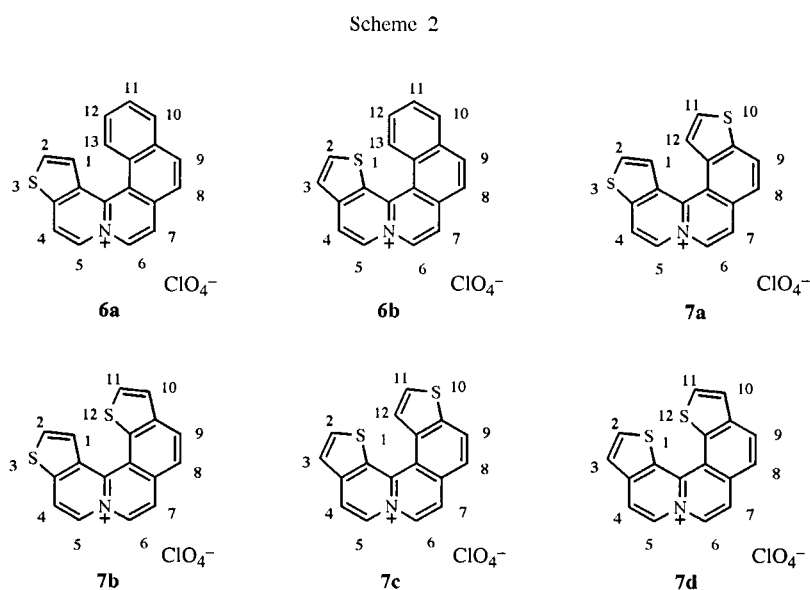
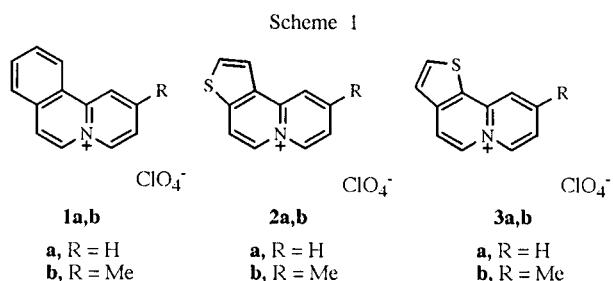
J. Heterocyclic Chem., **37**, 1009 (2000).**Introduction.**

The photocyclization of stilbene and its derivatives to phenanthrene and substituted phenanthrenes is now a well documented and useful synthetic reaction of polycyclic aromatic compounds [2]. This process has also been adapted to the preparation of fused heterocyclic systems [3]. Recently, Castle *et al.* have reported the synthesis of a number of polycyclic heterocyclic ring systems [4] containing thiophene and pyridine rings, however, there

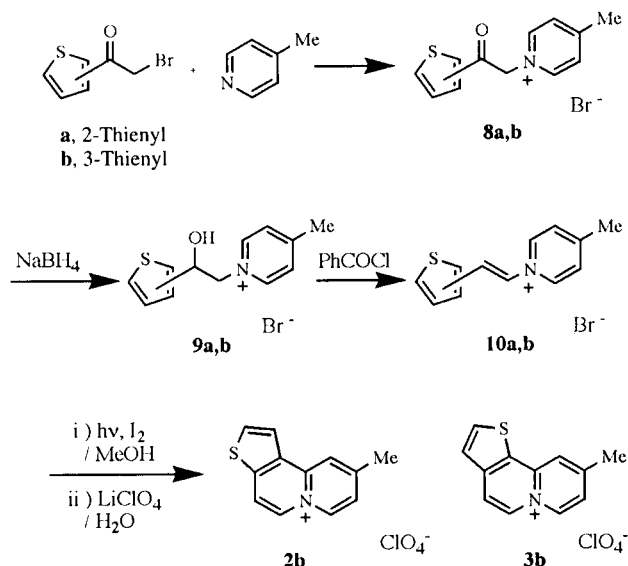
has been no examples of heterohelicenes having sulfur and bridgehead quaternary nitrogen atoms. In the course of our investigation for the synthesis of polycyclic azonia aromatic compounds by photocyclization [5], we reported the synthesis of benzo[*a*]quinolizinium salt (**1**) and thieno[*a*]-fused quinolizinium salts (**2a** and **3a**) in good yields (Scheme 1) [6]. We now describe here the photoreaction of 9-(arylviny)thieno[*a*]quinolizinium salts (**4a-c** and **5a-c**). These precursors can give hitherto unknown hetero[5]helicenes (**6a,b** and **7a-d**) containing both one quinolizinium unit and one or two thiophene rings as shown in Scheme 2.

Results and Discussion.

