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Syntheses and Properties of Novel Cyclic Sulfilimines, 2-Azathiabenzene Derivatives

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Novel cyclic sulfilimines (so-called azathiabenzenes), 2-methyl-1-aza-2-thianaphthalene (**7**) and 9-methyl- (**14a**) or 9-ethyl-10-aza-9-thiaphenanthrene (**14b**), were synthesized in high yields by deprotonation of the corresponding azasulfonium salts (**6**, **13a**, **13b**) with base. The ylidic properties of the azathiabenzenes were revealed by spectral and chemical evidence. The azathiabenzenes (**14a**, **14b**) were easily oxidized with potassium permanganate to yield the corresponding azathiabenzene oxides (**18a**, **18b**). Thermolysis of **14a** in refluxing xylene afforded the ring-expanded product 7*H*-dibenzo[*d*,*e*][1,3]thiazepine (**21**), while **14b** underwent β-elimination on refluxing in xylene to give 6*H*-dibenzo[*c*,*e*][1,2]thiazine (**24**). Reactions of the azathiabenzene derivatives with dimethyl acetylenedicarboxylate as an electrophile are also reported.

Keywords——cyclic sulfilimine; azathiabenzene; azathianaphthalene; azathiaphenanthrene; ring expansion; thermal rearrangement

Extensive studies have been reported on the chemistry of sulfilimines, particularly acyclic ones, which are recognized as very useful reagents in synthetic organic chemistry.[1] However, little work has been done on the synthesis or reactivities of cyclic sulfilimines except those having an N-sulfonyl or N-acyl group,[1] or two nitrogen atoms[2] in the ring. In connection with our interest in the aromaticities of conjugated six-membered cyclic sulfonium ylides, we have reported on the chemistry of thiabenzene derivatives.[3] It was next of interest to investigate the aromaticities of aza-analogues of thiabenzenes, so-called azathiabenzenes, in which a sulfur–nitrogen bond forms part of a cyclic conjugated ring system containing six π-electrons, and we succeeded in the first synthesis of 2-azathiabenzene derivatives.[4] Very recently, Moody *et al.* independently reported the preparation and some properties of other azathiabenzene derivatives.[5]

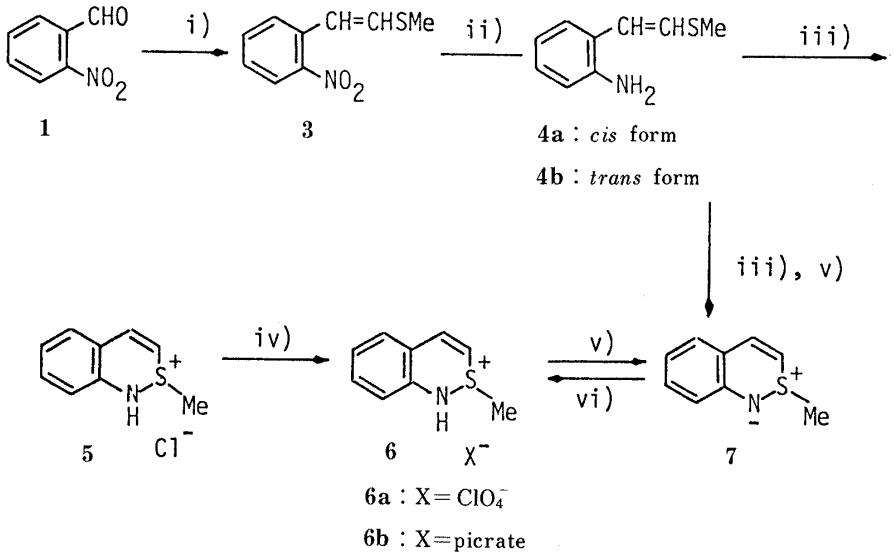
In this paper, we present the full details of our studies on the syntheses of azathianaphthalene **7** and azathiaphenanthrenes **14a**, **14b** and their properties, including the reactions with some electrophiles.

Results and Discussion

Synthesis of Azathianaphthalene 7 and Azathiaphenanthrenes 14a and 14b

Azathianaphthalene **7** was successfully synthesized by the method shown in Chart 1. Treatment of *o*-nitrobenzaldehyde (**1**) with triphenylphosphonium methylthiomethylide (**2**)[6] gave *o*-nitrostyryl methyl sulfide (**3**) in 89% yield as a 1 : 1 mixture of *cis* and *trans* products (by proton nuclear magnetic resonance (^{1}H-NMR)), which could not be separated by either column chromatography or preparative thin-layer chromatography (preparative TLC). This mixture was subsequently reduced with Zn–$CaCl_2$ in 80% ethanol to afford *o*-aminostyryl methyl sulfide (**4**) in 86% yield, which was easily separated into the *cis* product **4a** and *trans*

product **4b** by column chromatography on silica gel. The *cis* olefin **4a** was allowed to react with an equivalent amount of *N*-chlorosuccinimide (NCS) in dry dichloromethane at $-50\,°C$[7] to precipitate 2-methyl-1*H*-2,1-benzothiazin-2-ium chloride (**5**) which was subsequently treated with silver perchlorate to give the corresponding perchlorate **6a** in 41% yield. Deprotonation of **6a** using KOH at room temperature yielded 2-methyl-1-aza-2-thianaphthalene (**7**) as yellow prisms, mp 123—129 °C (dec.) in 57% yield. When the reaction mixture of **4a** with NCS was directly treated with an aqueous KOH solution without isolation of **5** or **6a**, azathianaphthalene **7** was isolated in 76% yield. All attempts to prepared **6a** or **7** from the *trans* olefin **4b** were unsuccessful.



1 3 4a : *cis* form 4b : *trans* form

5 6 7

6a : X = ClO_4^-

6b : X = picrate

i) $Ph_3\overset{+}{P}-\overset{-}{C}HSMe$ (**2**)–THF, ii) Zn–$CaCl_2$–80% EtOH, iii) NCS–CH_2Cl_2, $-50\,°C$, iv) $AgClO_4$, v) KOH–THF–H_2O, vi) picric acid

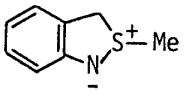


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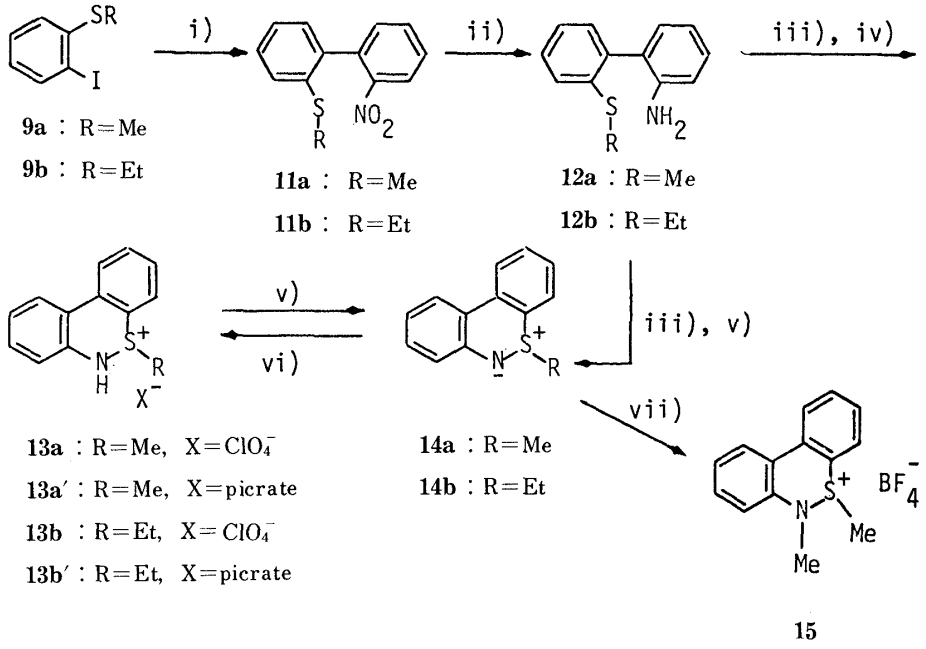
Chart 1

