Synthesis of polycyclic azonia-aromatic compounds by photo-induced intramolecular quaternization: Azonia derivatives of benzo[*c*]phenanthrene, [5]helicene and [6]helicene

Sadao Arai,*,† Masanori Ishikura and Takamichi Yamagishi

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

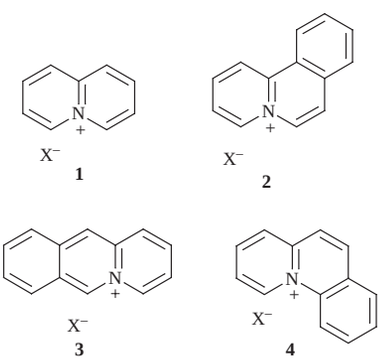
A series of new polycyclic azonia-aromatic compounds incorporating a benzo[*c*]quinolizinium ring have been synthesized by photo-induced intramolecular quaternization. Acetonitrile solutions of 2-[2-(2-chlorophenyl)vinyl]quinoline 8 and 2-[2-(1-chloro-2-naphthyl)vinyl]pyridine 9 have been irradiated with a high-pressure mercury lamp through a Pyrex filter to afford the azonia derivatives of benzo[*c*]phenanthrene, *viz* dibenzo[*cf*]quinolizinium salt 15 and naphtho[2,1-*c*]quinolizinium salt 18, respectively. On photoreaction of 2-[2-(1-chloro-2-naphthyl)vinyl]quinoline 10 and 2-[2-(2-chlorophenyl)-vinyl]benzo[*h*]quinoline 11 two successive cyclizations occur: the first converting substrates 10 and 11 into 10b-azonia[5]helicene salt 19 by photo-induced intramolecular quaternization and the second converting the salt 19 into 4c-azoniabenzo[*ghi*]perylene salt 20 by oxidative photocyclodehydrogenation. The photo-induced intramolecular quaternization of 2-[2-(2-chlorophenyl)vinyl]-1,10-phenanthroline 12 gives 10-aza-10c-azonia[5]helicene salt 21. The 12c-azonia[6]helicene salts 30 and 31, in which a carbon atom of the inner helix skeleton of [6]helicene is replaced by a quaternary nitrogen atom, have been synthesized by photo-induced quaternization of the corresponding olefins 13 and 14, respectively.

Introduction

Azonia-aromatic compounds, in which a bridgehead carbon of polycyclic aromatic compounds is replaced by a quaternary nitrogen, have been widely investigated in connection with their biological activities, because a similar structure is found in alkaloids such as coralyne, sempervirine, and flavopereurine.[1] There has also been interest in their application in a photographic process[1c] and as a new class of DNA-intercalating agents.[2] Since the first synthesis of unsubstituted bicyclic quinolizinium salt **1** by Boekelheide and Gall in 1954,[3] various synthetic methodologies have been reported for the construction of azonia-aromatic rings.

Of the three possible isomers of tricyclic benzoquinolizinium salts, benzo[*a*]- and benzo[*b*]-quinolizinium salts **2** and **3** have been synthesized by the cyclodehydrations of a 1-acetonyl-2-phenylpyridinium salt and a 1-benzyl-2-formylpyridinium salt under acidic conditions, respectively.[1,4] The cyclodehydrations also gave the tetra- and penta-cyclic compounds incorporating a benzo[*a*]- or benzo[*b*]-quinolizinium ring. The oxidative photocyclodehydrogenation of *N*-styrylpyridinium salts and 2-strylquinolizinium salts is also a convenient method for the synthesis of polycyclic azonia-aromatic compounds incorporating a benzo[*a*]quinolizinium ring such as 12a-azoniabenzo-[*ghi*]perylene, 8a-azonia[6]helicene, and 2a-azoniabenzo[*a*]-coronene salts.[5]

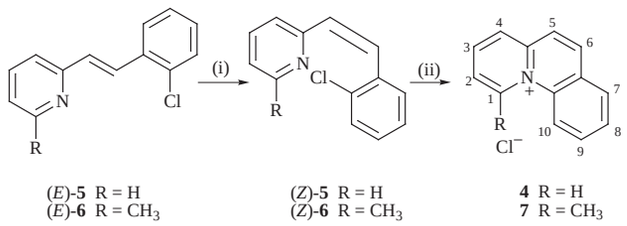
In contrast, the synthetic methodology available to attain polycyclic azonia-aromatic compounds incorporating a benzo-[*c*]quinolizinium ring is still very limited. Glover and Jones reported the synthesis of parent compound **4** by a three-step process from 2-cyanopyridine.[6] The Westphal condensation was used for the synthesis of this tricycle.[7] Bradsher developed a thermal quaternization method for the synthesis of compound **4**: (*Z*)-2-[2-(2-chlorophenyl)vinyl]pyridine (*Z*)-**5**, prepared by irradiation of a benzene solution of (*E*)-**5**, was heated at 170 °C to afford compound **4** (Scheme 1).[8a] The method was also applied to the synthesis of both the 1-methyl derivative **7** having a methyl group at the bay region and the dibenzo[*cf*]quinolizinium salt **15**. The thermal cyclization of compounds (*Z*)-**6** and (*Z*)-**8**, however, failed and respective isomers (*E*)-**6** and (*E*)-**8** were recovered.[8] In order to circumvent this difficulty we have devised a photocyclization method. Irradiation of compound (*E*)-**6** and (*E*)-**8** in acetonitrile gave the desired 1-methylbenzo-[*c*]quinolizinium salt **7** and compound **15**, respectively.[9a] These results prompted us to explore the generality of the photocyclization for the synthesis of polycyclic azonia-aromatic compounds incorporating a benzo[*c*]quinolizinium ring. Although oxidative photocyclization has been extensively used for the synthesis of numerous polycyclic aromatic compounds,[10] the photo-induced quaternization has received no attention to date. In this paper we detail the synthesis of novel polycyclic aromatic compounds with a bridgehead quaternary nitrogen by photo-induced intramolecular quaternization.



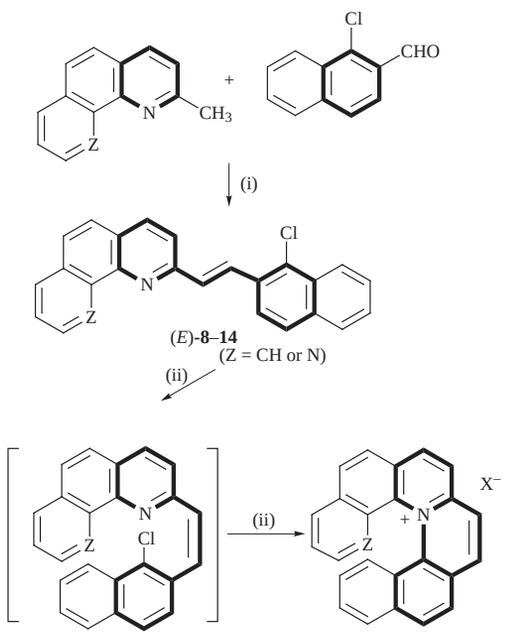
Results and discussion

New tetra-, penta-, and hexa-cyclic azonia-aromatic compounds incorporating a benzo[*c*]quinolizinium ring have been synthesized by means of photo-induced intramolecular quaternization from the corresponding stilbazoles. In most cases, the synthetic procedures follow the generalized pathway outlined in

† *Present address*: Chemical Research Laboratory, Tokyo Medical College, 6-1-1 Shinjuku, Shinjuku-ku, Tokyo 160, Japan.