9-Methylthieno[3,2-*a*]quinolizinium perchlorate (**2b**; R=Me) and 9-methylthieno[2,3-*a*]quinolizinium perchlorate (**3b**; R=Me) were prepared by a similar method to our previous paper [6] for the synthesis of the parent compounds (**2a** and **3a**; R=H) (Scheme 3). The reaction of 4-methylpyridine with bromoacetyl thiophenes



Scheme 3



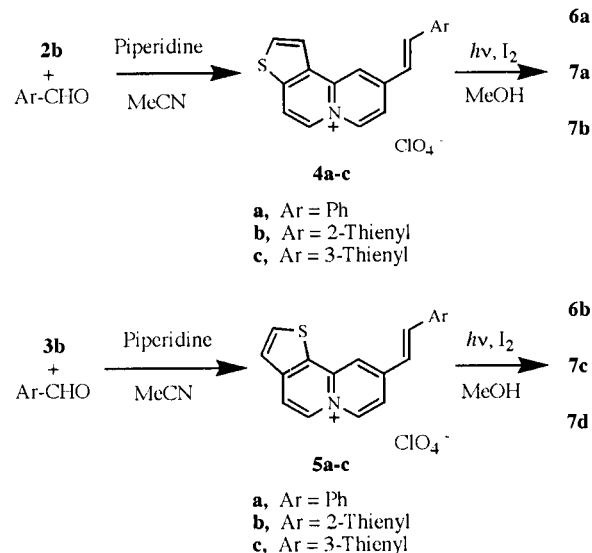
gave pyridinium salts **8a,b** (69% and 64% yields). The salts **8a,b** were reduced with sodium borohydride in water to afford the alcohols **9a,b** (76% and 77% yields). Dehydration of the alcohols **9a,b** with benzoyl chloride gave 1-[2-(thienyl)vinyl]-4-methylpyridinium bromides (**10a,b**) [7] (79% and 75% yields).

An aerated methanol solution of **10a** was irradiated with a high-pressure mercury lamp through a Pyrex-filter in the presence of iodine to yield the cyclized product **2b**. After counterion exchange with aqueous lithium perchlorate the perchlorate salt **2b** was obtained in 68% yield. The structure of **2b** was confirmed by spectral data and elemental analysis. The salt **10b** was also subjected to the irradiation under similar conditions used for **10a** and **3b** was obtained in 48% yield by ring closure at the 2-position of the 3-substituted thiophene ring.

The Knoevenagel condensation [8] of 9-methylthieno[*a*]quinolizinium salts (**2b** and **3b**) with benzaldehyde in the presence of piperidine in acetonitrile afforded (*E*)-9-styrylthieno[3,2-*a*]quinolizinium salt (**4a**, 90%) and (*E*)-9-styrylthieno[2,3-*a*]quinolizinium salt (**5a**, 89%), respectively (Scheme 4). Likewise, all four isomeric (*E*)-9-(2-thienylvinyl)thieno[*a*]quinolizinium salts (**4b,c** and **5b,c**) were obtained in excellent yields (92–99%) upon treatment of **2b** and **3b** with 2- or 3-thiophenecarbaldehydes, respectively.

A methanol solution of **4a** in the presence of iodine was irradiated with a Pyrex-filtered high-pressure mercury lamp ($\lambda > 280$ nm) until quantitative consumption of **4a**. The reaction of **4a** gave results different from the irradiation of 2-styrylbenzo[*a*]quinolizinium (**11**) [5e] as illustrated in Scheme 5. In the latter case, ring closure took place twice under the reaction conditions to yield the benzo[*ghi*]perylene skeleton accompanied by the loss of a total of four hydrogen atoms [5e]. However, the fab-ms