The nature of the S–N bond in **7** is shown to be ylidic by the following observations: (a) it exhibited a doublet signal ($J = 9$ Hz) due to C_3–H at δ 5.70 corresponding to an olefinic, not aromatic, region in the ^{1}H-NMR spectrum; (b) treatment of **7** with picric acid in ether afforded 2-methyl-1*H*-2,1-benzothiazin-2-ium picrate (**6b**) as yellow crystals, mp 168—172 °C (dec.) in quantitative yield; (c) the infrared (IR) spectrum showed strong bands at 950 and 920 cm^{-1} characteristic of the S–N stretching frequency of sulfilimines. The ylidic structure of azathiabenzene derivatives was also confirmed recently by an X-ray crystal structure determination of ethoxycarbonyl group-stabilized azathianaphthalene by Moody *et al.*[5a] Azathianaphthalene **7** seems to be much more stable than the cyclic sulfilimine **8** which was reported to decompose rapidly even at room temperature.[7] This stabilization of **7** might be attributed to the delocalization of the negative charge from nitrogen to the olefinic bond carbon (C_3-position) through the benzene ring.

The preparation of 9-methyl- (**14a**) or 9-ethyl-10-aza-9-thiaphenanthrene (**14b**) was performed as shown in Chart 2. *o*-Iodophenyl methyl sulfide (**9a**) was subjected to Ullman coupling reaction with *o*-iodonitrobenzene (**10**) at 200 °C in the presence of copper powder to give 2-methylthio-2′-nitrobiphenyl (**11a**) in 51% yield. Reduction of the nitro compound **11a**

using Zn–$CaCl_2$ in 80% ethanol afforded 2-amino-2′-methylthiobiphenyl (**12a**) in 48% yield. Treatment of the amino compound (**12a**) with NCS in dichloromethane at −50 °C, followed by deprotonation with an aqueous KOH solution gave 9-methyl-10-aza-9-thiaphenanthrene (**14a**) as yellow prisms, mp 168—172 °C (dec.) in quantitative yield. 5-Methyl-6*H*-dibenzo[*c*,*e*][1,2]thiazin-5-ium perchlorate (**13a**) was isolated in 64% yield by adding silver perchlorate to the reaction mixture of **12a** and NCS. The perchlorate **13a** was also converted in quantitative yield into **14a** by treatment with KOH in THF–water. 9-Ethyl-10-aza-9-thiaphenanthrene (**14b**) was also synthesized in 90% yield by a similar method starting from the Ullman coupling reaction of *o*-iodophenyl ethyl sulfide (**9b**) and *o*-iodonitrobenzene (**10**) as shown in Chart 2. Azathiaphenanthrenes **14a** and **14b** were converted into azasulfonium picrates **13a′** and **13b′** by treatment with picric acid in ether in 96.1 and 63% yields, respectively, showing that ylidic S–N bonding predominates in **14a** and **14b** as in the case of **7**.



i) *o*-$IC_6H_4NO_2$ (**10**)–Cu, 200 °C, ii) Zn–$CaCl_2$–80% EtOH, iii) NCS–CH_2Cl_2, −50 °C, iv) $AgClO_4$, v) KOH–THF–H_2O, vi) picric acid, vii) Me_3OBF_4

Chart 2

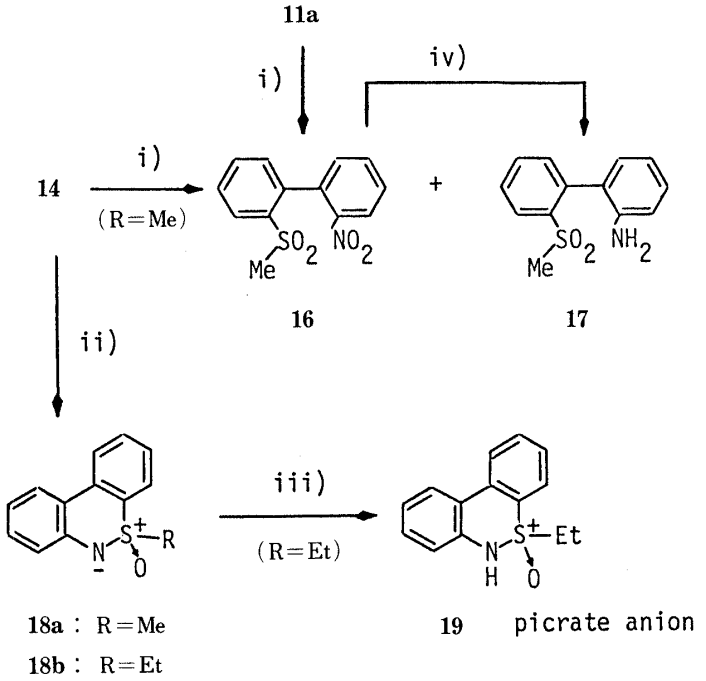
N-Alkylation of Azathiaphenanthrenes

Treatment of azathiaphenanthrenes **14a** and **14b** with methyl iodide in the presence of silver perchlorate gave no N-methylated products. Instead, the protonated products **13a** and **13b** were obtained in yields of 99 and 77%, respectively. This result might be attributed to the strong delocalization of the negative charge from the nitrogen atom to the benzene ring. In contrast, with a harder alkylating reagent,[10] trimethyloxonium tetrafluoroborate, **14a** gave the N-methylated salt **15** in 93.4% yield. The ^{1}H-NMR spectrum ($CDCl_3$) of **15** showed the N-methyl signal at δ 3.67.

Oxidation of Azathiaphenanthrenes

It is well-known that sulfilimines can be oxidized to the corresponding sulfoximines in good yields by reaction with potassium permaganate[7,11] or *m*-chloroperbenzoic acid (MCPBA).[12] We next examined the oxidation of this new class of heterocycles, as shown in

Chart 3. When **14a** was treated with MCPBA in acetone by the method reported by Cram *et al.*,[12a] ring-opening proceeded to afford 2-nitro-2′-mesylbiphenyl (**16**) and 2-amino-2′-mesylbiphenyl (**17**) in yields of 11 and 6%, respectively. The structures of these products were confirmed by comparison of the melting points and the spectral data with those of authentic samples prepared as shown in Chart 3. The nitro compound **11a** was oxidized with 2 eq of MCPBA to give **16**. Compound **16** was reduced with Zn–$CaCl_2$ in 80% ethanol to afford **17**. Next, we tried oxidation with potassium permanganate in dioxane–water, obtaining the



i) MCPBA, ii) $KMnO_4$, iii) picric acid, iv) Zn–$CaCl_2$–80% EtOH

Chart 3

expected 9-methyl-10-aza-9-thiaphenanthrene 9-oxide (**18a**) in 90% yield. Similarly, the azathiaphenanthrene **14b** was converted to the corresponding sulfoximine **18b** in 86% yield. This sulfoximine **18b** was led to the aminosulfoxonium salt **19** by treatment with picric acid.

