The Synthesis of Phenanthrodibenzothiophenes

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Received August 30, 1983

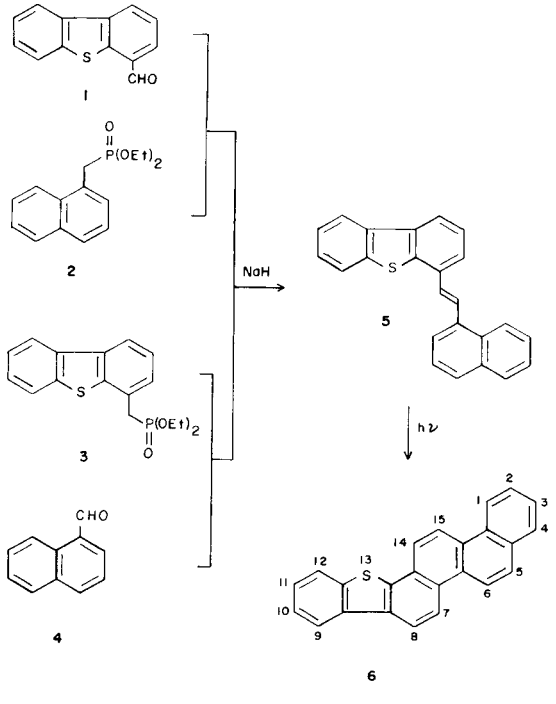
The synthesis of phenanthro[1,2-*c*]dibenzothiophene (**6**), phenanthro[4,3-*c*]dibenzothiophene (**10**), phenanthro[2,1-*a*]dibenzothiophene (**14**), phenanthro[3,4-*a*]dibenzothiophene (**16**), phenanthro[1,2-*a*]dibenzothiophene (**19**), phenanthro[2,1-*b*]dibenzothiophene (**20**), 8-methylphenanthro[3,2-*a*]dibenzothiophene (**24**), 7-methylphenanthro[1,2-*a*]dibenzothiophene (**25**), phenanthro[3,4-*b*]dibenzothiophene (**27**), phenanthro[4,3-*a*]-dibenzothiophene (**28**), 6-methylphenanthro[2,3-*a*]dibenzothiophene (**31**), and 5-methylphenanthro[4,3-*a*]dibenzothiophene (**32**) is described.

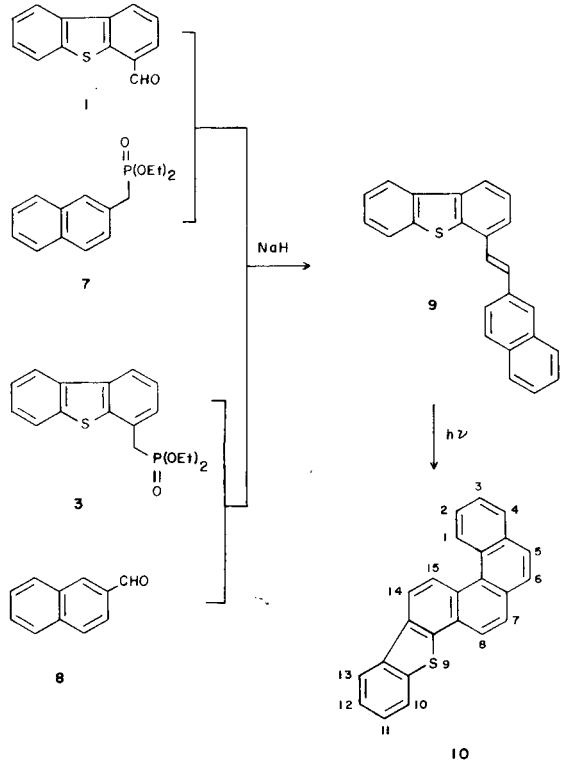
J. Heterocyclic Chem., **21**, 1833 (1984).

In this paper we report ten novel ring systems as part of our continuing studies [2-23] directed toward the synthesis of all of the potentially mutagenic unsubstituted polycyclic thiophenes and their monomethyl, dimethyl and monoethyl derivatives which occur or are suspected of occurring in coal liquids, shale oils and coal derived products.

The condensation of dibenzothiophene-4-carboxaldehyde (**1**) [24] with diethyl 1-naphthylmethylphosphonate (**2**) [25] gave in 60% yield 4-[β-(1-naphthyl)vinyl]dibenzothiophene (**5**) as fluorescent yellow flakes. Compound **5** was also obtained in 64% yield from the reaction of diethyl 4-dibenzothenylphosphonate (**3**) [21] with naphthalene-1-carboxaldehyde (**4**) using sodium hydride as the base.

Scheme I





When compound **5** was irradiated for four hours under a 450 watt Hanovia medium pressure mercury lamp using iodine and air as the oxidants it gave in 52% yield phenanthro[1,2-*c*]dibenzothiophene (**6**). Photocyclization yields were maximized by not adding the whole amount of iodine (0.1 g) at once in the reaction mixture, but by adding small amounts of iodine (0.033 g) every hour.

