K-Region Oxides and Imines of Benzo[*b*]phenanthro[2,3-*d*]thiophene and Benzo[*b*]phenanthro[3,2-*d*]thiophene

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The syntheses of the K-oxides and K-imine derivatives of benzo[*b*]phenanthro[2,3-*d*]thiophene and benzo[*b*]phenanthro[3,2-*d*]thiophene are described. The parent hydrocarbons **1** and **2** were oxidized with osmium tetroxide and sodium metaperiodate, and the dialdehydes **12** and **18** so formed, cyclized to the corresponding epoxides 1a,12b-dihydrobenz[*b*]oxireno[9,10]phenanthro[2,3-*d*]thiophene (**7**) and 1a,12b-dihydrobenz[*b*]oxireno[9,10]phenanthro[3,2-*d*]thiophene (**13**). Reaction of the oxiranes with sodium azide gave mixtures of azido-alcohols that, in turn, were transformed to the thiaarene imines 1a,12b-dihydro-1*H*-benz[*b*]azirino[9,10]phenanthro[2,3-*d*]thiophene (**8**) and 1a,12b-dihydro-1*H*-benz[*b*]azirino[9,10]phenanthro[3,2-*d*]thiophene (**14**), respectively, with the aid of tri-*n*-butylphosphine.

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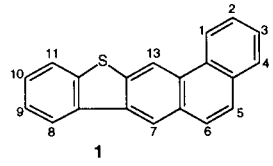
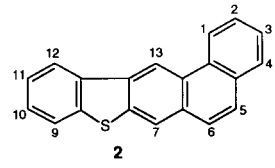
Many polycyclic thiaarenes are known to be widespread environmental pollutants and to have mutagenic and carcinogenic properties [1]. However, in contrast to the vast amount of research published on metabolic activation of carbocyclic polyarenes [2], only a few papers have been reported on the metabolism of the sulfur containing carcinogens [3]. Some thiaarenes have been found to form *in vivo* sulfoxides, sulfones and some hydroxylated compounds [3,4] but the possibility of metabolic transformation of the parent heterocycles into epoixdes and aziridines have not been investigated. Therefore, we found it imperative to prepare suitable standards for such studies.

In this paper we report the syntheses of the K-region oxides and imines of the carcinogenic benzo[*b*]phenanthro[2,3-*d*]- and benzo[*b*]phenanthro[3,2-*d*]thiophene (**1** and **2**) [5]. These nitrogen containing compounds are the first imine derivatives of biologically active polycyclic thiaarenes [6].

The parent thiaarenes **1** and **2** were prepared from benzo[*b*]thiophene and 1- and 2-naphthaldehyde, respectively, by the procedure of Tedjamulia *et al* [8] except that the amounts of chloromethyl methyl ether in the cyclization step of 2-(1-naphthylmethyl)- and of 2-(2-naphthylmethyl)-benzo[*b*]thiophene (**3** and **4**) were reduced. When the reported molar ratio of **3** (or **4**): stannic tetrachloride:ether of 1:2.6:2.6 was employed the main products were the isomeric 5- (or 6-) benzo[*b*]phenanthro[2,3-*d*]- and benzo[*b*]-phenanthro[3,2-*d*]thiophenecarboxaldehyde (**5** and **6**), respectively, as evidence by their ir, nmr and ms spectra. The aldehydes could be converted into the expected thiaarenes **1** and **2** by chlorotris(triphenylphosphine)rhodium-catalyzed decarbonylation at 260° [9]. The optimum ratio of **3**:stannic chloride:ether, by which aldehyde-free **1** could be obtained, was 1:2.6:1. The best yield of **2** was achieved when the corresponding molar ratio of the reactants was 1:2.4:1.1. The mps of the analytical samples of **1** and **2** formed by this procedure (242-245° and 186°, respectively) matched those reported by Croisy *et al* [5] rather than the very different ones found in earlier studies [8,10,11].