Thermal Rearrangement of Azathiaphenanthrenes

Conjugated sulfonium ylides, thiabenzenes, undergo thermal rearrangement of sulfur substituents to carbon *via* 1,2- or 1,4-shift.[3] It was therefore of interest to examine whether the azathiabenzene derivatives undergo this kind of thermal rearrangement. On investigating the thermal reaction of azathiabenzenes, we found a new ring expansion reaction instead of a 1,2-shift. Although azathianaphthalene **7** gradually decomposed on standing at room temperature for a long period to give complex mixtures, the azathiaphenanthrenes **14a** and **14b** are very stable and can be stored indefinitely without decomposition at room temperature. Compound **14a** was unchanged after being refluxed in benzene for 12 h. However, on refluxing in xylene for 3 h, **14a** underwent thermal ring expansion to yield 7*H*-dibenzo[*d*,*f*][1,3]thiazepine (**21**) in 26% yield. The amino group of **21** was easily acetylated with acetic anhydride to give the N-acetyl compound, which was subsequently oxidized with MCPBA to afford the N-acetyl sulfone derivative **22**. This ring expansion can be rationalized in terms of a Stevens-type rearrangement of the methylide intermediate **20** thermally derived from **14a** as shown in Chart 4. On the other hand, refluxing of the ethyl derivative **14b** in xylene for 1 h caused deethylation of **14b** to afford compound **24** in 40% yield. Attempts at N-

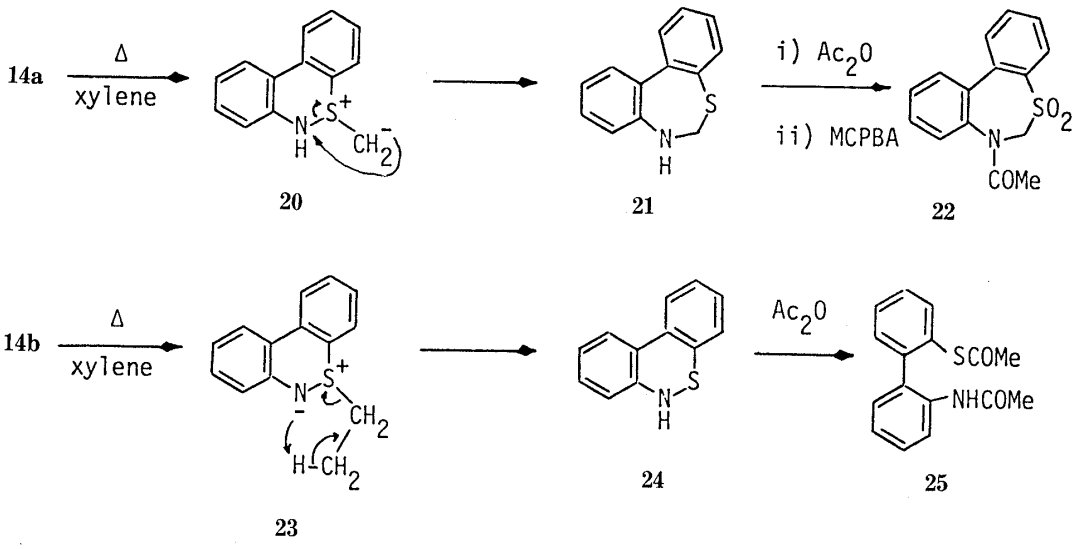


Chart 4

acetylation of **24** with acetic anhydride resulted in ring cleavage of the heterocycle to give 2-acetylthio-2′-acetamidobiphenyl (**25**). The formation of **24** is best explained in terms of a cyclo-elimination of the ethyl substituent as shown in Chart 4, a process which is commonly observed in the thermal reaction of acyclic sulfilimines bearing an S-alkyl group with a β-hydrogen atom.[13] We consider that this elimination reaction provides a new method for the preparation of dibenzo[*c*,*e*][1,2]thiazines.

Reactions of 2-Azathiabenzenes with Electrophiles

We have reported a number of interesting reactions of thiabenzene derivatives, 1-thianaphthalene,[3f] 2-thianaphthalenes,[3c,i] and 10-thiaanthracenes,[3b,g,h] with several electrophiles, and suggested that these reactivities of thiabenzene derivatives arise from the ylidic properties. It was thus of great interest to study the reactivities of azathiabenzene derivatives with electrophiles because these compounds possess the ylidic structure as described above.

Thus, we investigated the reactions of these compounds with dimethyl acetylenedicarboxylate (DMAD) as an electrophile. Treatment of **7** with DMAD in dry benzene for 91 h at room temperature afforded the crystalline adduct **26** as highly polar and yellow crystals in 20% yield (Chart 5). The structural proof of this novel adduct **26** was based on the spectroscopic data (experimental section). Similar addition products have been reported in the reaction of acyclic sulfilimines[14] and other cyclic sulfilimines[5c] with DMAD, the structure having been confirmed by X-ray diffraction analysis in the latter case.

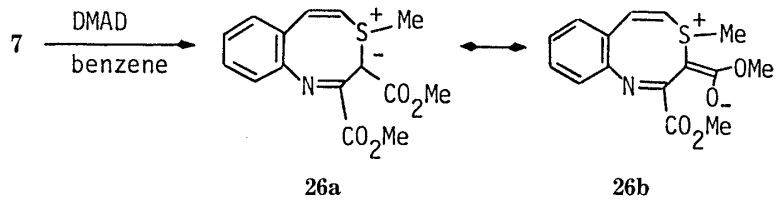
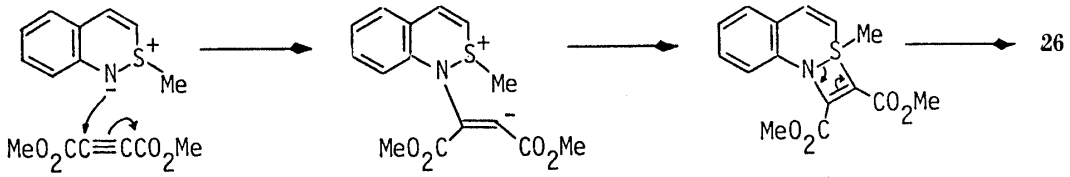


Chart 5

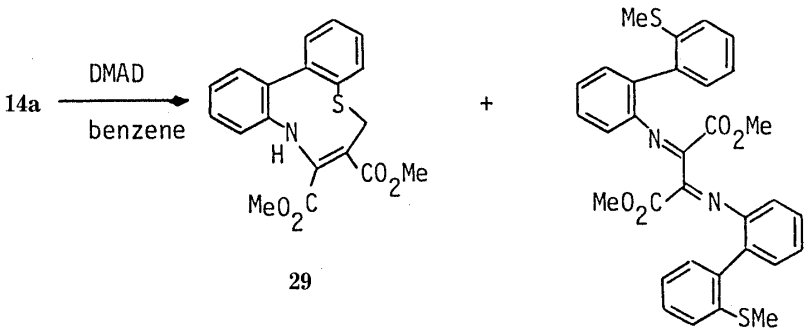
The course of the reaction is readily explained by a mechanism involving a four-center sulfurane intermediate **28** derived from the first intermediate **27** formed by the nucleophilic addition of the ylide anion to DMAD as shown in Chart 6, as proposed for the similar addition reaction of acyclic[14] and other cyclic sulfilimines.[5c]



