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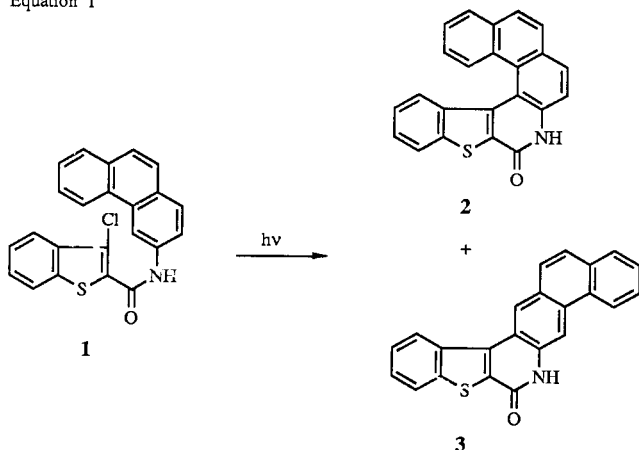
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Two previously unknown heterocyclic ring systems, namely, [1]benzothieno[2,3-*c*]naphtho[2,1-*f*]quinoline (**4**) and [1]benzothieno[2,3-*c*]naphtho[1,2-*g*]quinoline (**5**) were synthesized *via* photocyclization of 3-chloro-*N*-(2-phenanthryl)benzo[*b*]thiophene-2-carboxamide (**8**) followed by chlorination and dechlorination. The total assignment of their ¹H- and ¹³C-nmr spectra was determined by utilizing inverse-detected HMQC and HMBC two-dimensional nmr spectroscopic methods.

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In a related paper [2] we will report that the photocyclization of 3-chloro-*N*-(3-phenanthryl)benzo[*b*]thiophene-2-carboxamide (**1**) in cyclohexane in the presence of triethylamine afforded an isomeric mixture of [1]benzothieno[2,3-*c*]naphtho[1,2-*f*]quinolin-6(5*H*)-one (**2**) and [1]benzothieno[2,3-*c*]naphtho[2,1-*g*]quinolin-7(6*H*)-one (**3**) as shown in equation 1. Their structures were confirmed by two-di-

Equation 1



mensional nmr methods. As an extension of our studies on the synthesis of novel heterocyclic ring systems we now present the synthesis of two previously unknown ring systems, [1]benzothieno[2,3-*c*]naphtho[2,1-*f*]quinoline (**4**) and [1]benzothieno[2,3-*c*]naphtho[1,2-*g*]quinoline (**5**) *via* photocyclization.

When 3-chlorobenzo[*b*]thiophene-2-carbonyl chloride (**6**) [3-5] was allowed to react with 2-aminophenanthrene (**7**) [6] 3-chloro-*N*-(2-phenanthryl)benzo[*b*]thiophene-2-carboxamide (**8**) was obtained in 76% yield. Photocyclization of **8** afforded an isomeric mixture of [1]benzothieno[2,3-*c*]naphtho[2,1-*f*]quinolin-8(7*H*)-one (**9**) and [1]benzothieno[2,3-*c*]naphtho[1,2-*g*]quinolin-9(8*H*)-one (**10**) in a combined yield of 91%. Chlorination of the mixture of **9** and **10** with phosphorus oxychloride provided a mixture of the iso-

meric chloro analogs **11** and **12**. Separation of **11** and **12** afforded 8-chloro[1]benzothieno[2,3-*c*]naphtho[2,1-*f*]quinoline (**11**) in 60% yield and 9-chloro[1]benzothieno[2,3-*c*]naphtho[1,2-*g*]quinoline (**12**) in 16% yield. Catalytic dechlorination of **11** gave [1]benzothieno[2,3-*c*]naphtho[2,1-*f*]quinoline (**4**) in 62% yield. By the same method [1]benzothieno[2,3-*c*]naphtho[1,2-*g*]quinoline (**5**) was obtained in 57% yield from **12**.