1



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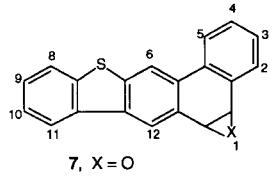

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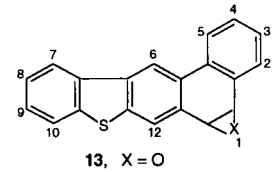
8, X = NH



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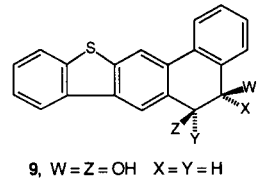
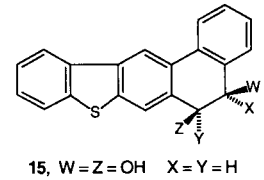
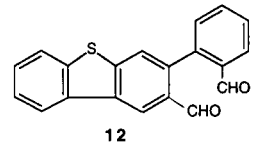
14, X = NH



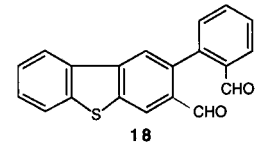
9, W = Z = OH X = Y = H
10, W = OH X = Z = H Y = N_3
11, W = Y = H X = N_3 Z = OH



15, W = Z = OH X = Y = H
16, W = OH X = Z = H Y = N_3
17, W = Y = H X = N_3 Z = OH



12



18

The preparation of 1a,12b-dihydrobenz[*b*]oxireno-[9,10]phenanthro[2,3-*d*]thiophene (**7**) was accomplished by osmium tetroxide oxidation of **1** in pyridine followed by treatment of the resulting diol **9** by sodium metaperiodate and cyclization of the dialdehyde **12** with tris(dimethylamino)phosphine. The overall yield of **7** from **1** was 44%. Nucleophilic ring opening of the oxirane moiety by azide ion furnished 83% of a 3:2 mixture of the *trans*-azido-alcohols **10** and **11** that could be cyclized in 38% yield to 1a,12b-dihydro-1*H*-benz[*b*]azirino[9,10]phenanthro[2,3-*d*]thiophene (**8**) upon treatment with tri-*n*-butylphosphine.

By the same sequence of reactions, 1a,12b-dihydrobenz-[*b*]oxireno[9,10]phenanthro[3,2-*d*]thiophene (**13**) was obtained in 35% from **2** *via* diol **15** and dialdehyde **18**. Transformation of **13** into a mixture of *trans*-azido-alcohols **16** and **17** (62% yield) followed by treatment with the phosphine afforded **14** in 32% yield.

EXPERIMENTAL

Benzo[*b*]phenanthro[2,3-*d*]thiophene **1** was prepared in 75% yield from 2-(1-naphthylmethyl)benzo[*b*]thiophene (**3**) as described in the literature [8], except that the ratio of **3**:stannic tetrachloride:chloromethyl methyl ether was 1:2.6:1. Likewise the reported method [8] was used for the preparation of benzo[*b*]-phenanthro[3,2-*d*]thiophene (**2**) from 2-(2-naphthylmethyl)benzo-[*b*]thiophene (**4**) (yield) 77%, but the ratio **4**:stannic tetrachloride: chloromethyl methyl ether was 1:2.4:1.1 and the ether was added portionwise during 16 hours.

cis-5,6-Dihydro-5,6-benzo[*b*]phenanthro[2,3-*d*]thiophenediol (**9**).

A mixture of 4.0 g (14.1 mmoles) of **1**, 7.0 g (27.5 mmoles) of osmium tetroxide and 150 ml of dry pyridine was stirred in the dark under exclusion of air for 10 days. The mixture was then treated for 3 hours with 150 ml of an aqueous 7% bisulfite solution. Addition of 500 ml of cold water furnished 3.0 g (68%) of **9** as light-sensitive colorless crystals. An analytical sample was obtained by chromatography on silica gel with a 4:1 mixture of ether-hexane as eluent, mp 201-202°; ir (nujol): 3280 cm^{-1} (OH); ^1H nmr (deuteriochloroform): 200 MHz δ 4.881 (d, 1H, $J_{5,6}$ = 3.5 Hz, H5 or H6), 4.997 (d, 1H, $J_{5,6}$ = 3.5 Hz, H5 or H6), 7.348-7.468 (m, 4H, H2, H3, H9, H10), 7.610 (d, 1H, $J_{3,4}$ = 7.1 Hz, H4), 7.760-7.894 (m, 2H, H1, H11), 8.187 (m, 1H, H8), 8.240 (s, 1H, H13), 8.383 (s, 1H, H7); ms (70 eV, 170°): m/z (relative intensity) 318 ($M^{+\cdot}$, 100), 301 ($C_{20}H_{13}OS^+$, 85), 287 ($C_{19}H_{12}OS^{+\cdot}$, 41), 284 ($C_{20}H_{12}S^{+\cdot}$, 5), 272 ($C_{19}H_{12}S^{+\cdot}$, 27), 271 ($C_{19}H_{11}S^+$, 74), 258 ($C_{18}H_{10}S^{+\cdot}$, 18).