Scheme 1 *Conditions*: (i) *hν*; (ii) *hν* or heat at 170 °C



Scheme 2 *Conditions*: (i) reflux in $(Ac)_2O$; (ii) *hν* in CH_3CN

Scheme 2. The (*E*)-stilbazoles **8**–**10** were synthesized by the condensation of 2-methylpyridine or 2-methylquinoline with *o*-chlorobenzaldehyde or 1-chloronaphthalene-2-carbaldehyde in boiling acetic anhydride in 26–59% yield. Similarly the olefins **11**–**14** were prepared from 2-methylbenzo[*h*]quinoline or 2-methyl-1,10-phenanthroline in 27–50% yield. The stereochemistry of the double bond was *E* as indicated by ^{1}H NMR coupling constants. For instance, the olefin protons in compound **8** appeared at δ 7.57 and 8.13 with a coupling constant $J = 16.3$ Hz, characteristic of an *E* configuration. The photocyclization of the olefins **8**–**14** was carried out as described below.

Photocyclization of 2-[2-(2-chlorophenyl)vinyl]quinoline 8

A benzene solution of (*E*)-**8** was irradiated with a high-pressure mercury lamp through a Pyrex-filter ($\lambda > 280$ nm) to afford *E*–*Z* mixtures of starting material and no cyclization products were observed.[8b] In contrast, by irradiation of an ethanolic solution of (*E*)-**8** the absorption band at 335 nm decreased and a new peak appeared at 410 nm. This result indicated the formation of dibenzo[*cf*]quinolizinium salt **15** (Scheme 3). The use of acetonitrile as a solvent was found to improve the yield dramatically as shown in Fig. 1. The yield determined by UV spectrophotometry, however, reached a maximum (34%) and then decreased. This result implies the photo-decomposition of the photo-product **15** under such reaction conditions. When substrates (*E*)- and (*Z*)-**8** were irradiated selectively without the irradiation of the first absorption band of compound **15** by the use of Pyrex-filtered light through an aq. nickel sulfate solution filter ($280 < \lambda < 360$ nm and $\lambda > 430$ nm),[11] the yield notably increased (67%) (Fig. 1). After anion exchange by treatment with lithium perchlorate, the salt **15** (X = ClO_4) was obtained as yellow crystals. The structural confirmation of salt **15** was established by its spectral and analytical data. The fast-atom

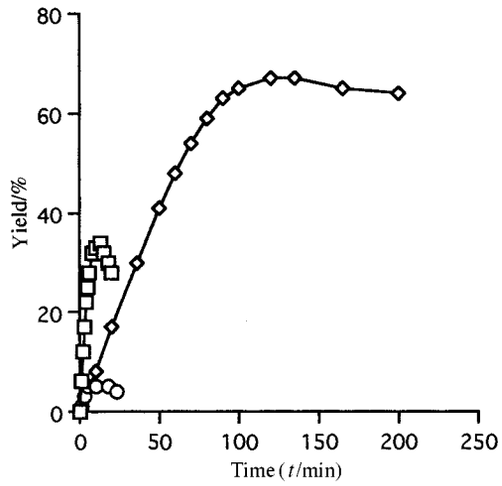
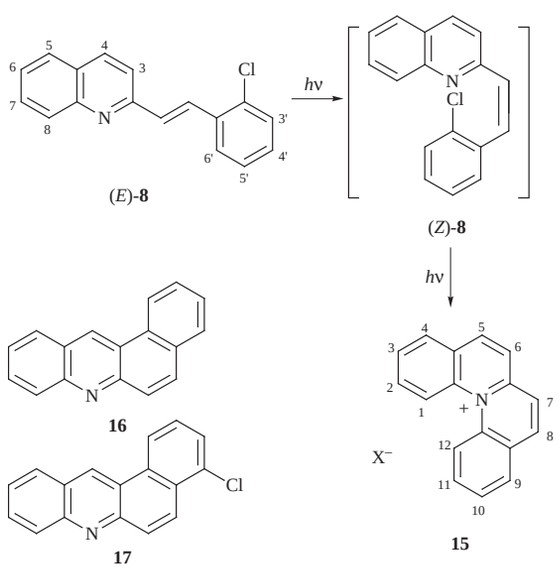


Fig. 1 Effect of irradiation conditions on the photocyclization of compound **8** (6.0×10^{-5} mol dm^{-3}). □, irradiation with Pyrex-filtered light in acetonitrile; ○, irradiation with Pyrex-filtered light in ethanol, ◇, irradiation with Pyrex-filtered light through an aq. nickel sulfate filter in acetonitrile.

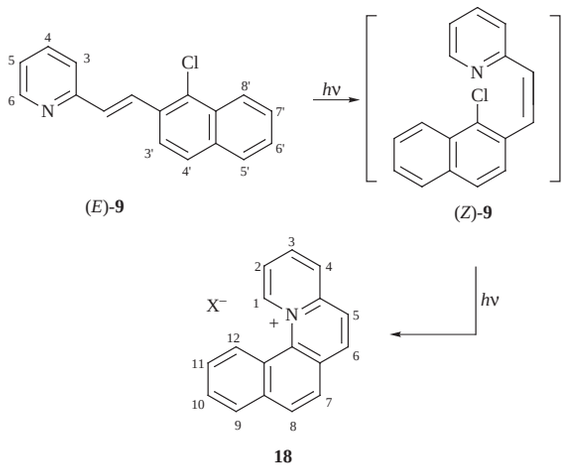


Scheme 3

bombardment (FAB) mass spectrum exhibited a molecular cation peak at *m*/*z* 230. The ^{1}H NMR spectrum showed a four-spin system and a two-spin system, and a typical cross-peak due to the long-range coupling between 1-H and 5-H was observed by the ^{1}H–^{1}H chemical-shift correlation (COSY) spectrum. The formation of benzo[*a*]acridine **16**, by photocyclization with a loss of hydrogen chloride, and its chloro derivative **17**, by oxidative photocyclodehydrogenation, were ruled out by the spectral and analytical data.

Photocyclization of 2-[2-(1-chloro-2-naphthyl)vinyl]pyridine 9

The irradiation of (*E*)-**9** in acetonitrile with Pyrex-filtered light afforded naphtho[2,1-*c*]quinolizinium salt **18** in 42% yield (Scheme 4). The use of an aq. nickel sulfate filter slightly increased the yield (48%). In this case the thermal cyclization of the *E*–*Z* mixtures **9** at 180 °C, prepared by irradiation of (*E*)-**9** in benzene, also afforded the salt **18**, in 60% yield.[8b] The different reactivity on thermal cyclization between isomers (*Z*)-**8** and (*Z*)-**9** is probably ascribable to the difference in nucleophilic character between quinoline (pK_a 4.94) and pyridine (pK_a 5.2).[12] The ^{1}H NMR spectrum of compound **18** showed that the proton (1-H) situated in the bay region is strongly deshielded (δ 10.33), similarly to the proton (1-H) of benzo[*c*]quinolizinium **4** (δ 10.39).[13] The downfield shift of the protons is