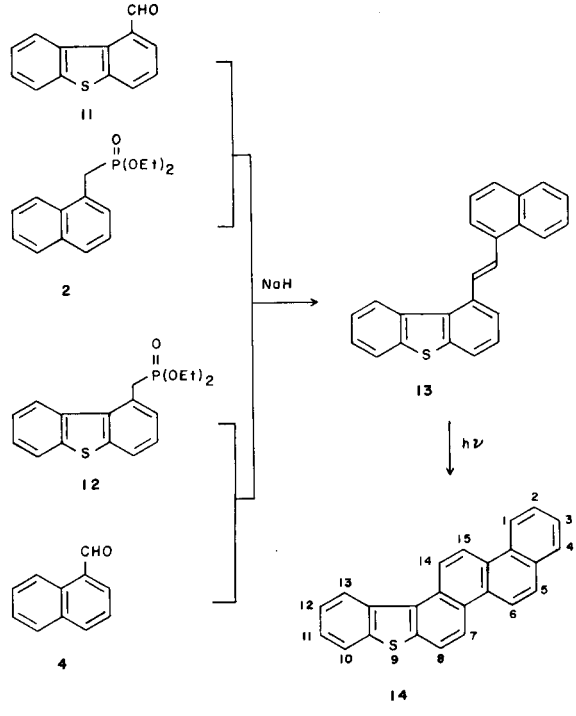
4-[β-(2-Naphthyl)vinyl]dibenzothiophene (**9**) was obtained under Wadsworth-Emmons conditions from the condensation of dibenzothiophene-4-carboxaldehyde (**1**) [24] with diethyl 2-naphthylmethylphosphonate (**7**) [25] in 83% yield and also from the condensation of diethyl 4-dibenzothenylphosphonate (**3**) [21] with naphthalene-2-carboxalde-

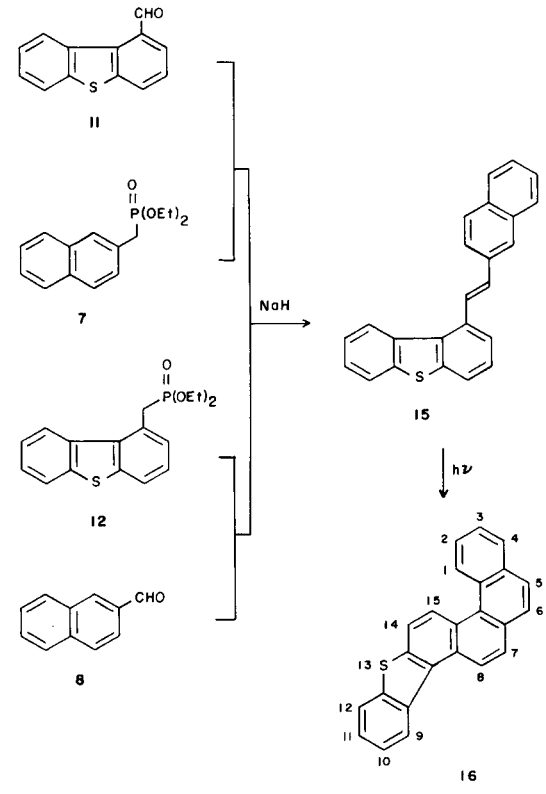
hyde (**8**) in 75% yield. Photocyclizing the pale yellow prisms **9** afforded phenanthro[4,3-*c*]dibenzothiophene (**10**) as colorless plates in 75% yield (Scheme I).

When diethyl 1-naphthylmethylphosphonate (**2**) [25] was allowed to react at room temperature for four hours with dibenzothiophene-1-carboxaldehyde (**11**) [22], 1-[β-(1-naphthyl)vinyl]dibenzothiophene (**13**) was isolated from the reaction mixture in 78% yield. The pale yellow crystals of **13** can also be obtained in better yield (83%) from the condensation of diethyl 1-dibenzothenylphosphonate (**12**) [21] with naphthalene-1-carboxaldehyde (**4**). Upon photocyclization, compound **13** gave phenanthro[2,1-*a*]dibenzothiophene (**14**) as silver flakes in 83% yield.

Phenanthro[3,4-*a*]dibenzothiophene (**16**) was obtained in two steps from dibenzothiophene-1-carboxaldehyde (**11**) [22] and also in two steps from diethyl 1-dibenzothenylphosphonate (**12**) [21]. When **11** [22] was allowed to react at room temperature with diethyl 2-naphthylmethylphosphonate (**7**) [25] or alternatively when **12** [20] was allowed to react with naphthalene-2-carboxaldehyde (**8**), 1-[β-(2-naphthyl)vinyl]dibenzothiophene (**15**) was isolated from these two separate reaction mixtures in 61% and 75% yield, respectively. By irradiation with a 450 watt Hanovia medium pressure mercury lamp compound **15** gave phenanthro[3,4-*a*]dibenzothiophene (**16**) in 52% yield as colorless needles (Scheme II).