Anal. Calcd. for $C_{20}H_{14}O_2S$: C, 75.45; H, 4.43; S, 10.07. Found: C, 75.15; H, 4.52; S, 9.80.

3-(2-Formylphenyl)-2-dibenzothiophenecarboxaldehyde (**12**).

To a mixture of 2.5 g (7.9 mmoles) of **9** in 250 ml of methanol was added a solution of 1.8 g (8.4 mmoles), of sodium metaperiodate in 60 ml water. The mixture was stirred under nitrogen at room temperature for 5 hours. The methanol was removed under reduced pressure and the residue extracted with dichloromethane. After the usual workup, the crude dialdehyde was chromatographed on silica gel using a mixture of 90% hexane and 10% ether as eluent. There was obtained 1.8 g (73%) of **12** as colorless crystals, mp 138°; ir (nujol): 1665 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): 200 MHz δ 7.409-7.735 (m, 5H, H4', H5', H6', H7, H8), 7.797 (s, 1H, H4), 7.895-7.909 (m, 1H, H6), 8.080 (dd, 1H, $J_{3',4'}$ = 7.4 Hz, $J_{3',5'}$ = 1.5 Hz, H3'), 8.272-8.318 (m, 1H, H9), 8.819 (s, 1H, H1), 9.878 (s, 1H, C*H*O), 9.905 (s, 1H, C*H*O); ms (70 eV, 110°): m/z (relative intensity) 316 ($M^{+\cdot}$, 26), 288 ($C_{19}H_{10}OS^{+\cdot}$, 4), 271 ($C_{19}H_{11}S^+$, 7), 260 ($C_{18}H_{12}S^{+\cdot}$, 4), 258 ($C_{18}H_{10}S^{+\cdot}$, 48).

Anal. Calcd. for $C_{20}H_{12}O_2S$: C, 75.93; H, 3.82; S, 10.13. Found: C, 76.25; H, 3.86; S, 10.11.

1a,12b-Dihydrobenz[*b*]oxireno[9,10]phenanthro[2,3-*d*]thiophene (**7**).

A solution of 1.2 g (3.8 mmoles) of **12** and 780 μl (4.3 mmoles) of tris(dimethylamino)phospine in 25 ml of dry benzene was refluxed under nitrogen for 8 hours. The solvent was evaporated under reduced pressure. The pale yellow residue was recrystallized from a mixture of ether and hexane to give 1.0 g (88%) of colorless epoxide, mp 221° dec; ^1H nmr (deuteriochloroform): 200 MHz δ 4.600 (d, 1H, $J_{1a,12b}$ = 4 Hz, H1a), 4.731 (d, 1H, $J_{1a,12b}$ = 4 Hz, H12b), 7.345-7.510 (m, 4H, H3, H4, H9, H10), 7.677 (dd, 1H, $J_{2,3}$ = 7.3 Hz, $J_{2,4}$ = 1.5 Hz, H2), 7.832-7.877 (m, 1H, H8), 8.163-8.210 (m, 2H, H5, H11), 8.376 (s, 1H, H12), 8.555 (s, 1H, H6); ms (m, 2H, H5, H11), (s, 1H, H12), (s, 1H, H6); (70 eV, 130°): m/z (relative intensity) 360 ($M^{+\cdot}$, 100), 284 ($C_{20}H_{12}S^{+\cdot}$, 17), 272 ($C_{19}H_{12}S^{+\cdot}$, 17), 271 ($C_{19}H_{11}S^+$, 59).

Anal. Calcd. for $C_{20}H_{12}OS$: C, 79.97; H, 4.03; S, 10.67. Found: C, 79.74; H, 4.11; S, 10.48.

Reaction of **7** with Sodium Azide.