27 28

Chart 6

Next, the reaction of **14a** with DMAD in benzene was carried out to afford a different type of 1 : 1 adduct **29**, mp 183—185 °C in 20% yield along with a small amount (3.2%) of 2 : 1 adduct **30**, mp 175—178 °C (Chart 7). The structures of **29** and **30** were determined on the basis of their spectroscopic data (experimental section). A similar 2 : 1 adduct was reported quite recently in the reaction of other cyclic sulfilimines with DMAD by Grant *et al.*[5c]



29 30

Chart 7

A plausible mechanism for the formation of **29** and **30** is depicted in Chart 8. The initial step of the reaction may be the nucleophilic attack of **14a** on the electron-deficient acetylene. The resulting zwitterionic intermediate **31** was converted to the next intermediate, the methylide **32**, by intramolecular proton abstraction from the proximate S-methyl group. This type of intramolecular proton abstraction has already been observed in some cases by us.[3f,h] The Michael-type addition of the anionic site of the methylide **32** to the double bond forms **33**, which is subsequently isomerized to the thermodynamically more stable compound **29**. The carbanion of the intermediate **31** is protonated by the small amount of water contaminating the reaction media to give the sulfonium ion intermediate **34**. The intermediate **34** is next attacked by a second molecule of **14a** to result in the formation of intermediate **35**, which affords the final product **30** after the loss of a proton.

The results of the reaction of azathiabenzenes with other electrophiles will be reported in the near future.

Experimental

Melting points were determined by using a Yanagimoto micromelting point apparatus and are uncorrected. IR spectra were taken on a JASCO IR A-1 infrared spectrometer and are expressed in reciprocal centimeters. ^{1}H-NMR spectra were recorded on Hitachi R-20B (60 MHz) and Bruker WH-200 (200 MHz) spectrometers. Chemical shifts are expressed in parts per million (ppm) with respect to Me_4Si as an internal standard. ^{13}C-NMR spectra were determined with a JEOL FX-100 or a Brucker WH-200 (50 MHz) spectrometer with Me_4Si as an internal standard;

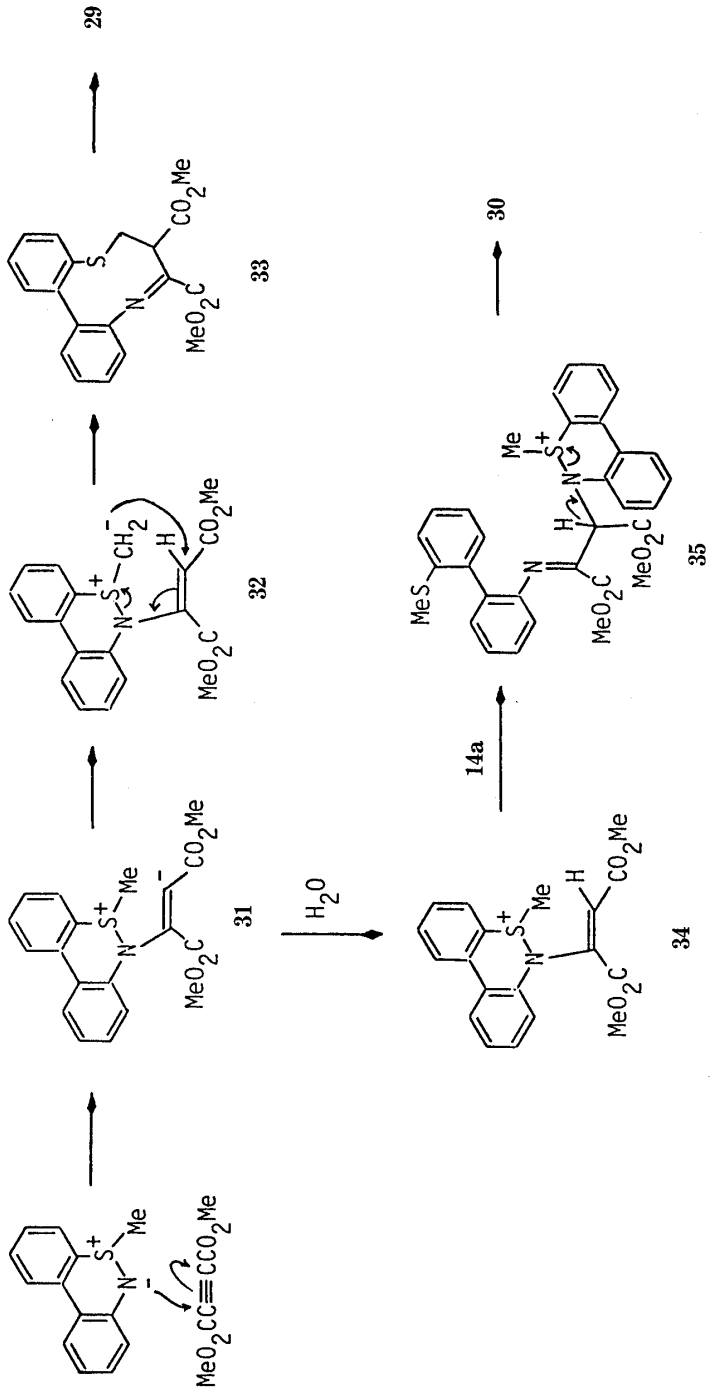


Chart 8

chemical shifts are expressed in δ values. The mass spectra (MS) were run on a JEOL D-300 mass spectrometer at an ionization voltage of 70 eV. Data are reported as *m/e*.

Methyl *o*-Nitrostyryl Sulfide (3)——A 0.64 N solution of phenyllithium in ether (150 ml, 96 mmol) was added dropwise under a nitrogen atmosphere to a stirred solution of well-pulverized methylthiomethyltriphenylphosphonium chloride (30 g, 84 mmol) in dry THF (200 ml). The phosphonium ylide **2** was formed exothermically with the development of a deep red color. After stirring of the mixture for 30 min at room temperature, *o*-nitrobenzaldehyde (**1**, 12.6 g, 83.6 mmol) was added as a solid to the mixture, and the whole was stirred under reflux in an atmosphere of nitrogen for 20 h. The reaction mixture was poured into 500 ml of cold water and extracted with ether. The ether layer was washed with water, dried over $MgSO_4$ and evaporated to dryness. The residue was extracted with pet. ether in a Soxhlet apparatus. The pet. ether was evaporated off and the residual oil was subjected to silica gel column chromatography with hexane–ether (20 : 1–5 : 1) as the eluent. The product was distilled to give 14.5 g (89%) of pure **3** as a yellow oil: bp 98 °C (2 mmHg). IR (neat): 1520, 1350 (NO_2) cm^{-1}. *Anal.* Calcd for $C_9H_9NO_2S$: C, 55.37; H, 4.65; N, 7.17. Found: C, 55.63; H, 4.66; N, 7.10. The ^{1}H-NMR spectrum of the product showed it to be a mixture of *trans*- and *cis*-*o*-nitrostyryl methyl sulfides in a ratio of 1 : 1. ^{1}H-NMR ($CDCl_3$) δ: 2.36 (3H, s, Me), 2.40 (3H, s, Me), 6.40 (1H, d, J=11 Hz, *cis* olefinic H), 6.70 (1H, d, J=15 Hz, *trans* olefinic H), 6.80 (1H, d, J=11 Hz, *cis* olefinic H), 6.97 (1H, d, J=15 Hz, *trans* olefinic H), 7.20—8.15 (8H, m, ArH).