Scheme II



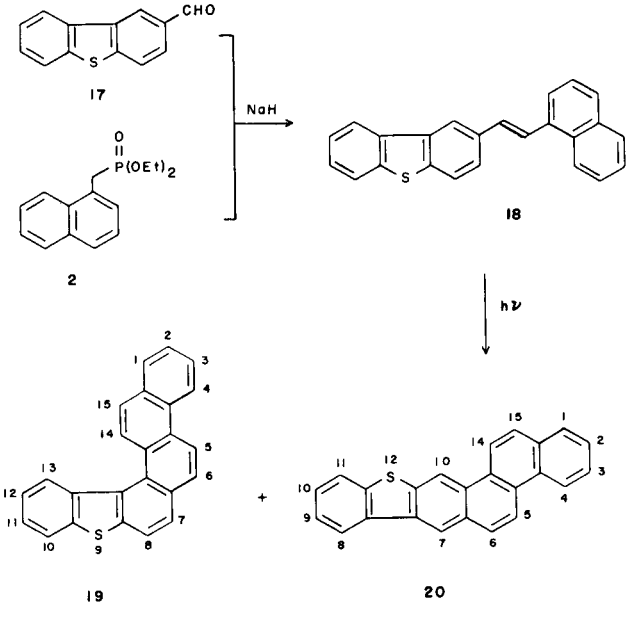


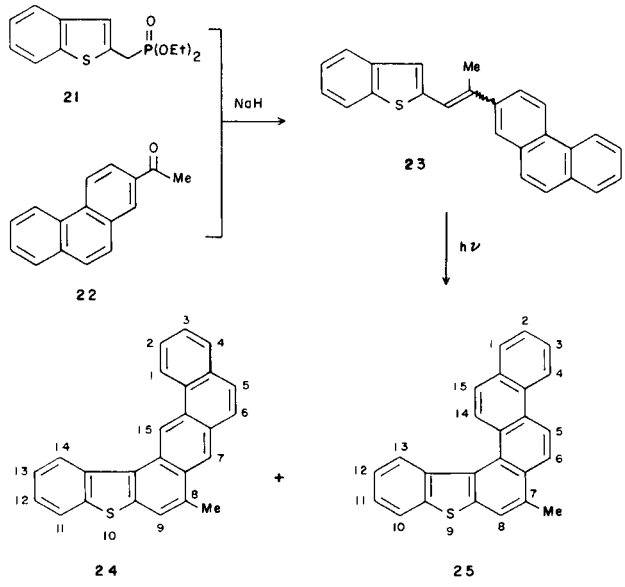
The Wadsworth-Emmons condensation between dibenzothiophene-2-carboxaldehyde (**17**) [26] and diethyl 1-naphthylmethylphosphonate (**2**) [25] afforded 2-[β-(1-naphthyl)vinyl]dibenzothiophene (**18**) in 83% yield. Photocyclization of **18** gave two chromatographically separable products. These are phenanthro[1,2-*a*]dibenzothiophene (**19**) and phenanthro[2,1-*b*]dibenzothiophene (**20**). Pure phenanthro[1,2-*a*]dibenzothiophene (**19**) eluted first with hexane as the eluent on a neutral alumina column. Compound **19** was obtained as colorless needles in 33% yield. Subsequent elution with benzene:hexane (3:1) gave pure phenanthro[2,1-*b*]dibenzothiophene (**20**) as pale yellow flakes in 23% yield. The structural assignment between **19** and **20** was based on nmr, melting point and solubility. The nmr spectra of phenanthro[1,2-*a*]dibenzothiophene (**19**) was similar to the aromatic region spectra of 7-methylphenanthro[1,2-*a*]dibenzothiophene (**25**) obtained from compound **23**. The nmr of compound **20** shows a singlet at δ 9.95 ppm due to the H-13 proton, the furthest downfield proton since it is in a bay region position. There is no singlet in the aromatic region of the nmr spectrum of **19**. Phenanthro[1,2-*a*]dibenzothiophene (**19**) is more angular than phenanthro[2,1-*b*]dibenzothiophene (**20**), therefore, **19** (mp 181°) should have a lower melting point and a greater solubility than compound **20** (mp 326°). Compound **20** eluted last and was much more insoluble in organic solvents than **19**. These data support the structural assignments given **19** and **20**.

When diethyl 2-benzo[*b*]thenylphosphonate (**21**) [13] was allowed to react with 2-acetylphenanthrene (**22**) at room temperature using sodium hydride as the base and 1,2-dimethoxyethane as the solvent, it gave 2-[β-methyl-β-(2-phenanthryl)vinyl]benzo[*b*]thiophene (**23**) in 52% yield as pale yellow crystals.

Compound **23** was a mixture of *E* and *Z* isomers, both of which can be photocyclized because of the photochemically initiated equilibrium between the *E* and *Z* isomers [27]. There are two methyl peak signals in the nmr of compound **23**: one at δ 2.62 ppm and the second peak at δ 2.30 ppm. From the integration of the methyl resonances, the ratio of *E* to *Z* was 1:1. Photocyclization of **23** gave a mixture of 8-methylphenanthro[3,2-*a*]dibenzothiophene (**24**) and 7-methylphenanthro[1,2-*a*]dibenzothiophene (**25**). The mixture of **24** and **25** was separated by chromatography on a neutral alumina column using hexane and cyclohexane as the eluents. Compound **25** eluted first in pure hexane. Further elution with hexane gave the second fraction which consisted of a mixture of **24** and **25**. Elution with cyclohexane gave the third fraction, which was pure 8-methylphenanthro[3,2-*a*]dibenzothiophene (**24**). A second column chromatography (basic alumina) was used to separate the second fraction. Pure *n*-pentane was used as the eluent which afforded pure **25** as the first fraction followed by pure **24** as the second fraction. The total yield from the two columns for 8-methylphenanthro[3,2-*a*]dibenzothiophene (**24**) was 31% and for 7-methylphenanthro[1,2-*a*]dibenzothiophene (**25**) was 34% (Scheme III).