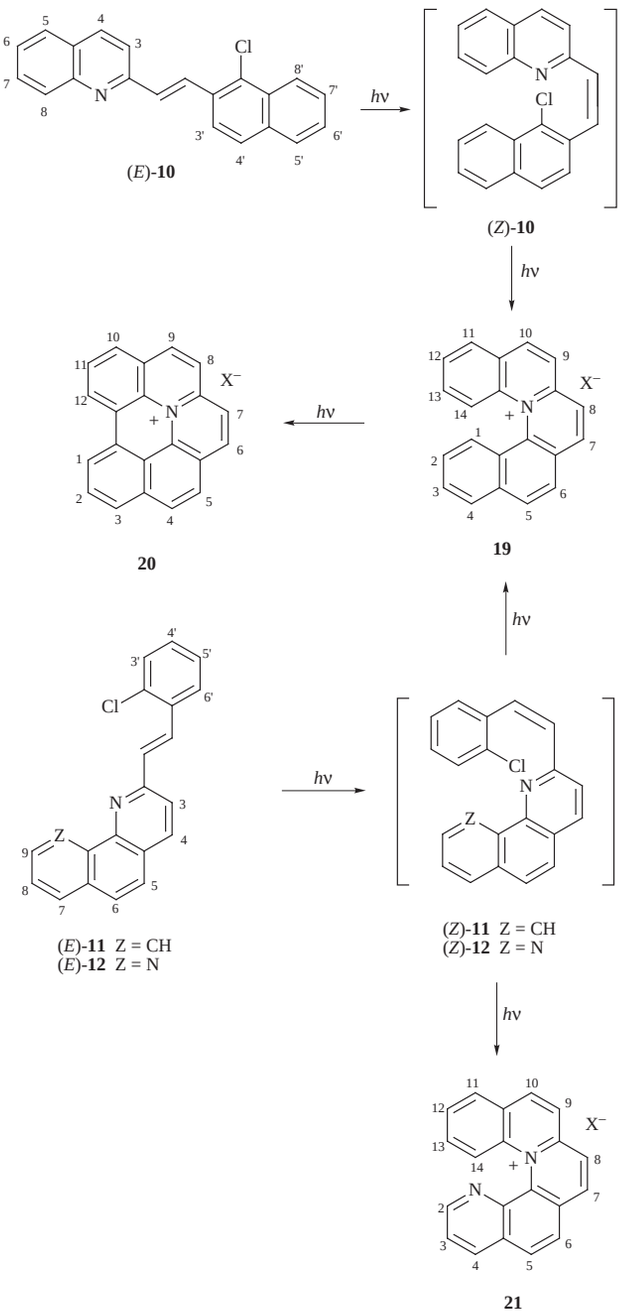


Scheme 4

attributed to the electron-withdrawing effect of the neighbouring quaternary nitrogen in addition to the mutual van der Waals compression effects between the overcrowded hydrogens situated in the bay region.

Photocyclization of 2-[2-(1-chloro-2-naphthyl)vinyl]quinoline 10, 2-[2-(2-chlorophenyl)vinyl]benzo[*h*]quinolines 11 and 2-[2-(2-chlorophenyl)vinyl]-1,10-phenanthroline 12

The cyclization of compound (*Z*)-**10** would yield the azonia derivative of [5]helicene (**19**), the lowest member in the helicene series[14] (Scheme 5). Attempted thermal cyclization at 170–200 °C, however, gave no cyclization products. When an acetonitrile solution of (*E*)-**10** was irradiated with Pyrex-filtered light, the first absorption band at 340 nm hypsochromically shifted to 330 nm, and a new peak appeared at 436 nm as shown in Fig. 2. During further irradiation the peak at 464 nm increased gradually. Before the clear appearance of the peak at 464 nm, the irradiation was ceased and anion exchange by treatment with lithium perchlorate yielded a yellow solid (~30% yield). Analysis of the ^{1}H NMR spectrum showed the presence of two products in the ratio 80:20, which were separated by column chromatography (SiO_2:CH_3CN–CF_3CO_2H 200:1). On the basis of their spectral and analytical data, the structures of the major and minor products were concluded to be the hitherto unknown 14b-azonia[5]helicene‡ perchlorate **19** (X = ClO_4) and 12b-azoniabenzo[*ghi*]perylene§ perchlorate **20** (X = ClO_4), respectively. The FAB mass spectrum of the major product **19** exhibited a molecular cation peak at *m*/*z* 280, while the molecular cation peak (*m*/*z* 278) of the minor product **20** pointed to the loss of two hydrogen atoms from the major product. The ^{1}H NMR spectrum of compound **19** showed three two-spin systems and two four-spin systems, which could be unambiguously assigned by ^{1}H–^{1}H COSY spectroscopy. The helical structure of product **19** was easily confirmed by characteristic upfield chemical shifts in the ^{1}H NMR spectrum.[15] The signals for 1-H (δ 7.67) and 2-H (δ 7.45) in the spectrum of compound **19** show large upfield shifts compared with the corresponding protons (8′-H and 7′-H) of the olefinic precursor (*E*)-**10**: $\Delta\delta$ {δ(**19**) − δ [(*E*)-**10**]} = −0.65 for 1-H and −0.28 for 2-H. The comparison of the signal (1-H) of compound **19** with that (12-H) of analogue **18** shows that the annelation of a benzene ring caused a large upfield shift of the signal (1-H) of pentacycle **19**: $\Delta\delta$ [δ(**19**) − δ(**18**)] = −1.40 (Fig. 3). On the other hand, all signals in the spectrum of fused hexacycle **20** appeared between δ 8.11 and 8.93, which corresponds to a typical region for planar polycyclic azonia-aromatic compounds.[5a,5c] The benzoperylene **20** was obtained in 45% yield as the major product after the peak at 464 nm reached a maximum. These results indicate two successive photocyclizations: the first converting substrate (*Z*)-**10** into [5]helicene **19** by photo-induced intramolecular quaternization and the second converting [5]-helicene **19** into the benzoperylene **20** by oxidative photocyclohydrogenation. In fact, an acetonitrile solution of [5]helicene **19** could be irradiated with Pyrex-filtered light to afford the benzoperylene **20**.



Scheme 5 Non-systematic numbering schemes for compounds **19**–**21**

Similar results were obtained by the photoreaction of substrate (*E*)-**11** (Scheme 5). In the photoreaction of (*E*)-**11** in acetonitrile stepwise spectral changes were observed and after prolonged irradiation the benzoperylene **20** was obtained in 55% yield.

Although carbocyclic [5]helicene **26** could be synthesized by the oxidative photocyclodehydrogenation of 1,2-bis-(2-naphthyl)ethylene **22** and 3-styrylphenanthrene **24**, these photocyclizations lead on to the formation of benzo[*ghi*]perylene **28** as shown in Scheme 6.[16] In the case of the azonia derivatives we found similar results: in the oxidative photocyclization of 2-[2-(2-naphthyl)vinyl]isoquinolinium salt **23** and 2-styrylbenzo-

‡ *Systematic name*: 10b-azoniapentahelicene.
§ *Systematic name*: 4c-azoniabenzo[*ghi*]perylene.

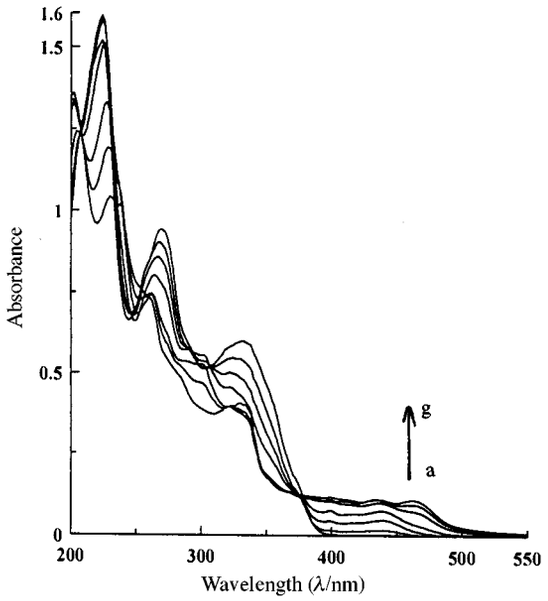


Fig. 2 Changes in the UV-VIS spectra during irradiation of (*E*)-**10** (3.17×10^{-5} mol dm^{-3}) in acetonitrile. (a) time $t = 0$, (b) after 40 s, (c) 2 min, (d) 4 min, (e) 9 min, (f) 14 min, (g) 45 min.