***cis*- and *trans*- *p*-Aminostyryl Methyl Sulfides (4a, 4b)**——A mixture of **3** (7 g, 35.9 mmol), Zn powder (7.1 g, 0.11 mmol) and $CaCl_2$ (5.2 g, 46.9 mmol) in 80% ethanol (160 ml) was refluxed with stirring for 6 h. The hot reaction mixture was filtered to remove solids, and the solids were well washed with hot ethanol. The combined ethanol solution was poured into ice-water and extracted with dichloromethane. The extract was washed with water, dried over $MgSO_4$ and evaporated. The residual oil was column-chromatographed on silica gel using hexane–ether chloroform (7 : 3 : 1) to afford 2.55 g (43.2%) of **4b** as a yellow oil from the first fraction: IR (neat): 3410, 3350 (NH_2) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.35 (3H, s, Me), 3.60 (2H, br, NH_2), 6.28 (1H, d, J=15 Hz, olefinic H), 6.65 (1H, d, J=15 Hz, olefinic H), 6.60—7.25 (4H, m, ArH).

The picrate of **4b**: yellow prisms (ether). mp 158—161 °C (dec.). IR (KBr): 3000 ($\overset{+}{N}H_3$), 1560, 1335 (NO_2) cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 2.45 (3H, s, Me), 6.40 (1H, d, J=18 Hz, olefinic H), 7.24 (1H, d, J=18 Hz, olefinic H), 7.00—7.85 (4H, m, ArH), 8.65 (2H, s, ArH); *Anal.* Calcd for $C_{15}H_{14}N_4O_7S$: C, 45.69; H, 3.58; N, 14.21. Found: C, 45.60; H, 3.66; N, 14.22. From the second fraction 2.5 g (42.4%) of **4a** was obtained as a yellow oil: IR (neat): 3420, 3350 (NH_2) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.30 (3H, s, Me), 3.60 (2H, br, NH_2), 6.18 (1H, d, J=10 Hz, olefinic H), 6.99 (1H, d, J=10 Hz, olefinic H), 6.40—7.40 (4H, m, ArH). The picrate of **4a**: yellow prisms (dichloromethane–hexane–ethanol). mp 173—175 °C (dec.). IR (KBr): 2900 ($\overset{+}{N}H_3$), 1550, 1330 (NO_2) cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 2.49 (3H, s, Me), 6.49 (1H, d, J=11 Hz, olefinic H), 6.78 (1H, d, J=11 Hz, olefinic H), 6.70—7.80 (4H, m, ArH), 8.63 (2H, s, ArH); *Anal.* Calcd for $C_{15}H_{14}N_4O_7S$: C, 45.69; H, 3.58; N, 14.21. Found: C, 45.61; H, 3.54; N, 14.14.

2-Methyl-1*H*-2,1-benzothiazin-2-ium Perchlorate (6a)——Compound **4a** (1.3 g, 7.9 mmol) was dissolved in dry dichloromethane (40 ml). The solution was cooled to −50 °C and stirred while a solution of NCS (1.1 g, 8.1 mmol) dissolved in dry dichloromethane (40 ml) was added dropwise over 30 min. Stirring was continued for a further 6 h during which time the temperature was gradually raised to 0 °C, and the mixture was left overnight at 0 °C. Dry ether (100 ml) was added to the reaction mixture. After the brown oil had sufficiently precipitated, the supernatant was discarded and the residual oil was dissolved in dry dichloromethane. Silver perchlorate (860 mg, 4.1 mmol) was added to the above dichloromethane solution and the mixture was stirred for 2.5 h. The precipitated silver chloride was filtered off and washed several times with dichloromethane. The filtrates were evaporated under reduced pressure to give 0.86 g (41%) of **6a** as colorless columns after recystallization from dichloromethane–hexane: mp 165—168 °C (dec.). IR (KBr): 3270 (NH), 1100 (ClO_4^-) cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 2.79 (3H, s, Me), 6.71 (1H, d, J=9 Hz, C_3–H), 7.00—7.70 (4H, m, ArH), 7.80 (1H, d, J=9 Hz, C_4–H). *Anal.* Calcd for $C_9H_{10}ClNO_4S$: C, 40.99; H, 3.82; N, 5.31. Found: C, 41.04; N, 3.86; N, 5.28.

2-Methyl-1-aza-2-thianaphthalene (7)——Method A: The reaction of **4a** (830 mg, 5 mmol) with NCS (700 mg, 5.3 mmol) in dichloromethane (70 ml) was carried out as described above. The reaction mixture was extracted with a diluted NaOH solution (NaOH (570 mg) in water (50 ml)) and the organic layer was separated, dried over $MgSO_4$ and evaporated to yield 620 mg (76.1%) of crude **7**. Recrystallization from dichloromethane–hexane gave pure **7** as yellow prisms: mp 123—129 °C (dec.). IR (KBr): 1600, 1255, 950, 920 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.22 (3H, s, Me), 5.70 (1H, d, J=9 Hz, C_3–H), 6.75—7.45 (5H, m, ArH and C_4–H). MS *m/e*: 163 (M^+). *Anal.* Calcd for C_9H_9NS: C, 66.22; H, 5.56; N, 8.58. Found: C, 66.44; H, 5.63; N, 8.46.

Method B: An aqueous KOH solution (KOH (86.3 mg) in water (1 ml)) was added to a solution of **6a** (200 mg, 0.76 mmol) in THF (5 ml) and the mixture was stirred for 5 min. The reaction mixture was extracted with dichloromethane. The extracts were washed with water, dried over $MgSO_4$ and evaporated to afford 70.4 mg (57%) of **7**.

Treatment of 7 with Picric Acid——An ethereal solution of equimolar amounts of picric acid was added to a solution of **7** (56.3 mg) in ether. The yellow precipitate was collected and recrystallized from dichloromethane–ether to afford 136 mg (quant) of 2-methyl-1*H*-2,1-benzothiazin-2-ium picrate (**6b**) as yellow crystals: mp 168—172 °C (dec.). IR (KBr): 1560, 1335 (NO_2) cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 2.79 (3H, s, Me), 6.71 (1H, d, J=9 Hz, C_3–H),

7.00—7.85 (4H, m, ArH), 7.80 (1H, d, $J=9$ Hz, C_4–H), 8.60 (2H, s, ArH). *Anal.* Calcd for $C_{15}H_{12}N_4O_2S$: C, 45.92; H, 3.08; N, 14.28. Found: C, 45.91; H, 3.10; N, 13.99.

2-Methylthio-2′-nitrobiphenyl (11a)——*o*-Iodonitrobenzene (**10**, 15 g, 60.2 mmol), *o*-iodophenyl methyl sulfide (**9a**, 16.6 g, 66.4 mmol) and copper powder (15.3 g, 0.24 mmol) were well mixed and heated at 200 °C with stirring for 1.5 h. Benzene was added to the reaction mixture and stirred for 30 min. The solids were filtered off and washed with benzene. The combined filtrates were evaporated to dryness *in vacuo*. The residual oil was purified by column chromatography on silica gel using hexane–benzene as an eluent to give 7.58 g (51.3%) of **11a**. Recrystallization from pet. ether afforded yellow plates: mp 40—42 °C. IR (KBr): 1530, 1350 (NO_2) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.30 (3H, s, Me), 6.90—8.13 (8H, m, ArH). *Anal.* Calcd for $C_{13}H_{11}NO_2S$: C, 63.65; H, 4.52; N, 5.71. Found: C, 63.59; H, 4.45; N, 5.71.