Scheme III

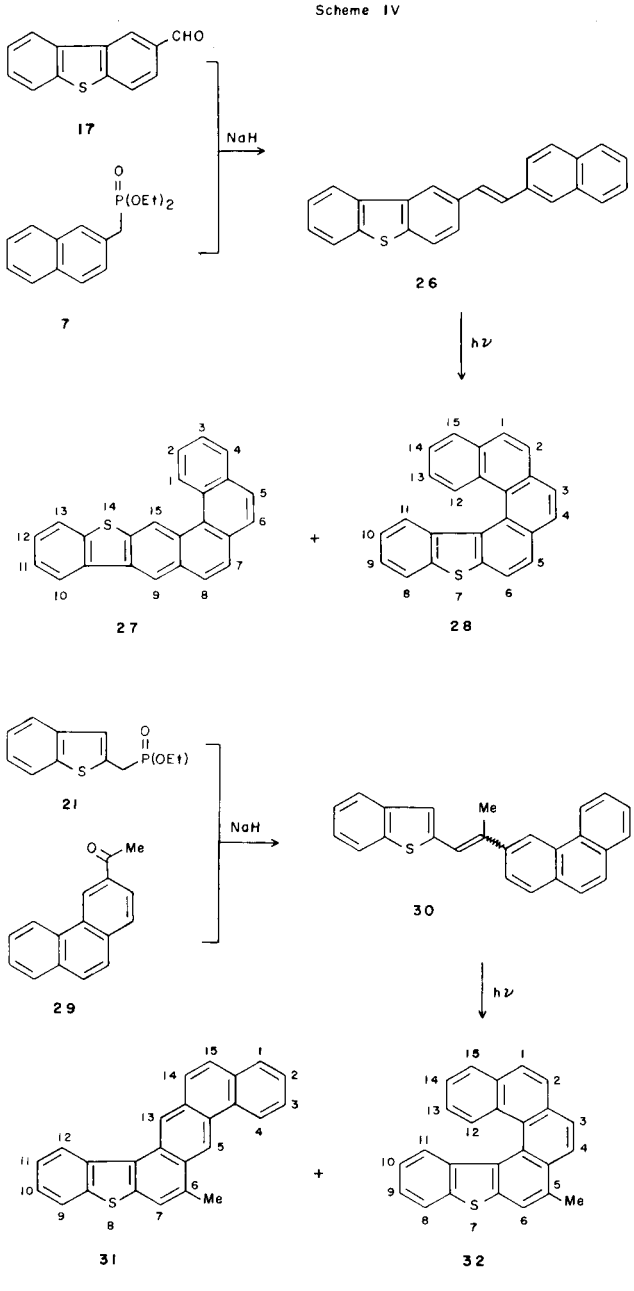




The parent compound, phenanthro[1,2-*a*]dibenzothiophene (**19**), which was previously synthesized from compound **18** helped us to identify 7-methylphenanthro[1,2-*a*]-dibenzothiophene (**25**) from the photocyclization products of **23**. Further evidence confirms our structural assignments. The nmr spectrum of **24** shows two singlets in the aromatic region, one at δ 8.47 due to H-7 and a second peak at δ 10.21 due to H-15. Compound **25** does not exhibit a singlet in the aromatic region of its nmr spectrum. The second compound **24** (mp 244°), from the column is slightly more linear than **25** (mp 222°), therefore **24** should have a higher melting point and a lower solubility than **25**. Compound **24** eluted last on both the neutral and basic alumina columns.

The reaction of dibenzothiophene-2-carboxaldehyde (**17**) [26] with diethyl 2-naphthylmethylphosphonate (**7**) [25] gave 2-[β-(2-naphthyl)vinyl]dibenzothiophene (**26**) in 80% yield as pale yellow flakes. Photocyclization of compound **26** gave a mixture of phenanthro[3,4-*b*]dibenzothiophene (**27**) and phenanthro[4,3-*a*]dibenzothiophene (**28**). The mixture was separated on a basic alumina column using hexane and benzene as the eluents. Phenanthro[4,3-*a*]dibenzothiophene (**28**) eluted first in pure hexane as colorless flakes in 25% yield. Elution with hexane:benzene (1:3) afforded phenanthro[3,4-*b*]dibenzothiophene (**27**) as colorless prisms in 19% yield. The best evidence for the structural assignment of **27** and **28** is the nmr spectra. The nmr spectrum of phenanthro[4,3-*a*]dibenzothiophene (**28**) was similar to the aromatic region of the nmr spectra of 9-methylphenanthro[4,3-*a*]dibenzothiophene (**32**). The nmr spectrum of compound **27** has two singlets, one at δ 8.66 due to H-9 and a second singlet at δ 9.56 due to H-15. The nmr spectrum of compound **28** does not exhibit a singlet [28]. Additionally **27** (mp 256°), being more linear

Scheme IV



than compound **28**, should have a higher melting point and a lower solubility than phenanthro[4,3-*a*]dibenzothiophene (**28**) (mp 198°).

2-[β-Methyl-β-(3-phenanthryl)vinyl]benzo[*b*]thiophene (**30**) was obtained in 63% yield as colorless crystals from the reaction of diethyl 2-benzo[*b*]thenylphosphonate (**21**) [13] with 3-acetylphenanthrene (**29**). Compound **30** was a mixture of *E* and *Z* isomers. There are two methyl signals in the nmr spectrum of **30**, one at δ 2.67 due to the *E* isomer and the second at δ 2.42 due to the *Z* isomer. The methyl signal of the *E* isomer is further downfield than the *Z* isomer due to the interaction with the H-3 proton of the thiophene ring. From the nmr peak areas, the ratio of *E* to *Z* was 2:1. When **30** was photocyclized, a mixture of two products was obtained from the reaction namely, 6-methylphenanthro[2,3-*a*]dibenzothiophene (**31**) and 5-methylphenanthro[4,3-*a*]dibenzothiophene (**32**) (Scheme IV). Compounds **31** and **32** were separated by neutral alumina column chromatography using hexane and benzene as the eluents. 5-Methylphenanthro[4,3-*a*]dibenzothiophene (**32**) eluted first in pure hexane as colorless needles in 30% yield. Elution with hexane:benzene (2:1) afforded 6-methylphenanthro[2,3-*a*]dibenzothiophene (**31**) as fluorescent yellow flakes in 38% yield. The 60 MHz nmr spectrum of **31** has a downfield singlet at δ 9.35 due to H-13 which readily distinguishes **31** from **32**. Furthermore the 60 MHz nmr spectrum of **32** is very similar to the high resolution spectrum (300 MHz) of **28** recently published [28] except for the methyl peak in the spectrum of **32** at δ 2.80. Thus there is no doubt about the correct structural assignments of **31** and **32**.

Some of the phenanthrodibenzothiophenes and the monomethyl derivatives are being screened against TA-98 and TA-100 in the Ames test (S9 liver homogenate activation) and these results will be published elsewhere.

EXPERIMENTAL

Melting points were determined in open capillary tubes on a Thomas-Hoover capillary melting point apparatus and are uncorrected. The proton magnetic resonance spectra (^{1}H-nmr) of all compounds were obtained on a Varian EM-360-A spectrometer in the solvents as indicated and were obtained by a simple sweep of the entire spectrum. Chemical shifts are reported in ppm from TMS as an internal standard and are given in δ units. Mass spectra were obtained on a Hewlett-Packard model 5980A mass spectrometer. The spectra were run using electron impact ionization. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona.