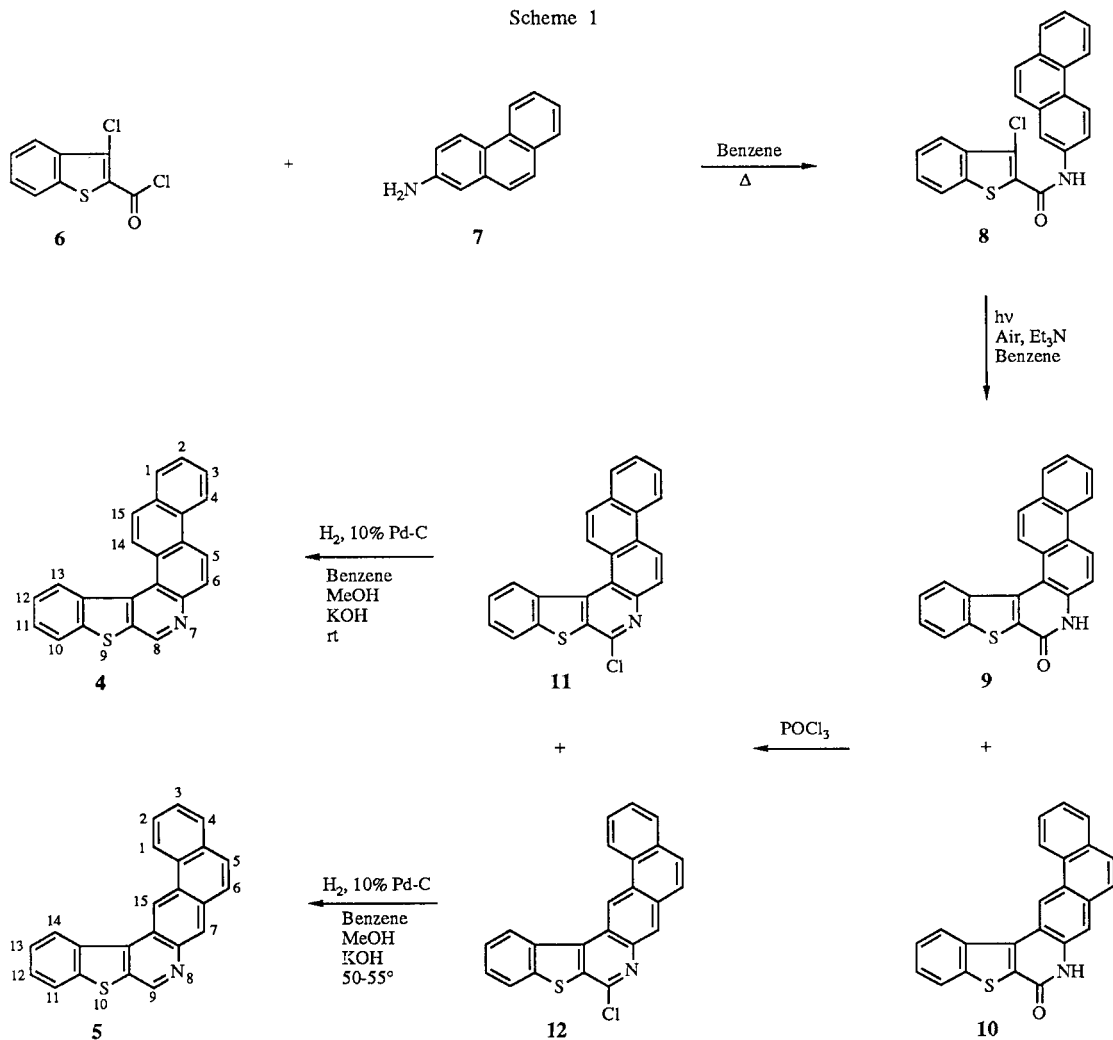
The structural confirmation of **12** was established by its ¹H nmr spectrum. Compound **12** exhibits two singlets at 9.84 and 8.53 ppm assigned to H15 and H7, respectively. Other physical properties such as the melting point and solubility further support our assignment of **11** and **12** [1].

NMR Spectroscopy.

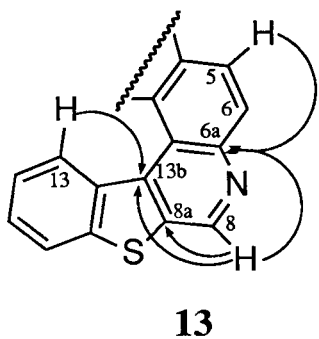
Direct (one bond, ¹J_{CH}) heteronuclear correlations were established for **4** using the HMQC pulse sequence originally described by Bax and Subramanian [7]. Vicinal proton-proton connectivities were obtained by using the COSY experiment [8].