***o*-Aminophenyl Ethyl Sulfide**——Sodium hydride (6.05 g, 0.25 mmol) was added in small amount to a stirred solution of *o*-aminobenzenethiol (30 g, 0.24 mol) in dry acetonitrile (200 ml) and the mixture was stirred for 1 h at room temperature. Ethyl iodide (39 g, 0.25 mol) was added to this solution at 0 °C with stirring. After being stirred for 7 h, the reaction mixture was poured into water (300 ml) and extracted with ether. The extract was washed, dried over $MgSO_4$ and evaporated to give 38.8 g (100%) of *o*-aminophenyl ethyl sulfide as an oil, whose ^{1}H-NMR spectrum ($CDCl_3$) showed signals due to ethyl protons at δ 1.30 (3H, t, $J=7$ Hz, CH_2CH_3), 2.40 (2H, q, $J=7$ Hz, CH_2CH_3), amino protons at δ 4.25 (2H, br) and aromatic protons at δ 6.25—7.55 (4H, m). This compound was used for the next reaction without further purification and characterization.

Ethyl *o*-Iodophenyl Sulfide (9b)——*o*-Aminophenyl ethyl sulfide (36.7 g, 0.24 mol) was dissolved in conc. HCl (130 ml) and crushed ice (100 g) was added. A solution of sodium nitrite (18.2 g, 0.26 mol) in water (80 ml) was slowly added to the above solution and the mixture was stirred for 2.5 h at room temperature. The resulting diazonium salt solution was slowly added to a solution of potassium iodide (160 g, 0.96 mol) in water (200 ml) and stirring was continued overnight. The reaction mixture was extracted with ether and the ether extract was washed first with sodium thiosulfinate and then water, dried over $MgSO_4$ and evaporated to dryness. The residual oil was purified by vacuum distillation under a nitrogen stream to give 47.65 g (75.3%) of **9b** as an orange oil: bp 133—135 °C (1 mmHg). ^{1}H-NMR ($CDCl_3$) δ: 1.35 (3H, t, $J=7.5$ Hz, $CH_2C\underline{H}_3$), 2.93 (2H, q, $J=7.5$ Hz, $C\underline{H}_2CH_3$), 6.60—7.90 (4H, m, ArH).

2-Ethylthio-2′-nitrobiphenyl (11b)——This compound was prepared from **10** (15 g, 60.2 mmol), **9b** (15.9 g, 60.2 mmol) and copper powder (15.3 g, 0.24 mol) by the same method as described above for **11a**: yellow oil. Yield: 6.65 g (42.6%). IR (neat): 1530, 1350 (NO_2) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.17 (3H, t, $J=7$ Hz, $CH_2C\underline{H}_3$), 2.76 (2H, q, $J=7$ Hz, $C\underline{H}_2CH_3$), 7.05—8.20 (8H, m, ArH). This oily compound was further characterized by leading it to the corresponding sulfone by oxidation with MCPBA in dichloromethane: mp 128—130 °C. IR (KBr): 1510, 1355 (NO_2), 1310, 1150 (SO_2) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.15 (3H, t, $J=7$ Hz, $CH_2C\underline{H}_3$), 2.84 (2H, q, $J=7$ Hz, $C\underline{H}_2CH_3$), 7.17—8.35 (8H, m, ArH). *Anal.* Calcd for $C_{14}H_{13}NO_4S$: C, 57.72; H, 4.50; N, 4.81. Found: C, 57.73; H, 4.46; N, 4.68.

2-Amino-2′-methylthiobiphenyl (12a)——A mixture of **11a** (10.3 g, 42 mmol), Zn powder (8.3 g, 127 mmol), and $CaCl_2$ (6.1 g, 55 mmol) in 80% ethanol (200 ml) was refluxed for 6 h and worked up as described for **4** to give a brown oil. The oil was purified by dissolving it in alkaline solution, followed by treatment with dil. HCl to give 4.33 g (47.9%) of **12a**, which was recrystallized from benzene–hexane to afford a pure product as colorless columns: mp 83—85 °C. IR (KBr): 3450, 3360 (NH_2) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.32 (3H, s, Me), 3.41 (2H, br, NH_2), 6.58—7.90 (8H, m, ArH). *Anal.* Calcd for $C_{13}H_{13}NS$: C, 72.52; H, 6.09; N, 6.51. Found: C, 72.52; H, 6.14; N, 6.36.

2-Amino-2′-ethylthiobiphenyl (12b)——A mixture of **11b** (1.2 g, 3.63 mmol), Zn powder (2.3 g, 35.2 mmol) and $CaCl_2$ (1.7 g, 15.3 mmol) in 80% ethanol (150 ml) was refluxed for 7 h and worked up as above to give 750 mg (71%) of **12b** as a yellow oil: IR (neat): 3430 (NH_2) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.24 (3H, t, $J=7$ Hz, $CH_2C\underline{H}_3$), 2.82 (2H, q, $J=7$ Hz, $C\underline{H}_2CH_3$), 3.33 (2H, br, NH_2), 6.60—7.70 (8H, m, ArH). Elemental analysis was performed on the picrate: *Anal.* Calcd for $C_{20}H_{18}N_4O_7S$: C, 52.40; H, 3.96; N, 12.22. Found: C, 52.37; H, 4.08; N, 11.96.

5-Methyl-6*H*-dibenzo[*c*,*e*][1,2]thiazin-5-ium Perchlorate (13a)——Compound **13a** was prepared by the same method as described for **6a** from the reaction of **12a** (1 g, 4.7 mmol) with NCS (640 mg, 4.78 mmol) in dry dichloromethane (75 ml), followed by treatment with silver perchlorate (810 mg, 3.92 mmol). Yield: 940 mg (64.1%). Colorless needles (hexane–dichloromethane). mp 187—191 °C (dec.). IR (KBr): 3360 (NH), 1115 (ClO_4^-) cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 2.93 (3H, s, Me), 3.75 (1H, br, NH), 7.25—8.45 (8H, m, ArH). *Anal.* Calcd for $C_{13}H_{12}ClNO_4S$: C, 49.77; H, 3.86; N, 4.46. Found: C, 49.52; H, 3.87; N, 4.45.

9-Methyl-10-aza-9-thiaphenanthrene (14a)——Method A: Compound **12a** (1.04 g, 4.84 mmol) was allowed to react with NCS (690 mg, 5.17 mmol) in dry dichloromethane (60 ml) and worked up as described for **7** to give 1.04 g (100%) of **14a**. Recrystallization from hexane–dichloromethane formed yellow prisms: mp 168—172 °C (dec.). IR (KBr): 1595, 1460, 1420, 1290, 1230, 935, 910 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.34 (3H, s, Me), 7.15—8.10 (8H, m, ArH). MS *m/e*: 213 (M^+), 198. *Anal.* Calcd for $C_{13}H_{11}NS$: C, 73.20; H, 5.20; N, 6.57. Found: C, 73.09; H, 5.09; N, 6.56.

Method B: An aqueous KOH solution (KOH (83.5 mg) in water (3 ml)) was added to a stirred solution of **13a** (200 mg, 0.64 mmol) in dry THF (5 ml). After being stirred for 30 min, the reaction mixture was extracted with dichloromethane. The extract was dried over $MgSO_4$ and evaporated to give 135 mg (100%) of **14a**. Treatment of **14a** (59.2 mg) with picric acid (68.3 mg) in dry ether (70 ml) gave 118 mg (96.1%) of the picrate **13a′** as yellow plates: mp 213—216 °C (dec.). IR (KBr): 3000 (NH), 1570, 1300 (NO_2) cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 2.93 (3H, s, Me), 7.10—

8.45 (8H, m, ArH), 8.60 (2H, m, ArH). *Anal.* Calcd for $C_{19}H_{14}N_4O_7S$: C, 51.58; H, 3.19; N, 12.66. Found: C, 51.44; H, 3.26; H, 12.44. On the other hand, treatment of **14a** (192.3 mg) in dry ether–dichloromethane (5 : 1) with 70% perchloric acid gave 208.8 mg (74%) of **13a**.