[*a*]quinolizinium salt **25** no stepwise spectral changes were observed and the azoniabenzo[*ghi*]perylene¶ salt **29** was obtained selectively.[5a,5c] These results imply that [5]helicenes **26** and **27** are easily photocyclized to give benzo[*ghi*]perylene derivatives **28** and **29** and that the construction of a [5]helicene framework is difficult under these conditions. The photochemical synthesis of [5]helicenes **26** and **27** has been reported to be accomplished with the aid of bromine auxiliaries.[5d,17] On the other hand, the photo-induced intramolecular quaternization of olefins **10** and **11** to afford azonia[5]helicene **19** is probably faster than the following oxidative photocyclodehydrogenation to afford benzoperylene **20** and, therefore azonia[5]helicene **19** could be isolated. By the replacement of C-1 or C-14 of azonia[5]helicene **19** with nitrogen, the [5]helicene would be photochemically stable. On irradiation of an acetonitrile solution of the phenanthroline (*E*)-**12**, the peak at 320 nm decreased, whilst a new peak at 423 nm increased monotonically and no stepwise spectral changes were observed. After work-up 1-aza-14b-azonia[5]helicene‖ salt **21** was obtained in 19% yield.

Photocyclization of 2-[2-(2-chloronaphthyl)vinyl]benzo[*h*]-quinolene 13 and 2-[2-(2-chloronaphthyl)vinyl]-1,10-phenanthroline 14

As a rational extension of the above results we have attempted the synthesis of novel azonia[6]helicenes with a quaternary nitrogen at the inner helix[14c] skeleton.[9b] Irradiation of an acetonitrile solution of the olefins **13** and **14** with Pyrex-filtered light and anion exchange with lithium perchlorate gave novel 16c-azonia[6]helicene** salts **30** and **31** (X = ClO_4) in 40% and 32% yield, respectively (Scheme 7). The helical structures of products **30** and **31** were confirmed by the ^{1}H NMR spectra. The signals for protons 1-H, 2-H, and 3-H of the azonia-helicene **30** appeared at δ 6.82, 6.87, and 7.52, respectively. These signals shifted upfield as compared with the corresponding resonances in the olefin precursor (*E*)-**13**. The signals (1-H, 2-H, and 3-H) of the terminal rings of the azonia[6]-helicene **30** also appeared upfield compared with those of the corresponding protons (1-H, 2-H, and 3-H) of the azonia[5]-helicenes **19** (Fig. 3). Similar results were observed in the case of

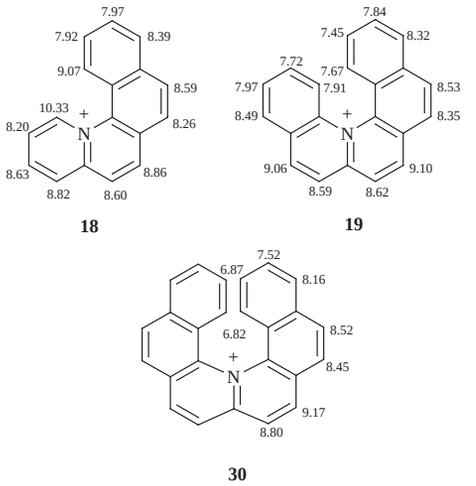
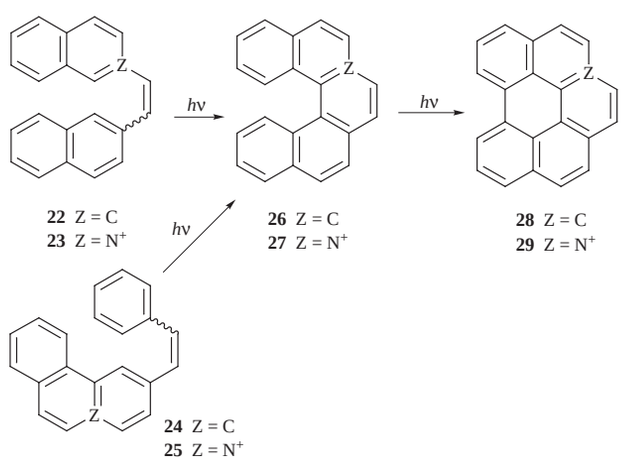
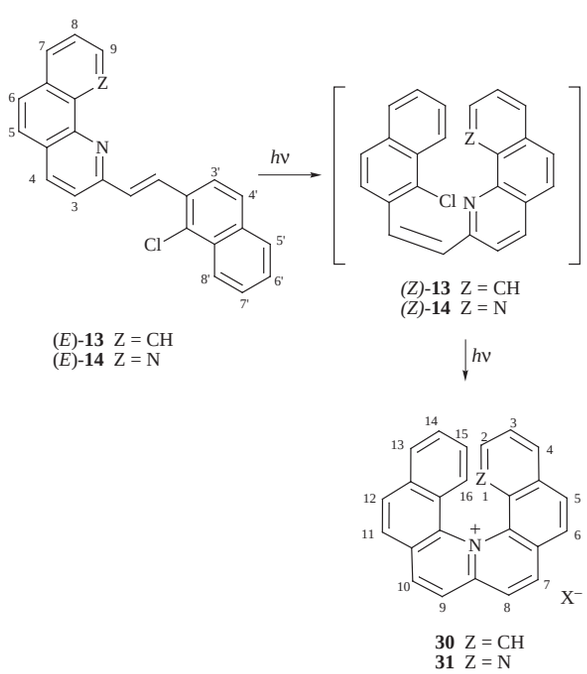


Fig. 3 ^{1}H NMR chemical shifts (δ [ppm]) in [$^2H_6$]DMSO



Scheme 6



Scheme 7 Non-systematic numbering for compounds **30**, **31**

azaazoniahelicenes **31** and **21**. These upfield shifts imply that the protons lie in the shielding region of the anisotropy effect originating from the opposite terminal rings and clearly support the helical structure.

In conclusion, we have developed a new approach to poly-

¶ *Systematic name*: 2a-azoniabenzo[*ghi*]perylene.
‖ *Systematic name*: 10-aza-10c-azoniapentahelicene.
** *Systematic name*: 12c-azoniahexahelicene.

cyclic azonia-aromatic compounds *via* photo-induced quaternization. This type of reaction has considerable generality for the synthesis of novel polycyclic azonia-aromatic systems incorporating a benzo[*c*]quinolizinium ring.

Experimental

Mps were determined on a Yamato melting point apparatus MP-21 and are uncorrected. UV spectra were obtained with an Hitachi 220A spectrophotometer. ^{1}H NMR spectra were measured with a JOEL-EX 270 (270 MHz) or EX400 (400 MHz) spectrometer using tetramethylsilane as internal standard. Chemical shifts were measured in ppm downfield from the internal standard and *J*-values are given in Hz. Spectral assignments are supported by ^{1}H–^{1}H COSY spectra. Protons are labelled as shown in the Schemes. These labels serve for NMR spectral comparisons and do not necessarily follow the numbering in the nomenclature of the individual compounds. Fast-atom bombardment (FAB) mass spectra were recorded with a JEOL JMS-DX300 spectrometer with *m*-nitrobenzyl alcohol as matrix. Elemental analyses were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. An Eikosha 300W or Ushio 450W high-pressure mercury lamp was used as the irradiation source. An aqueous solution of nickel sulfate ($NiSO_4 \cdot 6H_2O$ 500 g in 1000 cm^3 of water) was used as solution filter.[11] Column chromatography was carried out on silica gel (Merck Kieselgel 60) or alumina (Merck aluminium oxide 90 neutral).