4-[β-(1-Naphthyl)vinyl]dibenzothiophene (**5**). Method A.

Sodium hydride (50% dispersion in mineral oil, 0.62 g, 0.027 mole) was washed twice with hexane (60 ml) and then placed in dry 1,2-dimethoxyethane (100 ml). The slurry was cooled to 20° and diethyl 1-naphthylmethylphosphonate (**2**) (1.84 g, 0.0066 mole) [25] was added with stirring under a stream of dry nitrogen. After the addition, the solution was stirred at room temperature for 15 minutes. To the yellow solution maintained below 25°, dibenzothiophene-4-carboxaldehyde (**1**) (1.4 g, 0.0066 mole) [24] was slowly added. The solution was stirred at room temperature for four hours. The reaction mixture was slowly poured in a large excess of ice-water under a stream of dry nitrogen and the resulting precipitate was collected by filtration. The product was recrystallized from ethanol affording fluorescent yellow flakes in 60% yield (1.33 g), mp 181-182°.

Method B.

This compound was synthesized under Wadsworth-Emmons conditions from diethyl 4-dibenzothenylphosphonate (**3**) (0.5 g, 0.0015 mole) [21] and naphthalene-1-carboxaldehyde (**4**) (0.23 g, 0.0015 mole) in a similar manner to the preparation described under Method A affording fluorescent yellow flakes in 64% yield (0.323 g), mp 181-182°; nmr (deuteriochloroform): δ 7.24-8.33 (m, ethenyl-H and aromatic-H, 16H); ms: m/e 336 (M^+, 100).

Anal. Calcd. for $C_{24}H_{16}S$: C, 85.68; H, 4.79; S, 9.53. Found: C, 85.71; H, 4.84; S, 9.48.

Phenanthro[1,2-*c*]dibenzothiophene (**6**).

A solution of 4-[β-(1-naphthyl)vinyl]dibenzothiophene (**5**) (1.0 g, 0.003 mole) and iodine (0.10 g) in dry benzene (360 ml) was irradiated for four hours with a 450 watt Hanovia medium pressure mercury lamp. To maximize the yields the whole amount of iodine was not added to the photocyclization vessel at once, but rather was added in small amounts (0.033 g) every hour. During the course of the reaction a slow stream of air was passed through the solution. The solvent was evaporated *in vacuo* and the residue (dark oil) was chromatographed on a neutral alumina column using hexane:benzene (3:1) as the eluent affording colorless flakes in 52% yield (0.72 g, 0.0021 mole), mp 202-203°; nmr (deuteriobenzene): δ 7.31-8.65 (m, 14H, Ar*H*); ms: m/e 334 (M^+, 100).

Anal. Calcd. for $C_{24}H_{14}S$: C, 86.19; H, 4.22; S, 9.59. Found: C, 86.23; H, 4.34; S, 9.75.

4-[β-(2-Naphthyl)vinyl]dibenzothiophene (**9**). Method A.

Compound **9** was synthesized from the condensation of diethyl 2-naphthylmethylphosphonate (**7**) (3.1 g, 0.011 mole) [25] and dibenzothiophene-4-carboxaldehyde (**1**) (2.36 g, 0.011 mole) [24] in a manner similar to the synthesis of compound **5**. An analytical sample was recrystallized from benzene:hexane (1:2) affording pale yellow prisms in 83% yield (3.07 g, 0.0091 mole), mp 163-164°.

Method B.

Compound **9** was prepared from diethyl 4-dibenzothenylphosphonate (**3**) (0.5 g, 0.0015 mole) [21] and naphthalene-2-carboxaldehyde (**8**) (0.23 g, 0.0015 mole) in a similar manner to the preparation of compound **5** and pale yellow prisms were obtained in 75% yield (0.38 g, 0.0011 mole), mp 163-164°; nmr (deuteriochloroform): δ 7.25-8.29 (m, 2 × ethenyl-H and aromatic-H, 16H); ms: m/e 336 (M^+, 100).

Anal. Calcd. for $C_{24}H_{16}S$: C, 85.68; H, 4.79; S, 9.53. Found: C, 85.59; H, 4.75; S, 9.60.

Phenanthro[4,3-*c*]dibenzothiophene (**10**).

Compound **10** was prepared from the photocyclization of 4-[β-(2-naphthyl)vinyl]dibenzothiophene (**9**) (1.1 g, 0.0033 mole) and iodine (0.10 g) in a synthetic procedure similar to that employed in the preparation of compound **6**. After neutral alumina column chromatography using hexane:benzene (3:1) as the eluent, colorless plates were obtained in 75% yield (0.83 g, 0.0025 mole), mp 234-235°; nmr (deuteriochloroform): δ 7.33-8.42 (m, H-1, H-2, H-3, H-4, H-5, H-6, H-7, H-10, H-11, H-12, H-13, H-14, 12H, Ar*H*), 8.90-9.25 (m, H-8, H-9, 2H, Ar*H*); ms: m/e 334 (M^+, 100).

Anal. Calcd. for $C_{24}H_{14}S$: C, 86.19; H, 4.22; S, 9.59. Found: C, 86.06; H, 4.15; S, 9.67.

1-[β-(1-Naphthyl)vinyl]dibenzothiophene (**13**). Method A.

Compound **13** was prepared from the condensation of diethyl 1-naphthylmethylphosphonate (**2**) (1.1 g, 0.004 mole) [25] with dibenzothiophene-1-carboxaldehyde (**11**) (0.84 g, 0.004 mole) [22] in a manner similar to the condensation of compound **5**. Purification was accomplished on a silica gel column using hexane as the eluent affording pale yellow crystals in 78% yield (1.04 g, 0.0031 mole), mp 130-131°.