9-Ethyl-10-aza-9-thiaphenanthrene (14b)——This compound was prepared by the reaction of **13b** (1.71 g, 7.16 mmol) with NCS (1.02 g, 7.61 mmol) in dry dichloromethane (100 ml) followed by work-up as described for **7**: yellow oil. Yield: 1.47 g (90.3%). IR (neat): 1590, 1460, 1410, 1290, 1210, 915 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.04 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 2.10—3.25 (2H, m, $C\underline{H}_2CH_3$), 6.63—8.05 (8H, m, ArH). The structure was further confirmed by conversion to the picrate **13b′** in the usual way: yellow plates. mp 199—202 °C (dec.). IR (KBr): 3120 (NH), 1560, 1340 (NO_2) cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 1.18 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 3.03—3.48 (2H, m, $C\underline{H}_2CH_3$), 7.20—8.50 (8H, m, ArH), 8.61 (2H, m, ArH). *Anal.* Calcd for $C_{20}H_{16}N_4O_7S$: C, 52.63; H, 3.53; N, 12.28. Found: C, 52.73; H, 3.55; N, 12.24.

Attempts at N-Methylation of 14a and 14b——Silver perchlorate (348.5 mg, 1.68 mmol) was added to a stirred solution of **14a** (321 mg, 1.5 mmol) and methyl iodide (1.34 g, 9.4 mmol) in dichloromethane (40 ml) and the mixture was stirred for 24 h. The precipitates were filtered off and washed well with dichloromethane. The combined filtrates were concentrated to give 467 mg (99%) of **13a** as colorless columns (chloroform–ether), which were identified by comparison with authentic **13a** based on the spectroscopic data and mp. Similarly, the reaction of **14b** (401 mg, 1.76 mmol) with methyl iodide (5 g, 35.2 mmol) in the presence of silver perchlorate (430.2 mg, 2.08 mmol) afforded 444 mg (76.9%) of **13b**.

Treatment of 14a with Trimethyloxonium Tetrafluoroborate——A mixture of **14a** (331.6 mg, 1.55 mmol) and trimethyloxonium tetrafluoroborate (269.4 mg, 1.82 mmol) in dry dichloromethane (30 ml) was stirred for 1 d, and evaporated to dryness to give 456.4 mg (93.4%) of 5,6-dimethyldibenzo[*c*,*e*][1,2]thiazin-5-ium tetrafluoroborate (**15**) as crystals by trituration with dry ether. The product (**15**) was recrystallized from ether–dichloromethane to give colorless prisms: mp 164 °C (dec.). IR (KBr): 1030—1130 (BF_4^-) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.97 (3H, s, Me), 3.67 (3H, s, Me), 7.23—8.25 (8H, m, ArH). *Anal.* Calcd for $C_{14}H_{14}BF_4NS$: C, 53.36; H, 4.48; N, 4.44. Found: C, 53.14; H, 4.48; N, 4.45.

Oxidation of 14a with MCPBA——Sodium carbonate (1.26 g, 11.9 mmol) and 85% MCPBA (2.57 g, 14.9 mmol) were added to a solution of **14a** (633 mg, 2.97 mmol) in dry acetone (30 ml) and the mixture was stirred for 24 h at room temperature. Excess MCPBA was decomposed by addition of sodium thiosulfate (6 g, 38 mmol) dissolved in water (50 ml) followed by acidification with 6 N H_2SO_4 (3 ml). The reaction mixture was made basic (pH 12) with 6 N NaOH and extracted with dichloromethane. The extract was washed with water, dried over $MgSO_4$ and evaporated. The residue was subjected to preparative TLC on silica gel using hexane–dichloromethane. The first fraction gave 89.3 mg (10.9%) of **16** as yellow columns after recrystallization from dichloromethane–ether: mp 145—146 °C. From the second fraction, **17** was obtained in the yield of 44.2 mg (6%) as colorless columns (chloroform–hexane), mp 153—155 °C. Melting points and spectral data of these two products were identical with those of authentic samples, prepared as described below.

2-Nitro-2′-mesylbiphenyl (16)——85% MCPBA (2.46 g, 14.2 mmol) was added to a stirred solution of **11a** (1.28 g, 5.22 mmol) in dry dichloromethane (40 ml) and the mixture was stirred for 72 h at room temperature. An aqueous K_2CO_3 solution was added to this reaction mixture to make the solution basic, and the whole was stirred for 30 min. The organic layer was separated, washed with water, dried over $MgSO_4$ and evaporated. The residue was recrystallized from chloroform–ether to give 900 mg (62.3%) of **16** as yellow columns: mp 143—144 °C. IR (KBr): 1510, 1350 (NO_2), 1310, 1150 (SO_2) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.79 (3H, s, Me), 7.10—8.30 (8H, m, ArH). *Anal.* Calcd for $C_{13}H_{11}NO_4S$: C, 56.31; H, 4.00; N, 5.05. Found: C, 56.43; H, 4.03; N, 4.96.

2-Amino-2′-mesylbiphenyl (17)——Compound **16** (700 mg, 2.55 mmol) was reduced with Zn powder (500 mg) and $CaCl_2$ (400 mg) in 80% ethanol as described for **3** or **10**. The resulting product was recrystallized from chloroform–hexane to afford 310 mg (49%) of **17** as colorless columns: mp 153—155 °C. IR (KBr): 3450, 3360 (NH_2), 1290, 1140 (SO_2) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.81 (3H, s, Me), 3.52 (2H, br, NH), 6.65—8.40 (8H, m, ArH). *Anal.* Calcd for $C_{13}H_{13}NO_2S$: C, 63.14; H, 5.30; N, 5.66. Found: C, 62.89; H, 5.22; N, 5.70.

Oxidation of 14a with Potassium Permanganate——**14a** (1.21 g, 5.67 mmol) was dissolved in dioxane (100 ml). An aqueous 0.24 M potassium permanganate solution (50 ml, 12 mmol) was added dropwise to this solution and the mixture was stirred for 8 h at room temperature. The reaction mixture was poured into water (200 ml) then extracted with chloroform and the extract was drid over $MgSO_4$. After evaporation of the solvent, the residue was recrystallized from dichloromethane–hexane to give 1.17 g (89.9%) of 9-methyl-10-aza-9-thiaphenanthrene 9-oxide (**18a**) as colorless needles: mp 130—132 °C (dec.). IR (KBr): 1595, 1470, 1190, 1010 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.48 (3H, s, Me), 6.87—8.35 (8H, m, ArH). MS *m/e*: 229 (M^+), 166. *Anal.* Calcd for $C_{13}H_{11}NOS$: C, 68.10; H, 4.84; N, 6.11. Found: C, 67.99; H, 4.80; N, 6.00.