Scheme 4

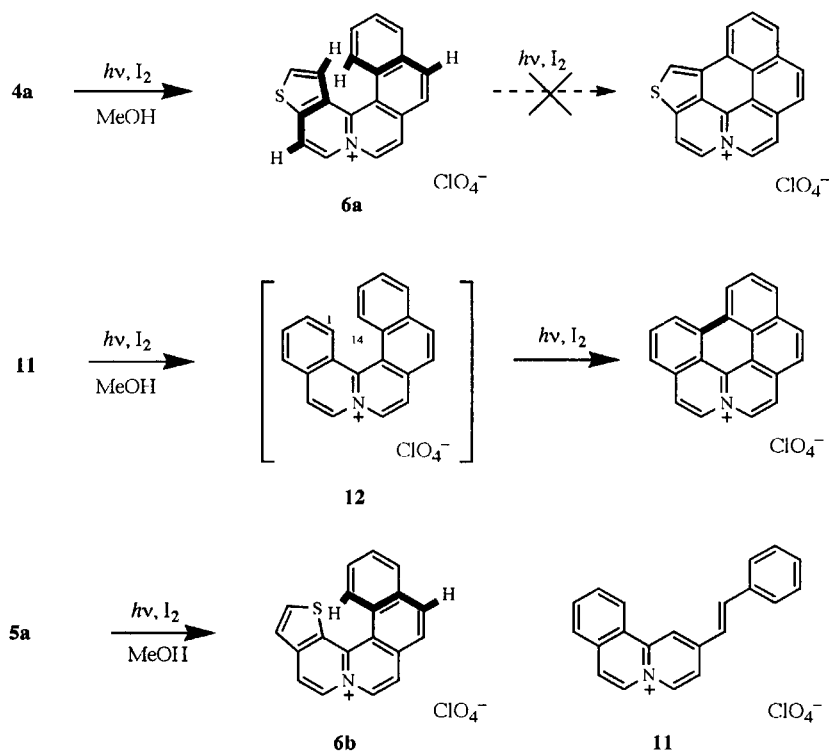


spectrum of the photoproduct from **4a** (m/z 288) showed a parent peak at m/z 286, which indicated the loss of only two hydrogen atoms during the reaction. The structure of the photoproduct was determined as 5a-azonia-3-thia[5]helicene (**6a**, 81% yield) on the basis of its ^1H -nmr spectrum, in which four pairs of doublets and one ABMX system appeared in the aromatic region. Two doublet peaks at 7.74 and 8.24 ppm showed a typical coupling constant (5.6 Hz) belonging to α,β -thiophene protons and the former signal was assigned to the H(1) proton by COSY spectrum because of the presence of the typical cross-peak due to the long-range coupling ($^5J_{\text{H-H}}$) between H(1) and H(4). In the NOE spectrum a correlation was found between H(1) (7.74 ppm) and a signal at 8.46 ppm and not between H(2) (8.24 ppm) and a signal at 8.46 ppm. So that, the signal resonating at 8.46 ppm was assigned as H(13). The similar long-range coupling between H(9) and H(13) was also observed and all the protons of the ABMX system H(10)–H(13) and the H(8) coupled with H(9) were assigned. Although the other two doublets were yet to be assigned from the COSY spectrum, a doublet centered at 9.24 ppm was tentatively assigned as H(6) based on its chemical shifts and the remaining one (8.43 ppm) as H(7).

The different behaviors between the final photoproducts from **4a** and **11** suggested that the non-bonding distance between C(1) and C(13) of **6a** is probably longer than C(1) and C(14) of 6a-azonia[5]helicene (**12**) [5c].

The photocyclization of **5a** was carried out under similar conditions to yield 5a-azonia-1-thia[5]helicene (**6b**) in 64% yield (Scheme 5). The ^1H -nmr spectral assignment of **6b** except for the thiophene protons was achieved in a similar way to that employed in the assignment of the spectrum of **6a**. The resonances of the terminal thiophene moiety, H(2) and H(3), were assigned by comparing with

Scheme 5



the previous spectroscopic data for thieno[2,3-*a*]quino-
lizinium salts **3a** [4]. Interestingly, one doublet peak
(8.81 ppm) of the four spin system in **6b**, which was
assigned to the H(13) proton by the presence of long-range
coupling with H(9) based upon the COSY spectrum, was
shifted to the lower field (by 0.35 ppm) compared with the
corresponding proton of **6a** (see Table I). This large down
field shift for H(13) of **6b** was probably ascribed to a
through-space effect of the non-bonding electrons of the
sulfur atom in the thiophene ring.

From the photocyclization of **4b,c** and **5b,c** under
similar conditions as used in **4a** and **5a**, the corresponding

four isomeric 5a-azoniadithia[5]helicenes (**7a-d**) were
obtained in 29-64%. All 1H nmr assignments of the
azoniadithia[5]helicenes **7a-d** were performed upon their
chemical shifts, coupling constants, and the basis of
two-dimensional nmr spectra. In Tables I and II details of
the 1H nmr data of the hetero[5]helicenes **6a,b** and **7a-d**,
all run at 270 MHz in DMSO- d_6 , are compared. The
following features may be noted: 1) The protons α
positioned to the nitrogen atom, H(5) and H(6), resonate at
the lowest field (over 9 ppm). 2) The protons α positioned
to the sulfur atom resonates at lower field than that β
positioned to it, except for the H(1) in **7b** and for the H(12)

Table 1
 1H Nmr Chemical Shifts (δ) of Compounds **6a,b** and **7a-d** in DMSO- d_6 [a]

Compounds	1H	2H	3H	4H	5H	6H	7H	8H	9H	10H	11H	12H	13H
6a	7.74	8.24	—	8.95	9.34	9.24	8.43	8.20	8.61	8.32	7.88	7.71	8.46
6b	—	8.46	7.90	8.66	9.36	9.24	8.39	8.17	8.61	8.33	7.91	7.75	8.81
7a	8.05	8.38	—	8.97	9.32	9.11	8.45	8.21	8.87	—	8.23	7.88	—
7b	8.47	8.43	—	9.00	9.32	9.10	8.47	8.26	8.69	7.86	8.12	—	—
7c	—	8.64	7.99	8.70	9.35	9.12	8.42	8.20	8.88	—	8.27	8.27	—
7d	—	8.65	8.05	8.76	9.37	9.12	8.45	8.26	8.72	7.91	8.14	—	—

[a] The numbering is given in Scheme 2.