A mixture of 900 mg (3 mmoles) of **7**, 2.0 g (30 mmoles) of sodium azide, 250 ml of acetone and 100 ml of water was stirred under nitrogen at 35° for 5 days. The acetone was removed under reduced pressure. Upon addition of 100 ml of water a mixture of *trans*-5-azido-5,6-dihydro-6-benzo[*b*]phenanthro[2,3-*d*]-thiophenol and *trans*-6-azido-5,6-dihydro-5-benzo[*b*]phenanthro-[2,3-*d*]thiophenol (**11**) precipitated. Chromatography on Florisil using a 1:1 mixture of ether and hexane as eluent afforded 850 mg (83%) of colorless azido alcohols, mp 195-196° dec; ir (nujol): 3300 (OH), 2150 cm^{-1} (N_3); ^1H nmr (deuteriochloroform): 200 MHz δ 2.15 (br s, 1H, O*H*), 4.795 (m, 2H, H5, H6), 7.358-7.524 (m, 4H, H2, H3, H9, H10), 7.602 (d, 1H, $J_{3,4}$ = 6.2 Hz, H4), 7.829-7.927 (m, 2H, H1, H11), 8.190 (m, 1H, H8), 8.248 (s, 0.6H, H13 of **10** or **11**), 8.272 (s, 0.4H, H13 of **10** or **11**), 8.329 (s, 0.6H, H7 of **10** or **11**), 8.385 (s, 0.4H, H7 of **10** or **11**); ms (70 eV, 140°): m/z (relative intensity) 343 ($M^{+\cdot}$, 36), 315 ($C_{20}H_{13}NOS^{+\cdot}$, 22), 301 ($C_{20}H_{13}OS^{+\cdot}$, 54), 287 ($C_{19}H_{11}OS^+$, 28), 286 ($C_{19}H_{12}NS^+$, 100), 284 ($C_{20}H_{12}S^{+\cdot}$), 271 ($C_{19}H_{11}S^+$, 38), 258 ($C_{18}H_{10}S^{+\cdot}$, 16).

Anal. Calcd. for $C_{20}H_{13}N_3OS$: C, 69.95; H, 3.82; N, 12.24; S, 9.34. Found: C, 70.18; H, 4.04; N, 11.95; S, 9.04.

1a,12b-Dihydro-1*H*-benz[*b*]azirino[9,10]phenanthro[2,3-*d*]thiophene (**8**).

A mixture of 50 mg (0.15 mmole) of **10** and **11**, 37μl (0.15 mmole) of tri-*n*-butylphosphine and 30 ml of dichloromethane was stirred under nitrogen at room temperature for 60 minutes and then refluxed for 3 hours. The solvent was evaporated, and the residue was chromatographed on silica gel deactivated with 15% of water using ether as eluent. The resulting pale yellow crystals were recrystallized (x3) from hexane to give 17 mg (38%) of pure **8**, mp 215° dec; ^1H nmr (deuteriochloroform): 200 MHz δ 3.660 (d, 1H, $J_{1a,12b}$ = 5.5 Hz, H1a), 3.801 (d, 1H, $J_{1a,12b}$ = 5.5 Hz), 7.349-7.488 (m, 4H, H3, H4, H9, H10), 7.618 (dd, 1H, $J_{2,3}$ = 7.2 Hz, $J_{2,4}$ = 1.8 Hz, H2), 7.820-8.198 (m, 2H, H5, H11), 8.326 (s,

1H, H12), 8.522 (s, 1H, H6); ms (70 eV, 140°): m/z (relative intensity) 299 ($M^{+\cdot}$, 100), 284 ($C_{20}H_{12}S^{+\cdot}$, 5), 272 ($C_{19}H_{12}S^{+\cdot}$, 7), 271 ($C_{19}H_{11}S^{+}$, 19).

Anal. Calcd. for $C_{20}H_{13}NS$: C, 80.24; H, 4.38; N, 4.68; S, 10.70. Found: C, 79.98; H, 4.46; N, 4.38; S, 10.41.

cis-5,6-Dihydro-5,6-benzo[*b*]phenanthro[3,2-*d*]thiophenediol (**15**).