(*E*)-2-[2-(2-Chlorophenyl)vinyl]quinoline 8

A mixture of 2-methylquinoline (7.04 g, 49.2 mmol) and *o*-chlorobenzaldehyde (6.97 g, 49.6 mmol) in acetic anhydride (16 cm^3) was refluxed for 12 h. After the solvent had been removed, the residue was chromatographed on aluminium oxide with benzene as eluent to give crude product, which was recrystallized from hexane (130 cm^3) to afford the olefin **8** as pale yellow crystals (6.5 g, 50%), mp 78 °C (lit.,[8b] 78–79 °C) (Found: C, 76.6; H, 4.4; N, 5.0. Calc. for $C_{17}H_{12}ClN$: C, 76.8; H, 4.55; N, 5.3%); $\lambda_{max}(CH_3CN)$/nm 277 (log ε 4.43), 323 (4.31) and 335 (4.30); δ_H(400 MHz; [$^2H_6$]DMSO) 7.40 (1 H, t, *J* 7.8 and 7.3, 4′-H), 7.44 (1 H, t, *J* 7.6 and 7.3, 5′-H), 7.56 (1 H, d, *J* 7.6, 6′-H), 7.57 (1 H, d, *J* 16.3, olefin-H), 7.59 (1 H, t, *J* 8.1 and 7.0, 6-H), 7.78 (1 H, t, *J* 7.8 and 7.0, 7-H), 7.85 (1 H, d, *J* 8.5, 3-H), 7.98 (1 H, d, *J* 8.1, 5-H), 8.03 (2 H, d, *J* 7.8, 8- and 3′-H), 8.13 (1 H, d, *J* 16.3, olefin-H) and 8.40 (1 H, d, *J* 8.5, 4-H); *m*/*z* 266 and 268 $(M + 1)^+$ and 230 $(M - Cl)^+$.

(*E*)-2-[2-(1-Chloro-2-naphthyl)vinyl]pyridine 9

A mixture of 2-methylpyridine (517 mg, 5.55 mmol), 1-chloronaphthalene-2-carbaldehyde[8b] (1.03 g, 5.43 mmol) and the zinc chloride complex of 2-methylpyridine (52 mg, 0.23 mmol) in acetic anhydride (10 cm^3) in a sealed tube was heated at 180 °C for 16 h. After column chromatography on silica gel with hexane–ethyl acetate (20:1) as eluent, recrystallization from hexane (20 cm^3)–benzene (1 cm^3) gave the olefin **9** (854 mg, 59%) as a pale yellow solid, mp 104–105 °C (lit.,[8b] 104–105 °C); $\lambda_{max}(CH_3CN)$/nm 270 (log ε 4.43), 282 (4.36), 323 (4.55) and 363sh; δ_H(270 MHz; $CDCl_3$) 7.33 (1 H, dd, *J* 4.8 and 7.4, 5-H), 7.58 (1 H, d, *J* 15.8, olefin-H), 7.59 (1 H, d, *J* 7.9, 3-H), 7.64 (1 H, t, *J* 7.9, 6′-H), 7.72 (1 H, t, *J* 7.6, 7′-H), 7.85 (1 H, t, *J* 7.7, 4-H), 7.98 (1 H, d, *J* 8.9, 3′-H), 8.02 (1 H, d, *J* 7.9, 5′-H), 8.10 (1 H, d, *J* 8.9, 4′-H), 8,28 (1 H, d, *J* 9.5, 8′-H), 8.33 (1 H, d, *J* 15.8, olefin-H) and 8.66 (1 H, d, *J* 4.7, 6-H); *m*/*z* 266 and 268 $(M + 1)^+$ and 230 $(M - Cl)^+$.

(*E*)-2-[2-(1-Chloro-2-naphthyl)vinyl]quinoline 10

A mixture of 2-methylquinoline (759 mg, 5.31 mmol), 1-chloronaphthalene-2-carbaldehyde[8b] (1.01 g, 5.31 mmol), and the zinc chloride complex of 2-methylquinoline (148 mg, 0.53 mmol) in acetic anhydride (10 cm^3) was refluxed for 8 h. Recrystallization from hexane (20 cm^3)–benzene (25 cm^3) gave the *olefin* **10** (437 mg, 26%) as yellow solid, mp 140–141 °C (Found: C, 79.6; H, 4.3; N, 4.4. $C_{21}H_{14}ClN$ requires C, 79.9; H, 4.5; N, 4.4%); $\lambda_{max}(CH_3CN)$/nm 274 (log ε 4.45) and 340 (4.33); δ_H(270 MHz; $CDCl_3$) 7.60 (1 H, t, *J* 7.5, 6-H), 7.66 (1 H, t, *J* 7.3, 6′-H), 7.73 (1 H, t, *J* 7.3, 7′-H), 7.74 (1 H, d, *J* 16.3, olefin-H), 7.79 (1 H, t, *J* 7.3, 7-H), 7.91 (1 H, d, *J* 8.3, 3-H), 7.99 (1 H, d, *J* 8.3, 5-H), 8.01 (1 H, d, *J* 8.3, 4′-H), 8.04 (1 H, d, *J* 7.8, 5′-H), 8.06 (1 H, d, *J* 8.3, 8-H), 8.17 (1 H, d, *J* 8.8, 3′-H), 8.32 (1 H, d, *J* 8.8, 8′-H), 8.42 (1 H, d, *J* 8.3, 4-H) and 8.44 (1 H, d, *J* 16.3, olefin-H); *m*/*z* 316 and 318 $(M + 1)^+$ and 280 $(M - Cl)^+$.

(*E*)-2-[2-(2-Chlorophenyl)vinyl]benzo[*h*]quinoline 11

2-Methylbenzo[*h*]quinoline[9b] (1.14 g, 5.91 mmol) reacted with *o*-chlorobenzaldehyde (1.37 g, 9.78 mmol) in the presence of zinc chloride (80 mg, 0.59 mmol) in boiling acetic anhydride (10 cm^3) for 23 h under nitrogen. After column chromatography on silica gel with benzene as the eluent, recrystallization from hexane (20 cm^3)–chloroform (2 cm^3) gave the *olefin* **11** as a solid (0.94 g, 50%), mp 109–110 °C (Found: C, 79.9; H, 4.5; N, 4.4. $C_{21}H_{14}ClN$ requires C, 79.9; H, 4.5; N, 4.4%); $\lambda_{max}(CH_3CN)$/nm 239 (log ε 4.65), 301 (4.41), 349 (4.22), 365 (4.28) and 368sh; δ_H(270 MHz; [$^2H_6$]DMSO) 7.41 (1 H, dd, *J* 7.3 and 7.3, 4′-H), 7.46 (1 H, dd, *J* 7.2 and 7.3, 5′-H), 7.58 (1 H, d, *J* 7.2, 6′-H), 7.67 (1 H, d, *J* 16.1, olefin-H), 7.78 (1 H, dd, *J* 6.6 and 7.8, 9-H), 7.82 (1 H, dd, *J* 6.6 and 6.8, 8-H), 7.88 (1 H, d, *J* 8.8, 5-H), 7.93 (1 H, d, *J* 8.3, 3-H), 7.94 (1 H, d, *J* 8.8, 6-H), 8.06 (1 H, d, *J* 6.8, 7-H), 8.06 (1 H, d, *J* 7.3, 3′-H), 8.33 (1 H, d, *J* 16.1, olefin-H), 8.45 (1 H, d, *J* 8.3, 4-H) and 9.29 (1 H, d, *J* 7.8, 10-H); *m*/*z* 316 and 318 $(M + 1)^+$ and 280 $(M - Cl)^+$.