Table 2
¹H Nmr Coupling Constants (J, Hz) of Compounds **6a,b** and **7a-d** in DMSO-d₆ [a]

Compounds	J _{1,2}	J _{2,3}	J _{4,5}	J _{6,7}	J _{8,9}	J _{10,11}	J _{11,12}	J _{12,13}
6a	5.6	-	7.1	7.1	8.6	7.9	7.3	7.9
6b	-	5.3	6.9	6.9	8.6	7.9	7.3	8.3
7a	5.6	-	6.9	7.1	8.6	-	5.6	-
7b	5.6	-	6.9	6.9	8.6	5.3	-	-
7c	-	5.4	6.8	6.8	8.3	-	5.6	-
7d	-	5.3	7.1	7.3	8.4	5.4	-	-

[a] The numbering is given in Scheme 2.

in **7c**. 3) Those above two special cases are due to deshielding effects by the lone pair of sulfur atom on the opposite terminal rings. The same observation is found in the case of H(13) of **6b**. 4) The small down field shifts of the H(4) in **6a** and **7a,b** and H(9) in **7a,c** are also attributed to the deshielding effects of the neighbouring sulfur atom. 5) The coupling constants of protons in the α and β positions to the sulfur atom are 5.3-5.6 Hz. 6) The coupling constants of protons α and β positions to the nitrogen atom are 6.8-7.3 Hz. 7) In the **6a** and **7a,b**, H(1) is coupled with H(4) by a five bond *epi-zig-zag* coupling. The long-range couplings between H(9) and H(13) of **6a,b** or H(9) and H(12) of **7a,c** are also observable.

In conclusion, the six novel thia and dithia analogues of azonias[5]helicenes (**6a,b** and **7a-d**) have been synthesized and their ¹H-nmr spectra were assigned. Further studies on the synthesis of higher fused heterohelicenes containing both quinolizinium unit and thiophene rings are now under way.

EXPERIMENTAL

General Procedure.

Melting points were determined on a Yamato melting point apparatus MP-21 and are uncorrected. The ¹H nmr spectra were obtained using a JEOL JNM-EX270 (270MHz) spectrometer. Chemical shifts are reported in ppm from DMSO-d₆ as 2.50 ppm. The uv and visible spectra were obtained with a Hitachi 220A spectrophotometer. The fast-atom bombardment mass spectra were recorded with a JEOL LX1000 spectrometer with m-nitrobenzyl alcohol as a matrix. Elemental analyses were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer.

2-[1-(4-Methylpyridinium)]-1-(2-thienyl)ethanone bromide (**8a**), 1-(2-hydroxy-2-thienylethyl)-4-methylpyridinium bromide (**9a**), and (*E*)-1-[2-(2-thienyl)vinyl]-4-methylpyridinium bromide (**10a**) were prepared according to the literature [7] with some modifications described below.

General Procedure for the Preparation of the 9-Methyl Derivatives of Thieno[3,2-*a*]- and Thieno[2,3-*a*]quinolizinium Perchlorates (**2b** and **3b**).

To a benzene solution (100 ml) of 2-bromoacetyl derivatives (100 mmoles), which were obtained by bromination of acetylthiophene with copper(II) bromide [9] and used without purification, 4-methylpyridine (120 mmoles) was added. The mixture was refluxed for 1-2 hours. The resulting solid was

filtered, washed with benzene and acetone, and recrystallized from ethanol to afford 1-(aroylmethyl)-4-methylpyridinium salts (**8a,b**).

To a solution of 27 mmoles of the pyridinium salt **8a,b** in water (150 ml), a solution of 0.3g (8 mmoles) of sodium borohydride in water (15 ml) was added portionwise at room temperature. After hydrolysis with HBr (48%), the solvent was removed under reduced pressure, and the residue was recrystallized from ethanol to give 1-(2-aryl-2-hydroxyethyl)-4-methylpyridinium bromides (**9a,b**). A solution of the alcohol **9a** or **9b** (10 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-ethyl acetate to yield (*E*)-1-(2-arylvinyl)-4-methylpyridinium salts (**10a,b**).

A methanol solution (1000 ml) of **10a,b** (1.0 g, 3.6 mmoles) and iodine (70 mg) in a Pyrex vessel was irradiated with a 450W 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 (100 ml). An insoluble brown solid was filtered off and a saturated aqueous solution of lithium perchlorate was added to the filtrate. The precipitate was filtered, washed with cold water, and recrystallized from acetonitrile-ethanol to afford **2b** and **3b** (R = Me).

2-[1-(4-Methylpyridinium)]-1-(2-thienyl)ethanone Bromide (**8a**).