In the manner described for the preparation of **9** 4.0 g (14 mmoles) of **2** was reacted for 8 days with 5.0 g (20 mmoles) of osmium tetroxide to give 3.1 g (69%) of air sensitive colorless crystals of **15**, mp 194-195°; ir (nujol): 3250 cm^{-1} (OH); ^1H nmr (deuteriochloroform): 200 MHz δ 4.854 (d, 1H, $J_{5,6}$ = 3.2 Hz, H5 or H6), 4.964 (d, 1H, $J_{5,6}$ = 3.2 Hz, H5 or H6), 7.351-7.501 (m, 4H, H2, H3, H10, H11), 7.594 (d, 1H, $J_{3,4}$ = 7.5 Hz, H4), 7.836-7.883 (m, 1H, H9), 7.982 (d, 1H, $J_{1,2}$ = 7.2 Hz, H1), 8.117 (s, 1H, H7), 8.230 (m, 1H, H12), 8.523 (s, 1H, H13); ms (70 eV, 160°): m/z (relative intensity) 318 ($M^{+\cdot}$, 100), 301 ($C_{20}H_{13}OS^{+}$, 73), 287 ($C_{19}H_{11}OS^{+}$, 47), 284 ($C_{20}H_{12}S^{+\cdot}$, 6), 272 ($C_{19}H_{12}S^{+\cdot}$, 33), 271 ($C_{19}H_{11}S^{+}$, 84), 258 ($C_{18}H_{10}S^{+\cdot}$, 18).

Anal. Calcd. for $C_{20}H_{14}O_2S$: C, 75.45; H, 4.43; S, 10.07. Found: C, 75.24; H, 4.37; S, 9.60.

2-(2-Formylphenyl)-3-dibenzothiophenecarboxaldehyde (**18**).

As for **9**, oxidation of 3.0 g (9.4 mmoles) of **15** with 3.0 g (14.0 mmoles) of sodium metaperiodate afforded 1.9 g (64%) of **18** as colorless crystals, mp 99°; ir (nujol): 1680 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): 200 MHz δ 7.418-7.739 (m, 5H, H4', H5', H6', H7, H8), 7.913 (dd, 1H, $J_{3',4'}$ = 7.1 Hz, $J_{3',5'}$ = 1.4 Hz, H3'), 8.084 (s, 1H, H1), 8.086-8.172 (m, 2H, H6, H9), 8.553 (s, 1H, H4), 9.888 (s, 1H, C*H*O), 9.899 (s, 1H, C*H*O); ms (70 eV, 120°): m/z (relative intensity) 316 ($M^{+\cdot}$, 37), 288 ($C_{19}H_{12}OS^{+\cdot}$, 21), 287 ($C_{19}H_{11}OS^{+\cdot}$, 100), 286 ($C_{19}H_{10}OS^{+\cdot}$, 31), 271 ($C_{19}H_{11}S^{+}$, 4), 260 ($C_{18}H_{12}S^{+\cdot}$, 14), 258 ($C_{18}H_{10}S^{+\cdot}$, 44).

Anal. Calcd. for $C_{20}H_{12}O_2S$: C, 75.93; H, 3.82; S, 10.13. Found: C, 75.75; H, 3.86; S, 10.24.

1a,12b-Dihydrobenz[*b*]oxireno[9,10]phenanthro[3,2-*d*]thiophene (**13**).

Treatment of 1.6 g (5.1 mmoles) of **18** with 950 μl (5.3 mmoles) of tris(dimethylamino)phosphine in boiling benzene for 3.5 hours gave 1.2 g (80%) of air sensitive colorless **13**, mp 172° dec (from ether-hexane mixture); ^1H nmr (deuteriochloroform): 200 MHz δ 4.572 (d, 1H, $J_{1a,12b}$ = 4 Hz, H1a), 4.635 (d, 1H, $J_{1a,12b}$ = 4 Hz, H12b), 7.348-7.571 (m, 4H, H3, H4, H8, H9), 7.686 (dd, 1H, $J_{2,3}$ = 7.4 Hz, $J_{2,4}$ = 1.5 Hz, H2), 7.857 (m, 1H, H10), 8.083 (s, 1H, H12), 8.208-8.300 (m, 2H, H5, H7), 8.813 (s, 1H, H6); ms (70 eV, 160°): m/z (relative intensity) 300 ($M^{+\cdot}$, 100), 284 ($C_{20}H_{12}S^{+\cdot}$, 17), 272 ($C_{19}H_{12}S^{+\cdot}$, 17), 271 ($C_{19}H_{11}S^{+}$, 59).