(*E*)-2-[2-(2-Chlorophenyl)vinyl]-1,10-phenanthroline 12

2-Methyl-1,10-phenanthroline[9b] (1.42 g, 7.01 mmol) reacted with *o*-chlorobenzaldehyde (1.42 g, 10.1 mmol) in boiling acetic anhydride (10 cm^3) for 2.5 h under nitrogen. After silica gel column chromatography with chloroform as eluent, recrystallization from hexane (30 cm^3)–chloroform (8 cm^3) at −40 °C gave the *olefin* **12** as a solid (0.76 g, 34%), mp 149–150 °C (Found: C, 75.6; H, 4.0; N, 8.7. $C_{20}H_{13}ClN_2$ requires C, 75.8; H, 4.1; N, 8.8%); $\lambda_{max}(CH_3CN)$/nm 257 (log ε 4.23), 297 (4.41), 320 (4.36), 355sh and 368sh; δ_H(270 MHz; [$^2H_6$]DMSO) 7.41 (1 H, ddd, *J* 2.0, 7.4 and 7.6, 4′-H), 7.46 (1 H, ddd, *J* 1.6, 7.4 and 7.6, 5′-H), 7.58 (1 H, dd, *J* 2.0 and 7.6, 6′-H), 7.70 (1 H, d, *J* 16.5, olefin-H), 7.80 (1 H, dd, *J* 4.3 and 8.3, 8-H), 7.99 (2 H, d, *J* 8.9, 5- and 6-H), 8.07 (1 H, dd, *J* 1.6 and 7.6, 3′-H), 8.08 (1 H, d, *J* 8.3, 3-H), 8.23 (1 H, d, *J* 16.5, olefin-H), 8.50 (1 H, dd, *J* 2.0 and 8.3, 7-H), 8.51 (1 H, d, *J* 8.3, 4-H) and 9.16 (1 H, dd, *J* 2.0 and 7.8, 9-H); *m*/*z* 317 and 319 $(M + 1)^+$ and 281 $(M - Cl)^+$.

(*E*)-2-[2-(1-Chloro-2-naphthyl)vinyl]benzo[*h*]quinoline 13

2-Methylbenzo[*h*]quinoline[9b] (1.94 g, 10.06 mmol) reacted with 1-chloronaphthalene-2-carbaldehyde[8b] (2.00 g, 10.49 mmol) in the presence of zinc chloride (68 mg, 0.50 mmol) in boiling acetic anhydride (20 cm^3) for 45 h under nitrogen. After the solvent had been removed, the residue was chromatographed on neutral alumina (benzene) to give a crude product, which was recrystallized from chloroform to afford the *olefin* **13** as a yellow solid (0.99 g, 27%), mp 146.5–147.5 °C (Found: C, 81.8; H, 4.2; N, 3.7. $C_{25}H_{16}ClN$ requires C, 82.1; H, 4.2; N, 3.8%); $\lambda_{max}(CH_3CN)$/nm 240 (log ε 4.64), 256 (4.53), 289 (4.48), 323 (4.43), 373 (4.47) and 388 (4.28); δ_H(400 MHz; [$^2H_6$]DMSO) 7.66 (1 H, dd, *J* 8.8 and 7.6, 6′-H), 7.74 (1 H, dd, *J* 7.6 and 8.8, 7′-H), 7.79 (1 H, dd, *J* 7.8 and 6.8, 8-H), 7.85 (1 H, dd, *J* 7.8 and 7.8, 9-H), 7.84 (1 H, d, *J* 16.1, olefin-H), 7.89 (1 H, d, *J* 8.8, 5-H), 7.95 (1 H, d, *J* 8.8, 6-H), 7.98 (1 H, d, *J* 8.3, 3-H), 8.03 (1 H, d, *J* 8.8, 5′-H), 8.05 (1 H, d, *J* 8.8, 4′-H), 8.07 (1 H, d, *J* 6.8, 7-H), 8.20 (1 H, d, *J* 8.8, 3′-H), 8.34 (1 H, d, *J* 8.8, 8′-H), 8.47 (1 H, d, *J* 8.3, 4-H), 8.64 (1 H, d, *J* 16.1, olefin-H) and 9.34 (1 H, d, *J* 7.8, 10-H); *m*/*z* 366 and 368 $(M + 1)^+$ and 330 $(M - Cl)^+$.

(*E*)-2-[2-(1-Chloro-2-naphthyl)vinyl]-1,10-phenanthroline 14
2-Methylphenanthroline[9b] reacted with 1-chloronaphthalene-2-carbaldehyde[8b] (2.08 g, 10.9 mmol) in boiling acetic anhydride (15 cm^3) for 2.5 h under nitrogen. After work-up according to the above procedure, followed by repeated purification with silica gel column chromatography (chloroform), recrystallization from hexane–chloroform gave title compound **14** as a yellow solid (2.39 g, 39% from 1,10-phenanthroline), mp 236–237 °C (Found: C, 78.85; H, 4.3; N, 7.8. $C_{24}H_{15}ClN_2$ requires C, 78.6; H, 4.1; N, 7.65%); λ_{max}(CH_3CN)/nm 256 (log ε 4.40), 2.85 (4.40), 330 (4.42), 343 (4.42) and 363 (4.37); δ_H(400 MHz; [$^2H_6$]DMSO) 7.66 (1 H, dd, *J* 8.8 and 7.7, 6′-H), 7.75 (1 H, dd, *J* 7.7 and 8.3, 7′-H), 7.81 (1 H, dd, *J* 4.4 and 8.1, 8-H), 7.87 (1 H, d, *J* 16.1, olefin-H), 8.00 (1 H, d, *J* 8.8, 5-H), 8.00 (1 H, d, *J* 8.8, 6-H), 8.04 (1 H, d, *J* 8.3, 4′-H), 8.06 (1 H, d, *J* 8.3, 5′-H), 8.14 (1 H, d, *J* 8.8, 3-H), 8.22 (1 H, d, *J* 8.3, 3′-H), 8.34 (1 H, d, *J* 8.3, 8′-H), 8.53 (1 H, d, *J* 8.1, 7-H), 8.54 (1 H, d, *J* 16.1, olefin-H), 8.54 (1 H, d, *J* 8.8, 4-H) and 9.18 (1 H, d, *J* 4.4, 9-H); *m*/*z* 367 and 369 $(M + 1)^+$ and 331 $(M - Cl)^+$.