Method B.

1-[β-(1-Naphthyl)vinyl]dibenzothiophene (**13**) was synthesized from diethyl 1-dibenzothenylphosphonate (**12**) (0.65 g, 0.0019 mole) [21] and naphthalene-1-carboxaldehyde (**4**) (0.30 g, 0.0019 mole) in a manner similar to the preparation of 4-[β-(1-naphthyl)vinyl]dibenzothiophene (**5**) affording pale yellow crystals in 83% yield (0.53 g, 0.0016 mole), mp 130-131°; nmr (deuteriochloroform): δ 7.14-7.87 (m, 2 × ethenyl-H, aromatic-H of naphthalene, H-2, H-3, H-7, H-8 of dibenzothiophene, 13H), 8.00-8.32 (m, H-4, H-6 of dibenzothiophene, 2H, Ar*H*), 8.52 (d, J = 6 Hz, H-9 of dibenzothiophene); ms: m/e 336 (M^+, 100).

Anal. Calcd. for $C_{24}H_{16}S$: C, 85.68; H, 4.79; S, 9.53. Found: C, 85.71; H, 4.79; S, 9.46.

Phenanthro[2,1-*a*]dibenzothiophene (**14**).

Photocyclization of **13** (1.1 g, 0.0033 mole) for four hours in a manner similar to the preparation of **6** gave a dark residue which was chromatographed on a neutral alumina column using hexane:benzene (1:1) as the eluent affording silver flakes in 83% yield (0.91 g, 0.0027 mole), mp 287-288°; nmr (deuteriochloroform): δ 7.21-8.28 (m, H-2, H-3, H-4, H-5, H-8, H-10, H-11, H-12, 8H, Ar*H*), 8.58-9.52 (m, H-1, H-6, H-7, H-13, H-14, H-15, 6H, Ar*H*); ms: m/e 334 (M^+, 100).

Anal. Calcd. for $C_{24}H_{14}S$: C, 86.19; H, 4.22; S, 9.59. Found: C, 86.25; H, 4.13; S, 9.41.

1-[β-(2-Naphthyl)vinyl]dibenzothiophene (**15**). Method A.

This compound was prepared from diethyl 2-naphthylmethylphosphonate (**7**) (0.92 g, 0.0033 mole) [25] and dibenzothiophene-1-carboxaldehyde (**11**) (0.7 g, 0.0033 mole) [22] in a similar manner to the preparation of **5**. Purification was accomplished on a neutral alumina column using cyclohexane as the eluent affording fluorescent pale yellow prisms in 61% yield (0.68 g, 0.002 mole), mp 102-103°.

Method B.

Compound **15** was synthesized from diethyl 1-dibenzothenylphosphonate (**12**) (2.2 g, 0.0066 mole) [21] and naphthalene-2-carboxaldehyde (**8**) (1.03 g, 0.0066 mole) in a manner similar to the preparation of **5** affording fluorescent pale yellow prisms in 75% yield (1.66 g, 0.005 mole), mp 102-103°; nmr (deuteriochloroform): δ 7.17-7.97 (m, 2 × ethenyl-H, aromatic-H of naphthalene, H-2, H-3, H-7, H-8, of dibenzothiophene, 13H), 8.02-8.36 (m, H-4, H-6 of dibenzothiophene, 2H, Ar*H*), 8.44-8.70 (m, H-9 of dibenzothiophene, 1H, Ar*H*); ms: m/e 336 (M^+, 100).

Anal. Calcd. for $C_{24}H_{16}S$: C, 85.68; H, 4.79; S, 9.53. Found; C, 85.60; H, 4.88; S, 9.41.

Phenanthro[3,4-*a*]dibenzothiophene (**16**).

Phenanthro[3,4-*a*]dibenzothiophene (**16**) was prepared from the photocyclization of **15** (1.0 g, 0.003 mole) in a manner similar to the preparation of **6**. An analytical sample was prepared by chromatography on a neutral alumina column using hexane:benzene (2:1) as the eluent affording colorless needles in 52% yield (0.52 g, 0.0016 mole), mp 173-174°; nmr (deuteriobenzene): δ 7.32-8.29 (m, H-2, H-3, H-4, H-5, H-6, H-7, H-10, H-12, H-13, H-14, 10H, Ar*H*), 8.53-9.28 (m, H-1, H-8, H-9, H-15, 4H, Ar*H*); ms: m/e 334 (M^+, 100).

Anal. Calcd. for $C_{24}H_{14}S$: C, 86.19; H, 4.22; S, 9.59. Found: C, 85.98; H, 4.38; S, 9.38.

2-[β-(1-Naphthyl)vinyl]dibenzothiophene (**18**).

This compound was synthesized from the condensation of dibenzothiophene-2-carboxaldehyde (**17**) (3.0 g, 0.014 mole) [26] with diethyl 1-naphthylmethylphosphonate (**2**) (3.9 g, 0.014 mole) [25] in a similar manner to the preparation of **5**. An analytical sample was recrystallized from hexane:benzene (1:1) affording pale yellow crystals in 83% yield (3.91 g, 0.012 mole), mp 155-156°; nmr (deuteriochloroform): δ 7.23-8.61 (m, 16H, Ar*H*); ms: m/e 336 (M^+, 100).

Anal. Calcd. for $C_{24}H_{16}S$: C, 85.68; H, 4.79; S, 9.53. Found: C, 85.81; H, 4.90; S, 9.79.

Phenanthro[1,2-*a*]dibenzothiophene (**19**) and Phenanthro[2,1-*b*]dibenzothiophene (**20**).