This compound was obtained as brown prisms (69%), mp 232-233° dec. (ref. [7] 239-240°); ¹H nmr (DMSO-d₆): δ 2.67 (s, 3H, CH₃), 6.39 (s, 2H, CH₂), 7.41 (dd, J = 4.1 and 4.9 Hz, 1H, thienyl-4), 8.09 (d, J = 6.3 Hz, 2H, pyridyl-3,5), 8.21 (d, J = 4.1 Hz, 1H, thienyl-3), 8.23 (d, J = 4.9 Hz, 1H, thienyl-5), 8.88 (d, J = 6.3 Hz, 2H, pyridyl-2,6); ms: *m/z* 218 (M-Br)⁺.

2-[1-(4-Methylpyridinium)]-1-(3-thienyl)ethanone Bromide (**8b**).

This compound was obtained as brown prisms (64%), mp 214-215° dec.; ¹H nmr (DMSO-d₆): δ 2.67 (s, 3H, CH₃), 6.33 (s, 2H, CH₂), 7.61 (d, J = 5.3 Hz, 1H, thienyl-4), 7.79 (dd, J = 2.6 and 5.3 Hz, 1H, thienyl-5), 8.09 (d, J = 5.8 Hz, 2H, pyridyl-3,5), 8.77 (d, J = 2.6 Hz, 1H, thienyl-2), 8.86 (d, J = 5.8 Hz, 2H, pyridyl-2,6); ms: *m/z* 218 (M-Br)⁺.

Anal. Calcd. for C₁₂H₁₂NOSBr: C, 48.34; H, 4.06; N, 4.70. Found: C, 48.64; H, 4.16; N, 4.41.

1-{2-[Hydroxy-(2-thienyl)]ethyl}-4-methylpyridinium Bromide (**9a**).

This compound was obtained as white prisms (76%), mp 176.5-178° (ref. [7] 177-179°); ¹H nmr (DMSO-d₆): δ 2.62

(s, 3H, CH₃), 4.65 (dd, *J* = 8.6 and 12.9 Hz, 1H, CH₂), 4.94 (dd, *J* = 3.1 and 12.9 Hz, 1H, CH₂), 5.35 (m, 1H, CH), 6.44 (broad s, 1H, OH), 7.06 (dd, *J* = 3.6 and 5.0 Hz, 1H, thienyl-4), 7.14 (d, *J* = 3.6 Hz, 1H, thienyl-3), 7.50 (dd, *J* = 5.0 and 1.0 Hz, 1H, thienyl-5), 8.00 (d, *J* = 6.3 Hz, 2H, pyridyl-3,5), 8.88 (d, *J* = 6.3 Hz, 2H, pyridyl-2,6); ms: *m/z* 220 (M-Br)⁺.

1-{2-[Hydroxy-(3-thienyl)]ethyl}-4-methylpyridinium Bromide (9b).

This compound was obtained as white prisms (77%), mp 178-179°; ¹H nmr (DMSO-*d*₆): δ 2.62 (s, 3H, CH₃), 4.61 (dd, *J* = 8.6 and 12.9 Hz, 1H, CH₂), 4.90 (dd, *J* = 3.1 and 12.9 Hz, 1H, CH₂), 5.0 Hz, 1H, thienyl-4), 7.42 (d, *J* = 3.0 Hz, 1H, thienyl-2), 7.58 (dd, *J* = 3.0 and 5.0 Hz, 1H, thienyl-5), 7.99 (d, *J* = 5.8 Hz, 2H, pyridyl-3,5), 8.84 (d, *J* = 5.8 Hz, 2H, pyridyl-2,6); ms: *m/z* 220 (M-Br)⁺.

Anal. Calcd. for C₁₂H₁₄NOSBr: C, 48.01; H, 4.70; N, 4.67. Found: C, 47.79; H, 4.59; N, 4.52.

(E)-4-Methyl-1-[2-(2-thienyl)vinyl]pyridinium Bromide (10a).

This compound was obtained as yellow micro needles (79%), mp 233-234° dec. (ref. [7] 239-240°); ¹H nmr (DMSO-*d*₆): δ 2.66 (s, 3H, CH₃), 7.19 (dd, *J* = 5.3 and 3.6 Hz, 1H, thienyl-4), 7.47 (d, *J* = 3.6 Hz, 1H, thienyl-3), 7.74 (d, *J* = 5.3 Hz, 1H, thienyl-5), 7.99 (d, *J* = 14.2 Hz, 1H, CH=CH), 8.08 (d, *J* = 6.3 Hz, 2H, pyridyl-3,5), 8.09 (d, *J* = 14.2 Hz, 1H, CH=CH), 9.20 (d, *J* = 6.3 Hz, 2H, pyridyl-2,6); ms: *m/z* 202 (M-Br)⁺.

(E)-4-Methyl-1-[2-(3-thienyl)vinyl]pyridinium Bromide (10b).