Photocyclization
A typical photocyclization procedure is described for the synthesis of dibenzo[*cf*]quinolizinium perchlorate **15** from chloride (*E*)-**8**. A solution of the chloride (*E*)-**8** (53 mg, 0.2 mmol) in acetonitrile (1000 cm^3) in a Pyrex reaction vessel was irradiated through an aq. nickel sulfate filter 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 405 nm reached a maximum, the solvent was evaporated. The residue was dissolved in water and insoluble solids were filtered off. Saturated aq. lithium perchlorate was added to the filtrate and the resulting yellow solid was filtered off, washed with cold water, and recrystallized from ethanol to give compound **15** (X = ClO_4) (27 mg, 41%) as yellow crystals, mp 255–257 °C (Found: C, 61.7; H, 3.7; N, 4.1. $C_{17}H_{12}ClNO_4$ requires C, 61.9; H, 3.7; N, 4.25%); λ_{max}(CH_3CN)/nm 268 (log ε 4.49), 277sh, 384 (4.11) and 405 (4.26); δ_H(400 MHz; [$^2H_6$]DMSO) 8.08 (2 H, t, *J* 8.5 and 7.5, 2- and 11-H), 8.14 (2 H, t, *J* 9.0 and 7.2, 3- and 10-H), 8.48 (2 H, d, *J* 8.5, 6- and 7-H), 8.51 (2 H, d, *J* 9.0, 4- and 9-H), 9.00 (2 H, d, *J* 8.5, 1- and 12-H) and 9.04 (2 H, d, *J* 8.5, 5- and 8-H); *m*/*z* 230 $(M - ClO_4)^+$.

Naphtho[2,1-*c*]quinolizinium perchlorate 18 (X = ClO_4). The same procedure was used as for the preparation of compound **15**. Yield 42%; mp 215–216 °C (lit.,[8b] 215.5–216 °C) (Found: C, 61.8; H, 3.8; N, 4.0. Calc. for $C_{17}H_{12}ClNO_4$: C, 61.9; H, 3.7; N, 4.25%); λ_{max}(CH_3CN)/nm 246 (log ε 4.54), 270 (4.25), 304 (4.30), 374 (3.73) and 393 (3.80); δ_H(270 MHz; [$^2H_6$]DMSO) 7.92 (1 H, t, *J* 6.4, 11-H), 7.97 (1 H, t, *J* 6.4, 10-H), 8.20 (1 H, t, *J* 7.1, 2-H), 8.26 (1 H, d, *J* 8.6, 7-H), 8.39 (1 H, d, 8.4, 9-H), 8.59 (1 H, d, *J* 8.6, 8-H), 8.60 (1 H, d, *J* 8.4, 5-H), 8.63 (1 H, t, *J* 7.9, 3-H), 8.82 (1 H, d, *J* 7.3, 4-H), 8.86 (1 H, d, *J* 8.6, 6-H), 9.07 (1 H, d, *J* 7.9, 12-H) and 10.33 (1 H, d, *J* 6.9, 1-H); *m*/*z* 230 $(M - ClO_4)^+$.

10b-Azonia[5]helicene perchlorate 19 (X = ClO_4) and 4c-azoniabenzo[*ghi*]perylene perchlorate 20 (X = ClO_4). By irradiation of the olefin **10**, the crude product (~30% yield) was obtained as a mixture of products **19** and **20** in the ratio 80 : 20. The mixture was separated by column chromatography (silica gel) with acetonitrile–TFA (200 : 1). These products were dissolved in water and saturated aq. lithium perchlorate was added. The precipitate was filtered off, washed with cold water, and recrystallized from acetonitrile–ethyl acetate and acetonitrile–ethanol to afford compounds **19** and **20**, respectively.

The *pentahelicene* **19**: Yield 15%; mp 300–303 °C (decomp.) (Found: C, 66.7; H, 3.7; N, 3.5. $C_{21}H_{14}ClNO_4$ requires C, 66.4; H, 3.7; N, 3.7%); λ_{max}(CH_3CN)/nm 258 (log ε 4.22), 271 (4.22), 286 (4.37), 310 (4.35), 320 (4.34), 393sh, 418sh and 436 (4.16); δ_H(270 MHz; [$^2H_6$]DMSO) 7.45 (1 H, ddd, *J* 8.6, 7.9 and 1.3, 2-H), 7.67 (1 H, dd, *J* 8.6 and 1.0, 1-H), 7.72 (1 H, ddd, *J* 7.9, 8.6 and 1.3, 13-H), 7.84 (1 H, dd, *J* 8.6 and 1.0, 3-H), 7.91 (1 H, dd, *J* 8.6 and 1.0, 14-H), 7.97 (1 H, ddd, *J* 8.2, 7.9 and 1.0, 12-H), 8.32 (1 H, dd, *J* 8.6 and 1.3, 4-H), 8.35 (1 H, d, *J* 8.6, 6-H), 8.49 (1 H, dd, *J* 8.2 and 1.3, 11-H), 8.53 (1 H, d, *J* 8.6, 5-H), 8.59 (1 H, d, *J* 8.9, 9-H), 8.62 (1 H, d, *J* 8.6, 8-H), 9.06 (1 H, d, *J* 8.9, 10-H) and 9.10 (1 H, d, *J* 8.6, 7-H); *m*/*z* 280 $(M - ClO_4)^+$.

The *fused hexacycle* **20**: Yield 5%; mp >325 °C (Found: C, 66.5; H, 3.05; N, 3.7. $C_{21}H_{12}ClNO_4$ requires C, 66.8; H, 3.2; N, 3.7%); λ_{max}(CH_3CN)/nm 237 (log ε 4.59), 260 (4.59), 333 (4.45), 363 (3.56), 383 (3.43), 437 (3.73) and 464 (3.89); δ_H(270 MHz; [$^2H_6$]DMSO) 8.11 (1 H, dd, *J* 7.8, 11-H), 8.12 (1 H, d, *J* 8.8, 8-H), 8.14 (1 H, dd, *J* 7.8, 2-H), 8.19 (1 H, d, *J* 9.3, 5-H), 8.22 (1 H, d, *J* 8.8, 9-H), 8.23 (1 H, d, *J* 7.8, 10-H), 8.26 (1 H, dd, *J* 7.8 and 1.4, 3-H), 8.51 (1 H, d, *J* 8.3, 6-H), 8.53 (1 H, d, *J* 8.8, 4-H), 8.64 (1 H, d, *J* 7.8, 12-H), 8.86 (1 H, dd, *J* 7.8 and 1.4, 1-H) and 8.93 (1 H, d, *J* 8.8, 7-H); FAB-MS 278 $(M - ClO_4)^+$. Compound **20** was also obtained in 55% yield by prolonged irradiation of the olefin **11**.

10-Aza-10c-azonia[5]helicene perchlorate 21 (X = ClO_4). The same procedure was used as for the preparation of compound **15** to give *compound* **21**. Yield 19%; mp 250–252 °C (decomp.) (Found: C, 63.3; H, 3.2; N, 7.5. $C_{20}H_{13}ClN_2O_4$ requires C, 63.1; H, 3.4; N, 7.4%); λ_{max}(CH_3CN)/nm 259 (log ε 4.46), 299 (4.24), 359 (3.76), 401 (3.87) and 423 (3.96); δ_H(270 MHz; [$^2H_6$]DMSO) 7.67 (1 H, ddd, *J* 8.6, 7.7 and 1.6, 13-H), 7.84 (1 H, d, *J* 8.6, 14-H), 7.91 (1 H, dd, *J* 4.5 and 8.2, 3-H), 7.93 (1 H, dd, *J* 8.1 and 7.7, 12-H), 8.42 (1 H, dd, *J* 8.1 and 1.6, 11-H), 8.49 (1 H, d, *J* 8.7, 6-H), 8.59 (1 H, d, *J* 8.7, 5-H), 8.61 (1 H, d, *J* 8.2, 9-H), 8.63 (1 H, dd, *J* 4.5 and 1.6, 2-H), 8.71 (1 H, d, *J* 8.6, 8-H), 8.78 (1 H, dd, *J* 8.2 and 1.6, 4-H), 9.12 (1 H, d, *J* 8.2, 10-H) and 9.14 (1 H, d, *J* 8.6, 7-H); *m*/*z* 281 $(M - ClO_4)^+$.