Oxidation of 14b with Potassium Permanganate——**14b** (1.25 g, 5.5 mmol) was oxidized with potassium permanganate (12 mmol) in a mixture of dioxane and water as described for **14a** to give 1.15 g (85.8%) of 9-ethyl-10-aza-9-thiaphenanthrene 9-oxide (**18b**) as a yellow oil. IR (neat): 1600, 1480, 1420, 1220, 920 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.16 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 3.35—3.85 (2H, m, $C\underline{H}_2CH_3$), 6.83—8.35 (8H, m, ArH). MS *m/e*: 243 (M^+), 214. *Anal.* Calcd for $C_{20}H_{16}N_4O_8S$ (picrate): C, 50.85; H, 3.41; N, 11.86. Found: C, 50.87; H, 3.33; N, 11.65.

Thermal Ring Expansion of 14a——A solution of **14a** (133.8 mg, 0.63 mmol) in dry xylene (15 ml) was refluxed for 3 h. The reaction mixture was concentrated and the residual oil was purified by preparative TLC on silica gel with dichloromethane–hexane to afford 34.8 mg (26%) of 7*H*-dibenzo[*d,f*][1,3]thiazepine (**21**) as a colorless oil. IR (neat): 3380 (NH) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.60 (1H, br, NH), 4.65 (2H, CH_2), 6.50—7.70 (8H, m, ArH). MS *m/e*: 213 (M^+), 184.

7-Acetyldibenzo[*d,f*][1,3]thiazepine 1,1-Dioxide (22)——A solution of **21** (77.7 mg, 0.36 mmol) in acetic anhydride (15 ml) was refluxed for 3 h. The reaction mixture was concentrated and the residue was dissolved in dichloromethane. The solution was washed with an aqueous K_2CO_3 solution, then water, dried over $MgSO_4$ and evaporated. The oily residue (76.3 mg) was dissolved in dichloromethane (20 ml) and 85% MCPBA (135.1 mg) was added to the solution. The mixture was stirred for 88 h at room temperature, then an aqueous K_2CO_3 solution was added to the reaction mixture and the whole was stirred for 1 h. The organic layer was separated, washed with water, dried over $MgSO_4$ and evaporated to dryness. The residue was purified by preparative TLC on silica gel using ethyl acetate–hexane (1 : 1) as a solvent to afford 33.2 mg (21.7%) of **22** as colorless columns from chloroform–ether: mp 223—226 °C. IR (KBr): 1670 (CO), 1305, 1135 (SO_2) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.59 (3H, s, Me), 4.59 (1H, d, J= 15 Hz, C_6–H), 6.42 (1H, d, J=15 Hz, C_6–H), 7.10—8.30 (8H, m, ArH). *Anal.* Calcd for $C_{15}H_{13}NO_3S$: C, 62.70; H, 4.56; N, 4.87, Found: C, 62.52; H, 4.56; N, 4.73.

Thermal Reaction of 14b——14b (293.3 mg, 1.29 mmol) was dissolved in dry xylene (30 ml) and the solution was refluxed for 1 h. The solvent was removed *in vacuo* to leave an oil, which was purified by preparative TLC on silica gel with ethyl acetate–hexane (1 : 6) to afford 103.5 mg (40.3%) of 6*H*-dibenzo[*c,e*][1,2]thiazine (**24**) as a colorless oil. IR (neat): 3240 (NH) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.83 (1H, br, NH), 7.00—8.20 (8H, m, ArH). MS *m/e*: 199 (M^+).

Acetylation of 24 with Acetic Anhydride——A solution of **24** (79.8 mg, 0.4 mmol) in acetic anhydride (15 ml) was refluxed for 4 h. The excess acetic anhydride was removed *in vacuo* and the residue was dissolved in dichloromethane. The dichloromethane solution was washed with an aqueous $NaHCO_3$ solution, then with water to remove a trace amount of acetic anhydride, dried over $MgSO_4$ and evaporated. The residue was purified by preparative TLC on silica gel with hexane–ether (1 : 2) to give 58.1 mg (51%) of 2-acetylthio-2′-acetamidobiphenyl (**25**) as colorless prisms after recrystallization from dichloromethane–hexane: mp 199—199.5 °C. IR (KBr): 3400 (NH), 1700 (CO) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.96 (3H, s, Me), 2.38 (3H, s, Me), 7.00—7.90 (9H, m, ArH and NH). MS *m/e*: 285 (M^+), 184. *Anal.* Calcd for $C_{16}H_{15}NO_2S$: C, 67.34; H, 5.30; N, 4.91. Found: C, 67.07; H, 5.18; N, 4.69.

Reaction of 7 with DMAD——A solution of DMAD (283.2 mg, 1.99 mmol) in dry benzene (5 ml) was added to a solution of **7** (278.3 mg, 1.71 mmol) in dry benzene (20 ml) and the mixture was stirred for 91 h at room temperature. Benzene was evaporated off under reduced pressure at room tempeature to leave an oil, which was subjected to preparative TLC on silica gel with hexane–ethyl acetate (1 : 1). The fraction obtained from the origin of the plate afforded 104.7 mg (20.1%) of 2,3-bismethoxycarbonyl-4-methyl-4-thionia-1-benzazocin-3-ide (**26**), which was recrystallized from dichloromethane–hexane to give yellow columns: mp 171—173 °C. IR (KBr): 1720 (ester), 1650 (ester) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.97 (3H, s, Me), 3.64 (3H, s, Me), 3.86 (3H, s, Me), 6.25 (1H, d, J=9 Hz, olefinic H), 6.75—7.70 (4H, m, ArH), 7.83 (1H, d, J=9 Hz, olefinic H). ^{13}C-NMR ($CDCl_3$) δ: 32.99 (q), 51.11 (q), 52.72 (q), 53.9 (s), 114.22 (d), 121.93 (d), 123.44 (d), 124.38 (s), 127.52 (d), 132.24 (d), 147.48 (d), 151.62 (s), 160.16 (s), 167.03 (s), 167.61 (s). MS *m/e*: 305 (M^+). *Anal.* Calcd for $C_{15}H_{15}NO_4S$: C, 59.01; H, 4.95; N, 4.59. Found: C, 58.73; H, 5.04; N, 4.63.

Reaction of 14a with DMAD——A mixture of **14a** (634.5 mg, 2.97 mmol) and DMAD (428.8 mg, 3.02 mmol) in dry benzene (50 ml) was stirred for 6 h at room temperature. Benzene was removed *in vacuo* and the residue was purified by preparative TLC on silica gel with pet. ether–ether (1 : 1) to afford 212.3 mg (20.1%) of 7,8-bismethoxycarbonyl-6*H*,9*H*-dibenzo[*f,h*][1,5]thiazonine (**29**) and 27.2 mg (3.2%) of dimethyl 1,2-bis-(2-methylthio-2′-biphenylylimino)ethane-1,2-dicarboxylate (**30**). **29**: colorless needles (benzene). mp 183—185 °C. IR (KBr): 3300 (NH), 1690 (CO) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.26 (2H, s, CH_2), 3.62 (2H, s, OMe), 3.65 (3H, s, OMe), 6.18 (1H, br, NH), 6.70—7.80 (8H, m, ArH). MS *m/e*: 355 (M^+), 296. *Anal.* Calcd for $C_{19}H_{17}NO_4S$: C, 64.21; H, 4.82; N, 3.94. Found: C, 64.26; H, 4.82; N, 4.08. **30**: yellow needles (benzene). mp 175—178 °C. IR (KBr): 1735 (CO) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.29 (6H, s, 2 × SMe), 3.36 (6H, s, 2 × OMe), 6.80—7.60 (8H, m, ArH). MS *m/e*: 568 (M^+). *Anal.* Calcd for $C_{32}H_{28}N_2O_4S$: C, 67.59; H, 4.96; N, 4.93. Found: C, 67.53; H, 4.93; N, 4.81.

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