This compound was obtained as yellow micro needles (75%), mp 194-196° dec.; ¹H nmr (DMSO-*d*₆): δ 2.66 (s, 3H, CH₃), 7.53 (d, *J* = 4.9 Hz, 1H, thienyl-4), 7.72 (dd, *J* = 2.5 and 4.9 Hz, 1H, thienyl-5), 7.76 (d, *J* = 14.4 Hz, 1H, CH=CH), 7.87 (d, *J* = 2.5 Hz, 1H, thienyl-2), 8.08 (d, *J* = 6.6 Hz, 2H, pyridyl-3,5), 8.24 (d, *J* = 14.4 Hz, 1H, CH=CH), 9.18 (d, *J* = 6.6 Hz, 2H, pyridyl-2,6); ms: *m/z* 202 (M-Br)⁺.

Anal. Calcd. for C₁₂H₁₂NSBr: C, 51.07; H, 4.29; N, 4.96. Found: C, 51.19; H, 4.57; N, 4.66.

9-Methylthieno[3,2-*a*]quinolizinium Perchlorate (2b).

This compound was obtained as orange needles (68%), mp 214-215°; ¹H nmr (DMSO-*d*₆): δ 2.73 (s, 3H, CH₃), 7.99 (d, *J* = 6.9 Hz, 1H, 8-H), 8.39 (d, *J* = 5.4 Hz, 1H, 2-H), 8.49 (d, *J* = 5.4 Hz, 1H, 1-H), 8.62 (d, *J* = 7.1 Hz, 1H, 4-H), 8.98 (s, 1H, 10-H), 9.01 (d, *J* = 7.1 Hz, 1H, 5-H), 9.29 (d, *J* = 6.9 Hz, 1H, 7-H); ms: *m/z* 200 (M-ClO₄)⁺.

Anal. Calcd. for C₁₂H₁₀NSClO₄: C, 48.09; H, 3.36; N, 4.67. Found: C, 48.04; H, 3.32; N, 4.64.

9-Methylthieno[2,3-*a*]quinolizinium Perchlorate (3b).

This compound was obtained as pale yellow needles (48%), mp 168-169°; ¹H nmr (DMSO-*d*₆): δ 2.72 (s, 3H, CH₃), 7.90 (d, *J* = 5.1 Hz, 1H, 3-H), 7.96 (dd, *J* = 6.9 and 1.3 Hz, 1H, 8-H), 8.36 (d, *J* = 6.9 Hz, 1H, 4-H), 8.59 (d, *J* = 5.1 Hz, 1H, 2-H), 8.67 (s, 1H, 10-H), 9.02 (d, *J* = 6.9 Hz, 1H, 5-H), 9.29 (d, *J* = 6.9 Hz, 1H, 7-H); ms: *m/z* 200 (M-ClO₄)⁺.

Anal. Calcd. for C₁₂H₁₀NSClO₄: C, 48.09; H, 3.36; N, 4.67. Found: C, 47.90; H, 3.23; N, 4.60.

General Procedure for the Preparations of the (E)-9-(Arylviny)thieno[*a*]quinolizinium Salts (4a-c and 5a-c).

To a refluxing acetonitrile solution (5 ml) of **2b** or **3b** (1.7 mmoles) and arylaldehyde (7 mmoles) was added piperidine (4 mmoles). The mixture was refluxed for 1 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 filtered, washed with diethyl ether, and dried *in vacuo* to give (E)-9-(2-arylviny)thieno[*a*]quinolizinium salts (**4a-c** and **5a-c**). The analytical samples were obtained by recrystallization from acetonitrile-ethanol.

(E)-9-Styrylthieno[3,2-*a*]quinolizinium Perchlorate (4a).

This compound was obtained as yellow needles (90%), mp 280-281° dec.; ¹H nmr (DMSO-*d*₆): δ 7.48 (t, *J* = 7.3 Hz, 1H, phenyl-4), 7.52 (dd, *J* = 6.9 and 7.3 Hz, 2H, phenyl-3,5), 7.58 (d, *J* = 16.2 Hz, 1H, CH=CH), 7.76 (d, *J* = 6.9 Hz, 2H, phenyl-2,6), 8.07 (d, *J* = 16.2 Hz, 1H, CH=CH), 8.36 (d, *J* = 6.9 Hz, 1H, 8-H), 8.44 (d, *J* = 5.3 Hz, 1H, 2-H), 8.53 (d, *J* = 5.3 Hz, 1H, 1-H), 8.61 (d, *J* = 7.3 Hz, 1H, 4-H), 9.00 (d, *J* = 7.3 Hz, 1H, 5-H), 9.14 (s, 1H, 10-H), 9.34 (d, *J* = 6.9 Hz, 1H, 7-H); ms: *m/z* 288 (M-ClO₄)⁺.

Anal. Calcd. for C₁₉H₁₄NSClO₄: C, 58.84; H, 3.64; N, 3.61. Found: C, 59.10; H, 3.53; N, 3.42.

(E)-2-[2-(2-Thienyl)vinyl]thieno[3,2-*a*]quinolizinium Perchlorate (4b).