When **18** (1.3 g, 0.0039 mole) was photocyclized in a manner similar to the preparation of **6**, a chromatographically separable mixture was obtained, namely phenanthro[1,2-*a*]dibenzothiophene (**19**) and phenanthro[2,1-*b*]dibenzothiophene (**20**). Separation was achieved *via* neutral alumina column chromatography using hexane and benzene as the eluents. Compound **19** eluted first in pure hexane and it was obtained as colorless needles in 33% yield (0.43 g, 0.0013 mole). Compound **20** eluted in benzene:hexane (3:1) as pale yellow flakes in 23% yield (0.30 g, 0.0009 mole).

Compound **19**.

The colorless needles **19** had mp 181-182°; nmr (deuteriochloroform): δ 7.20-8.29 (m, H-1, H-2, H-3, H-6, H-7, H-8, H-10, H-11, H-12, H-15, 10H, Ar*H*), 8.50-9.06 (m, H-4, H-5, H-13, H-14, 4H, Ar*H*); ms: m/e 336 (M^+, 100).

Anal. Calcd. for $C_{24}H_{14}S$: C, 86.19; H, 4.22; S, 9.59. Found: C, 85.93; H, 4.38; S, 9.41.

Compound **20**.

The pale yellow flakes of **20** had mp 326-327°; nmr (deuteriochloroform): δ 7.34-8.28 (m, H-2, H-3, H-4, H-5, H-8, H-9, H-10, H-11, H-12, H-13, 10H, Ar*H*), 8.81-9.40 (m, H-1, H-6, H-7, 3H, Ar*H*), 9.95 (s, H-15, 1H, Ar*H*); ms: m/e 336 (M^+, 100).

Anal. Calcd. for $C_{24}H_{16}S$: C, 86.19; H, 4.22; S, 9.59. Found: C, 86.24; H, 4.03; S, 9.68.

2-[β-Methyl-β-(2-phenanthryl)vinyl]benzo[*b*]thiophene (**23**).

Compound **23** was prepared from diethyl 2-benzo[*b*]thenylphosphonate (**21**) (2.5 g, 0.0088 mole) [13] and 2-acetylphenanthrene (**22**) (1.94 g, 0.0088 mole) in a similar manner to the preparation of **5** affording the crude product. Purification was accomplished on a neutral alumina column using benzene:hexane (1:1) as the eluent giving pale yellow crystals in 52% yield (1.6 g, 0.0046 mole), mp 172-173°; nmr (deuteriochloroform): δ 2.30 (s, C*H*$_3$ for *Z* isomer, 3H), 2.62 (s, C*H*$_3$ for *E* isomer, 3H), 6.88-8.28 (m, ethenyl-H, aromatic-H of benzo[*b*]thiophene, H-1, H-3, H-6, H-7, H-8, H-9, H-10 of phenanthrene, 14H), 8.51-8.84 (m, H-4, H-5 of phenanthrene, 2H, Ar*H*); ms: m/e 350 (M^+, 100).

Anal. Calcd. for $C_{25}H_{18}S$: C, 85.67; H, 5.18; S, 9.15. Found: C, 85.73; H, 5.09; S, 9.27.

8-Methylphenanthro[3,2-*a*]dibenzothiophene (**24**) and 7-Methylphenanthro[1,2-*a*]dibenzothiophene (**25**).

The chromatographically separable mixture of **24** and **25** was prepared from **23** (1.3 g, 0.0037 mole) in a manner similar to the preparation of **6**. The dark residue was chromatographed on a neutral alumina column using hexane and cyclohexane as the eluents. Compound **25** eluted first in hexane. The second fraction consisted of a mixture of **24** and **25** upon continued elution with hexane. Upon elution with cyclohexane **24** was obtained. The second fraction was separated by a second column chromatography (basic alumina). Compound **25** again eluted first in pentane in pure form, followed by pure **24**. The total yield from both columns for **24** was 31% (0.4 g, 0.0011 mole) and for **25** was 34% (0.44 g, 0.0013 mole).

Compound **24**.

This compound eluted last and it was obtained as colorless crystals, mp 244°; nmr (deuteriochloroform): δ 2.85 (s, C*H*$_3$, 3H), 7.35-8.12 (m, H-2, H-3, H-4, H-5, H-6, H-9, H-11, H-12, H-13, 9H, Ar*H*), 8.47 (s, H-7, 1H, Ar*H*), 8.78-9.15 (m, H-1, H-14, 2H, Ar*H*), 10.21 (s, H-15, 1H, Ar*H*); ms: m/e 348 (M^+, 100).

Anal. Calcd. for $C_{25}H_{16}S$: C, 86.17; H, 4.63; S, 9.20. Found: C, 85.96; H, 4.41; S, 9.42.

Compound **25**.

This compound eluted first and it was obtained as colorless needles, mp 222°; nmr (deuteriochloroform): δ 2.91 (s, C*H*$_3$, 3H), 7.20-8.29 (m, H-1, H-2, H-3, H-6, H-8, H-10, H-11, H-12, H-15, 9H, Ar*H*), 8.50-9.06 (m, H-4, H-5, H-13, H-14, 4H, Ar*H*); ms: m/e 348 (M^+, 100).

Anal. Calcd. for $C_{25}H_{16}S$: C, 86.17; H, 4.63; S, 9.20. Found: C, 86.03; H, 4.60; S, 9.38.

2-[β-(2-Naphthyl)vinyl]dibenzothiophene (**26**).

This compound was prepared from the condensation of diethyl 2-naphthylmethylphosphonate (**7**) (4.7 g, 0.017 mole) [25] with dibenzothiophene-2-carboxaldehyde (**17**) 3.6 g, 0.017 mole) [26] in a manner similar to the preparation of **5**. An analytical sample was recrystallized in ethanol affording pale yellow flakes in 80% yield (4.6 g, 0.014 mole), mp 208-209°; nmr (deuteriochloroform): δ 7.19-8.00 (m, 2 × ethenyl-H, aromatic-H of naphthalene, H-3, H-4, H-6, H-7, H-8 of dibenzothiophene, 14H), 8.01-8.35 (m, H-1, H-9 of dibenzothiophene, 2H, Ar*H*); ms: m/e 336 (M^+, 100).