12c-Azonia[6]helicene perchlorate 30 (X = ClO_4). The same procedure was used as for the preparation of compound **15** to give *compound* **30**. Yield 40%; mp 322–325 °C (decomp.) (Found: C, 69.75; H, 3.6; N, 3.4. $C_{25}H_{16}ClNO_4$ requires C, 69.85; H, 3.75; N, 3.3%); λ_{max}(CH_3CN)/nm 253 (log ε 4.62), 318 (4.30), 340 (4.21) and 459 nm (3.89); δ_H(270 MHz; [$^2H_6$]DMSO) δ 6.82 (1 H, dd, *J* 8.2 and 1.3, 1-H), 6.87 (1 H, ddd, *J* 8.2, 6.7 and 1.3, 2-H), 7.52 (1 H, ddd, *J* 8.2, 6.7 and 1.3, 3-H), 8.16 (1 H, dd, *J* 8.2 and 1.3, 4-H), 8.45 (1 H, d, *J* 8.7, 6-H), 8.52 (1 H, d, *J* 8.7, 5-H), 8.80 (1 H, d, *J* 8.6, 8-H) and 9.17 (1 H, d, *J* 8.6, 7-H); FAB-MS *m*/*z* 330 $(M - ClO_4)^+$.

12-Aza-12c-azonia[6]helicene perchlorate 31 (X = ClO_4). The same procedure was used as for the preparation of compound **15** to give *compound* **31**. Yield 32%; mp 304–306 °C (decomp.) (Found: C, 66.65; H, 3.4; N, 6.45. $C_{24}H_{15}ClN_2O_4$ requires C, 66.9; H, 3.5; N, 6.5%); λ_{max}(CH_3CN)/nm 256 (log ε 4.64), 311 (4.29) and 453 nm (3.80); δ_H(400 MHz; [$^2H_6$]DMSO) 6.85 (1 H, dd, *J* 8.3 and 7.3, 15-H), 7.06 (1 H, d, *J* 8.3, 16-H), 7.51 (1 H, dd, *J* 7.8 and 7.3, 14-H), 7.51 (1 H, dd, *J* 8.3 and 3.9, 3-H), 7.95 (1 H, dd, *J* 3.9 and 1.5, 2-H), 8.15 (1 H, d, *J* 7.8, 13-H), 8.35 (1 H, d, *J* 8.8, 11-H), 8.45 (1 H, d, *J* 8.8, 12-H), 8.53 (1 H, d, *J* 8.3, 5-H), 8.57 (1 H, d, *J* 8.3, 6-H), 8.59 (1 H, dd, *J* 8.3 and 1.5, 4-H), 8.79 (1 H, d, *J* 9.3, 9-H), 8.86 (1 H, d, *J* 8.3, 8-H), 9.18 (1 H, d, *J* 8.3, 7-H) and 9.21 (1 H, d, *J* 9.3, 10-H); FAB-MS *m*/*z* 331 $(M - ClO_4)^+$.

Acknowledgements

This work was supported in part by a Grant-in-aid for Scientific Research No. 04650781 from the Ministry of Education, Science and Culture, Japan. We are indebted to Dr. Takehiko Suzuki for his help in microanalyses.

References

1 Reviews on azonia-aromatic compounds: (*a*) B. S. Thyyagarajan, *Adv. Heterocycl. Chem.*, 1965, **5**, 291; (*b*) G. Jones, *Adv. Heterocycl. Chem.*, 1982, **31**, 1; (*c*) C. K. Bradsher, in *Comprehensive Heterocyclic Chemistry*, ed. A. R. Katritzky and C. W. Rees,

Pergamon Press, Oxford, 1984, vol. 2, p. 525; (*d*) S. Arai and M. Hida, *Adv. Heterocycl. Chem.*, 1992, **55**, 261.
2 I. Santiesteban, J. G. Siro, J. J. Vaquero, J. L. Garcia-Navio, J. Alvarez-Builla and O. Castano, *J. Org. Chem.*, 1995, **60**, 5667.
3 V. Boekelheide and W. G. Gall, *J. Am. Chem. Soc.*, 1954, **76**, 1832.
4 C. K. Bradsher, *Chem. Rev.*, 1987, **87**, 1277 and references therein.
5 (*a*) S. Arai, T. Takeuchi, M. Ishikawa, T. Takeuchi, M. Yamazaki and M. Hida, *J. Chem. Soc.*, *Perkin Trans. 1*, 1987, 481; (*b*) S. Arai, T. Yafune, M. Ohkubo and M. Hida, *Tetrahedron Lett.*, 1989, **30**, 7217; (*c*) S. Arai, N. Nakanura, H. Yamaguchi, M. Okazaki and M. Hida, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 1996; (*d*) K. Sato, K. Nakajima, S. Arai and T. Yamagishi, *Liebiegs Ann. Chem.*, 1996, 439; (*e*) S. Arai, T. Yamagishi and M. Hida, *Yuki Gosei Kagaku Kyokaishi* (*J. Synth. Org. Chem. Jpn.*), 1993, **51**, 62.
6 E. E. Glover and G. Jones, *J. Chem. Soc.*, 1958, 3021.
7 O. Westphal, K. Jann and W. Heffe, *Arch. Pharm.* (*Weinheim*, *Ger.*), 1961, **294**, 37.
8 A. Fozard and C. K. Bradsher, *J. Org. Chem.*, 1966, **31**, (*a*) 2346; (*b*) 3683.
9 For preliminary communication of portions of this work, see: (*a*) S. Arai, K. Tabuchi, H. Arai, H. Yamagishi and M. Hida, *Chem. Lett.*, 1991, 1355; (*b*) S. Arai, M. Ishikura, K. Sato and T. Yamagishi, *J. Heterocycl. Chem.*, 1995, **32**, 1081.
10 F. B. Mallory and C. W. Mallory, *Org. React.*, 1984, **30**, 1.
11 S. L. Murov, *Handbook of Photochemistry*, Marcel Dekker, New York, 1973, p. 99.
12 J. A. Joule, K. Mills and G. F. Smith, *Heterocyclic Chemistry*, Chapman and Hall, London, 1995.
13 S. Arai, H. Arai, K. Tabuchi, T. Yamagishi and M. Hida, *J. Heterocycl. Chem.*, 1992, **29**, 215.
14 (*a*) R. H. Martin, *Angew. Chem.*, *Int. Ed. Engl.*, 1974, **13**, 649; (*b*) W. H. Laarhoven and W. J. C. Prinsen, *Top. Curr. Chem.*, 1984, **125**, 63; (*c*) K. P. Meurer and F. Vögtle, *Top. Curr. Chem.*, 1984, **127**, 1.
15 N. Dwfay and R. H. Martin, *Bull. Soc. Chim. Belg.*, 1984, **93**, 313.
16 M. Scholz, M. Mühlstädt and P. Dietz, *Tetrahedron Lett.*, 1967, 665; W. Carruthers, *J. Chem. Soc. C*, 1967, 1525; E. Blackburn, C. E. Loader and C. J. Timmons, *J. Chem. Soc. C.*, 1970, 163.
17 L. Liu and T. J. Katz, *Tetrahedron Lett.*, 1991, **32**, 6831.

Paper 7/08886H
Received 10*th December* 1997
Accepted 19*th February* 1998