This compound was obtained as orange needles (98%), mp 256-257° dec.; ¹H nmr (DMSO-*d*₆): δ 7.22 (dd, *J* = 3.6 and 5.0 Hz, 1H, thienyl-4), 7.25 (d, *J* = 16.2 Hz, 1H, CH=CH), 7.49 (d, *J* = 3.6 Hz, 1H, thienyl-3), 7.78 (d, *J* = 5.0 Hz, 1H, thienyl-5), 8.27 (d, *J* = 16.2 Hz, 1H, CH=CH), 8.31 (d, *J* = 7.3 Hz, 1H, 8-H), 8.42 (d, *J* = 5.6 Hz, 1H, 2-H), 8.50 (d, *J* = 5.6 Hz, 1H, 1-H), 8.58 (d, *J* = 7.3 Hz, 1H, 4-H), 8.96 (d, *J* = 7.3 Hz, 1H, 5-H), 9.11 (s, 1H, 10-H), 9.29 (d, *J* = 7.3 Hz, 1H, 7-H); ms: *m/z* 294 (M-ClO₄)⁺.

Anal. Calcd. for C₁₇H₁₂NS₂ClO₄: C, 51.84; H, 3.07; N, 3.56. Found: C, 51.71; H, 3.33; N, 3.45.

(E)-2-[2-(3-Thienyl)vinyl]thieno[3,2-*a*]quinolizinium Perchlorate (4c).

This compound was obtained as yellow needles (92%), mp 261-262° dec.; ¹H nmr (DMSO-*d*₆): δ 7.38 (d, *J* = 16.2 Hz, 1H, CH=CH), 7.58 (d, *J* = 5.0 Hz, 1H, thienyl-4), 7.72 (dd, *J* = 3.0 and 5.0 Hz, 1H, thienyl-5), 7.91 (d, *J* = 3.0 Hz, 1H, thienyl-2), 8.07 (d, *J* = 16.2 Hz, 1H, CH=CH), 8.28 (d, *J* = 7.3 Hz, 1H, 8-H), 8.42 (d, *J* = 5.6 Hz, 1H, 2-H), 8.52 (d, *J* = 5.6 Hz, 1H, 1-H), 8.58 (d, *J* = 7.3 Hz, 1H, 4-H), 8.97 (d, *J* = 7.3 Hz, 1H, 5-H), 9.07 (s, 1H, 10-H), 9.29 (d, *J* = 7.3 Hz, 1H, 7-H); ms: *m/z* 294 (M-ClO₄)⁺.

Anal. Calcd. for C₁₇H₁₂NS₂ClO₄: C, 51.84; H, 3.07; N, 3.56. Found: C, 51.84; H, 3.30; N, 3.31.

(E)-9-Styrylthieno[2,3-*a*]quinolizinium Perchlorate (5a).

This compound was obtained as yellow needles (89%), mp 246-247° dec.; ¹H nmr (DMSO-*d*₆): δ 7.45 (t, *J* = 7.3 Hz, 1H, phenyl-4), 7.52 (dd, *J* = 6.9 and 7.3 Hz, 2H, phenyl-3,5), 7.70 (d, *J* = 16.2 Hz, 1H, CH=CH), 7.77 (d, *J* = 6.9 Hz, 2H, phenyl-2,6), 7.91 (d, *J* = 5.1 Hz, 1H, 3-H), 8.06 (d, *J* = 16.2 Hz, 1H, CH=CH), 8.35 (d, *J* = 7.1 Hz, 1H, 4-H), 8.40 (d, *J* = 7.3 Hz, 1H, 8-H), 8.61 (d, *J* = 5.1 Hz, 1H, 2-H), 8.77 (s, 1H, 10-H), 9.00 (d, *J* = 7.1 Hz, 1H, 5-H), 9.33 (d, *J* = 7.3 Hz, 1H, 7-H); ms: *m/z* 288 (M-ClO₄)⁺.

Anal. Calcd. for $C_{19}H_{14}NSClO_4$: C, 58.84; H, 3.64; N, 3.61. Found: C, 59.08; H, 3.92; N, 3.51.

(*E*)-2-[2-(2-Thienyl)vinyl]thieno[2,3-*a*]quinolizinium Perchlorate (**5b**).

This compound was obtained as yellow needles (99%), mp 244–245° dec.; 1H nmr (DMSO- d_6): δ 7.23 (dd, *J* = 3.0 and 5.0 Hz, 1H, thienyl-4), 7.38 (d, *J* = 16.2 Hz, 1H, CH=CH), 7.51 (d, *J* = 3.0 Hz, 1H, thienyl-3), 7.78 (d, *J* = 5.0 Hz, 1H, thienyl-5), 7.90 (d, *J* = 5.3 Hz, 1H, 3-H), 8.27 (d, *J* = 16.2 Hz, 1H, CH=CH), 8.32 (d, *J* = 7.3 Hz, 1H, 4-H), 8.34 (d, *J* = 6.9 Hz, 1H, 8-H), 8.60 (d, *J* = 5.3 Hz, 1H, 2-H), 8.79 (s, 1H, 10-H), 8.96 (d, *J* = 7.3 Hz, 1H, 5-H), 9.29 (d, *J* = 6.9 Hz, 1H, 7-H); ms: *m/z* 294 (M-ClO $_4$) $^+$.