Anal. Calcd. for $C_{24}H_{16}S$: C, 85.68; H, 4.79; S, 9.53. Found: C, 85.73; H, 4.61; S, 9.68.

Phenanthro[3,4-*b*]dibenzothiophene (**27**) and Phenanthro[4,3-*a*]dibenzothiophene (**28**).

Compounds **27** and **28** were obtained from **26** (1.30 g, 0.0039 mole) in a manner similar to the preparation of **6**. The residue was chromatographed on a basic alumina column using hexane and benzene as the eluents. Elution with pure hexane gave **28** in 25% yield (0.33 g, 0.001 mole) as colorless flakes. The second fraction which eluted in hexane:benzene (1:3), gave pure **27** in 19% yield (0.25 g, 0.0007 mole) as colorless prisms.

Compound **27**.

This compound was obtained in 19% yield as colorless prisms, mp 256°; nmr (deuteriochloroform): δ 7.20-8.41 (m, H-2, H-3, H-4, H-5, H-6, H-7, H-8, H-10, H-11, H-12, H-13, 11H, Ar*H*), 8.66 (s, H-9, 1H, Ar*H*), 9.01-9.30 (m, H-1, 1H, Ar*H*), 9.56 (s, H-15, 1H, Ar*H*); ms: m/e 334 (M^+, 100).

Anal. Calcd. for $C_{24}H_{14}S$: C, 86.19; H, 4.22; S, 9.59. Found: C, 86.23; H, 4.36; S, 9.42.

Compound **28**.

The colorless flakes **28** eluted first and it was obtained in 25% yield, mp 197°; nmr (deuteriochloroform): δ 6.86-8.29 (m, H-2, H-3, H-4, H-5, H-6, H-7, H-8, H-9, H-10, H-12, H-13, H-14, H-15, 13H, Ar*H*), 8.62-8.82 (m, H-1, 1H, Ar*H*); ms: m/e 334 (M^+, 100).

Anal. Calcd. for $C_{24}H_{14}S$: C, 86.19; H, 4.22; S, 9.59. Found: C, 86.30: H, 4.41; S, 9.40.

2-[β-Methyl-β-(3-phenanthryl)vinyl]benzo[*b*]thiophene (**30**).

Compound **30** was prepared under Wadsworth-Emmons conditions from diethyl 2-benzo[*b*]thenylphosphonate (**21**) (2.5 g, 0.0088 mole) [13] and 3-acetylphenanthrene (**29**) (1.9 g, 0.0088 mole) in a manner similar to the preparation of **5** and red crystals were obtained. Purification was accomplished on a neutral alumina column using hexane:benzene (1:1) as the eluent affording colorless crystals in 63% yield (1.9 g, 0.0055 mole), mp 136-137°; nmr (deuteriochloroform): δ 2.42 (s, C*H*$_3$ of *Z* isomer, ⅓ × 3H), 2.67 (s, C*H*$_3$ of *E* isomer, ⅔ × 3H), 6.92-8.21 (m, ethenyl-H, aromatic-H of benzo[*b*]thiophene, H-1, H-2, H-6, H-7, H-8, H-9, H-10 of phenanthrene, 13H), 8.48-8.98 (m, H-4, H-5 of phenanthrene, 2H, Ar*H*); ms: m/e 350 (M^+, 100).

Anal. Calcd. for $C_{25}H_{18}S$: C, 85.67; H, 5.18; S, 9.15. Found: C, 85.83; H, 5.31; S, 9.30.

6-Methylphenanthro[2,3-*a*]dibenzothiophene (**31**) and 5-Methylphenanthro[4,3-*a*]dibenzothiophene (**32**).

Compounds **31** and **32** were obtained from the photocyclization of **30** (1.2 g, 0.0034 mole) in a manner similar to the preparation of **6**. Separation of the mixture was accomplished on a neutral column using hexane and benzene as the eluents. Compound **32** eluted first in pure hexane in 30% yield (0.34 g, 0.001 mole) as colorless needles. Upon elution with hexane:benzene (2:1) **31** was obtained as fluorescent yellow flakes in 38% yield (0.45 g, 0.0013 mole).

Compound **31**.

Compound **31** was obtained as fluorescent yellow flakes, mp 236°; nmr (deuteriochloroform): δ 7.30-8.30 (m, H-1, H-2, H-3, H-4, H-5, H-9, H-11, H-12, H-13, H-14, 10H, Ar*H*), 8.68-9.13 (m, H-6, H-7, 2H, Ar*H*), 9.35 (s, H-15, 1H, Ar*H*); ms: m/e 348 (M^+, 100).

Anal. Calcd. for $C_{25}H_{16}S$: C, 86.17; H, 4.63; S, 9.20. Found: C, 86.35; H, 4.81; S, 9.47.

Compound **32**.

This compound was obtained as colorless needles, mp 230°; nmr (deuteriochloroform): δ 2.80 (s, C*H*$_3$, 3H), 6.86-8.29 (m, H-2, H-3, H-4, H-5, H-6, H-7, H-8, H-10, H-12, H-13, H-14, H-15, 13H, Ar*H*), 8.53-8.79 (m, H-1, 1H, Ar*H*); ms: m/e 348 (M^+, 100).

Anal. Calcd. for $C_{25}H_{16}S$: C, 86.17; H, 4.63; S, 9.20. Found: C, 86.21; H, 4.72; S, 9.03.

Acknowledgement.

This study was supported by the U. S. Department of Energy, Office of Health and Environmental Research, Contract No. DE-AC0279EV10237.

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