Anal. Calcd. for $C_{20}H_{12}OS$: C, 79.97; H, 4.03; S, 10.67. Found: C, 79.69; H, 4.11; S, 10.45.

trans-5-Azido-5,6-dihydro-6-benzo[*b*]phenanthro[3,2-*d*]thiophenol (**16**) and *trans*-6-Azido-5,6-dihydro-5-benzo[*b*]phenanthro[3,2-*d*]-thiophenol (**17**).

In the manner described for **7**, 1.0 g (3.3 mmoles) of **13** was reacted for 48 hours with 1.0 g (15 mmoles) of sodium azide to give (after chromatography on Florisil with 1:1 mixture ether-hexane) 0.7 g (62%) of azido alcohols **16** and **17**, mp 206° dec; ir (nujol): 3290 (OH), 2120 cm^{-1} (N_3); ^1H nmr (deuteriochloroform): 200 MHz δ 4.772 (m, 2H, H5, H6), 7.366-7.518 (m, 4H, H2, H3, H10, H11), 7.612 (d, 1H, $J_{3,4}$ = 6 Hz, H4), 7.857 (m, 1H, H9), 7.922 (m, 1H, H1), 7.990 (s, 0.6H, H7 of **16** or **17**), 8.060 (s, 0.4H, H7 of **16** or **17**), 8.203-8.249 (m, 1H, H12), 8.516 (s, 0.4H, H13 of **16** or **17**), 8.538 (s, 0.6H, H13 of **16** or **17**); ms (70 eV, 140°): m/z (relative intensity) 343 ($M^{+\cdot}$, 17), 315 ($C_{20}H_{13}NOS^{+\cdot}$, 26), 301 ($C_{20}H_{13}OS^{+}$, 13), 287 ($C_{19}H_{11}OS^{+}$, 88), 286 ($C_{19}H_{12}NS^{+}$, 100), 284 ($C_{20}H_{12}S^{+\cdot}$, 20), 271 ($C_{19}H_{11}S^{+}$, 27), 258 ($C_{18}H_{10}S^{+\cdot}$, 27).

Anal. Calcd. for $C_{20}H_{13}N_3OS$: C, 69.95; H, 3.82; N, 12.24; S, 9.34. Found: C, 70.22; H, 4.03; N, 11.86; S, 8.93.

1a,12b-Dihydro-1*H*-benz[*b*]azirino[9,10]phenanthro[3,2-*d*]thiophene (**14**).

As for the preparation of **8** a mixture of 50 mg (0.15 mmole) of the above azido alcohols, 37μl (0.15 mmole) of tri-*n*-butylphosphine and 25 ml of dichloromethane was stirred for 60 minutes at 25° and additional 60 minutes at 42°. Chromatography on silica gel deactivated with 12% water (ether as eluent) afforded 140 mg (32%) of **14** as pale yellow crystals, mp 207° dec (from ether-hexane); ^1H nmr (deuteriochloroform): 200 MHz δ 3.680 (d, 1H, $J_{1a,12b}$ = 5.1 Hz, H1a), 3.757 (d, 1H, $J_{1a,12b}$ = 5.1 Hz, H12b), 7.340-7.538 (m, 4H, H3, H4, H8, H9), 7.642 (dd, 1H, $J_{2,3}$ = 7.3 Hz, $J_{2,4}$ = 1.7 Hz, H2), 7.870 (m, 1H, H10), 8.072 (s, 1H, H12), 8.229-8.308 (m, 2H, H5, H7), 8.842 (s, 1H, H6); ms (70 eV, 120°): m/z (relative intensity) 299 ($M^{+\cdot}$, 100), 284 ($C_{20}H_{12}S^{+\cdot}$, 10), 272 ($C_{19}H_{12}S^{+\cdot}$, 13), 271 ($C_{19}H_{11}S^{+}$, 34).

Anal. Calcd. for $C_{20}H_{13}NS$: C, 80.24; H, 4.38; N, 4.68; S, 10.70. Found: C, 80.16; H, 4.47; N, 4.56; S, 10.41.

Acknowledgement.

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[1] See *e.g.*, J. Jacob, Sulfur Analogues of Polycyclic Aromatic Hydrocarbons, Environmental Occurrence, Chemical and Biological Properties, Cambridge University Press, Cambridge, UK, 1990, and references cited therein.

[2] R. G. Harvey, Polycyclic Aromatic Hydrocarbons, Chemistry and Carcinogenicity, Cambridge University Press, Cambridge, UK, 1991, and references cited therein.

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