Anal. Calcd. for $C_{17}H_{12}NS_2ClO_4$: C, 51.84; H, 3.07; N, 3.56. Found: C, 51.66; H, 3.25; N, 3.83.

(*E*)-2-[2-(3-Thienyl)vinyl]thieno[2,3-*a*]quinolizinium Perchlorate (**5c**).

This compound was obtained as yellow needles (98%), mp 217–218° dec.; 1H nmr (DMSO- d_6): δ 7.49 (d, *J* = 16.2 Hz, 1H, CH=CH), 7.58 (d, *J* = 4.8 Hz, 1H, thienyl-4), 7.72 (dd, *J* = 2.8 and 4.8 Hz, 1H, thienyl-5), 7.89 (d, *J* = 2.8 Hz, 1H, thienyl-2), 7.90 (d, *J* = 5.3 Hz, 1H, 3-H), 8.06 (d, *J* = 16.2 Hz, 1H, CH=CH), 8.32 (d, *J* = 7.3 Hz, 2H, 4-H and 8-H), 8.60 (d, *J* = 5.3 Hz, 1H, 2-H), 8.68 (s, 1H, 10-H), 8.98 (d, *J* = 7.3 Hz, 1H, 5-H), 9.29 (d, *J* = 7.3 Hz, 1H, 7-H); ms: *m/z* 294 (M-ClO $_4$) $^+$.

Anal. Calcd. for $C_{17}H_{12}NS_2ClO_4$: C, 51.84; H, 3.07; N, 3.56. Found: C, 52.05; H, 3.35; N, 3.57.

General Procedure for Photocyclization of **4a-c** and **5a-c**.

A solution of **4** or **5** (150–200 mg; 0.4–0.5 mmoles) and iodine (25–50 mg; 0.1–0.2 mmoles) in methanol (1000 ml) was irradiated at room temperature with a 450 W high-pressure mercury lamp (Ushio UM-452) inside a Pyrex immersion well. The reaction was monitored by the UV and visible spectra. When the spectra of the *cis* form of **4** or **5** disappeared, irradiation was stopped and the solvent was removed under reduced pressure. The residue was recrystallized from acetonitrile-ethanol.

5a-Azonias-3-thia[5]helicene Perchlorate (**6a**).

This compound was obtained as pale yellow needles, yield 81% from **4a**, mp 290–291° dec.; ms: *m/z* 286 (M-ClO $_4$) $^+$.

Anal. Calcd. for $C_{19}H_{12}NSClO_4$: C, 59.15; H, 3.14; N, 3.63. Found: C, 59.37; H, 3.01; N, 3.30.

5a-Azonias-1-thia[5]helicene Perchlorate (**6b**).

This compound was obtained as pale yellow needles, yield 64% from **5a**, mp 234–236° dec.; ms: *m/z* 286 (M-ClO $_4$) $^+$.

Anal. Calcd. for $C_{19}H_{12}NSClO_4$: C, 59.15; H, 3.14; N, 3.63. Found: C, 59.06; H, 3.21; N, 3.25.

5a-Azonias-3,10-dithia[5]helicene Perchlorate (**7a**).

This compound was obtained as pale yellow needles, yield 40% from **4b**, mp 228.5–229.5° dec.; ms: *m/z* 292 (M-ClO $_4$) $^+$.

Anal. Calcd. for $C_{17}H_{10}NS_2ClO_4$: C, 52.11; H, 2.57; N, 3.58. Found: C, 52.36; H, 2.93; N, 3.69.

5a-Azonias-3,12-dithia[5]helicene Perchlorate (**7b**).

This compound was obtained as pale yellow needles, yield 40% from **4c**, mp >300°; ms: *m/z* 292 (M-ClO $_4$) $^+$.

Anal. Calcd. for $C_{17}H_{10}NS_2ClO_4$: C, 52.11; H, 2.57; N, 3.58. Found: C, 52.28; H, 2.58; N, 3.34.

5a-Azonias-1,10-dithia[5]helicene Perchlorate (**7c**).

This compound was obtained as pale yellow needles, yield 29% from **5b**, mp 239–241° dec.; ms: *m/z* 292 (M-ClO $_4$) $^+$.

Anal. Calcd. for $C_{17}H_{10}NS_2ClO_4$: C, 52.11; H, 2.57; N, 3.58. Found: C, 52.00; H, 2.63; N, 3.37.

5a-Azonias-1,12-dithia[5]helicene Perchlorate (**7d**).

This compound was obtained as pale yellow needles, yield 21% from **5c**, mp 243–244° dec.; ms: *m/z* 292 (M-ClO $_4$) $^+$.

Anal. Calcd. for $C_{17}H_{10}NS_2ClO_4$: C, 52.11; H, 2.57; N, 3.58. Found: C, 52.17; H, 2.75; N, 3.83.

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