With direct ¹H-¹³C chemical shift correlations, we turn our attention to the orientation of the spin systems relative to one another and to the assignment of the quaternary carbon resonances using a long-range heteronuclear chemical shift correlation experiment (Figure 1) [9]. The key long-range connectivity in the assignment of **4** is afforded by the H8 singlet resonating at 9.38 ppm which is directly correlative with the carbon resonating at 145.0 ppm. Long-range couplings to H8 are observed from three quaternary carbons resonating at 134.7, 136.3 and 144.8 ppm. The quaternary carbon resonating furthest upfield of this group has no other long-range couplings. By examining the structure of **4**, C8a would be expected to reveal this behavior and the coupling observed attributed to ²J_{CH}. The carbon resonating at 136.3 ppm exhibits coupling to both the H8 resonance and to the doublet resonating at 8.71 ppm. Although the carbon resonating furthest downfield in this group also exhibits couplings to

Scheme 1



both the H8 resonance and to the doublet resonating at 8.90 ppm, upon consideration of the chemical shift and our past experience [2] this quaternary carbon may be assigned unequivocally as C6a and the proton thus must be H5. Therefore, the middle carbon of this group may be assigned as C13b through elimination and a consideration of the chemical shift and the proton resonating at 8.71 ppm must be H13. These correlation pathways are shown in **13**.



Given the unequivocal assignment of the resonance at 8.71 ppm as H13, the balance of the proton and carbon resonances in the ring containing H13 can be readily assigned through concerted usage of COSY, HMQC and HMBC spectra. These assignments are summarized in Table 1.

Continuing to the long-range couplings of H5 assigned as above, the assignment and orientation of H5 and H6 relative to C6a is straightforward. The H5 long-range

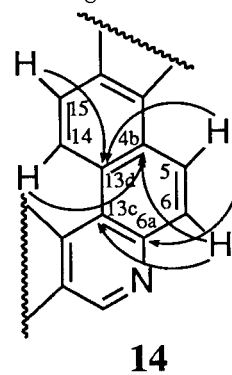


Table 1

Resonance Assignments of [1]Benzothieno[2,3-*c*]naphtho[2,1-*f*]-quinoline (**4**) in Deuteriochloroform

Position	Chemical Shift (ppm)		Long-Range Correlation
	Proton	Carbon	
1	7.98	128.4	H3, H15
2	7.68	127.0	H4
3	7.74	127.0	H1
4	8.81	123.5	H2
4a		130.1	H1, H3, H5, H15
4b		122.8	H4, H6, H14
5	8.90	123.7	
6	8.33	128.4	
6a		144.8	H5, H8
8	9.38	145.0	
8a		134.7	H8
9a		141.4	H11, H13
10	8.02	123.5	H12
11	7.56	128.0	H13
12	7.42	123.8	H10
13	8.71	127.0	H13
13a		135.3	H10, H12
13b		136.3	H8, H13
13c		129.6	H6, H14
13d		126.4	H5, H15
14	8.79	126.4	
15	7.83	124.9	H1
15a		132.5	H2, H4, H14, H15

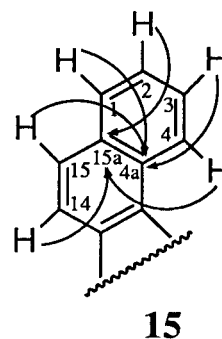
Table 2

Resonance Assignments of [1]Benzothieno[2,3-*c*]naphtho[1,2-*g*]quinoline (**5**) in Deuteriochloroform

Position	Chemical Shift (ppm)		Long-Range Correlation
	Proton	Carbon	
1	8.92	123.02	H3
2	7.79	127.12	H4
3	7.70	127.55	H1
4	7.92	128.98	H2, H5
4a		132.36	H1, H3, H6
5	7.74	127.92	H4
6	7.89	127.01	H7
6a		131.62	H5, H15
7	8.77	129.15	H6
7a		143.44	H9, H15
9	9.40	146.46	
9a		132.98	H9
10a		141.50	H12, H14
11	8.12	123.95	H13
12	7.68	127.40	H14
13	7.81	125.71	H11
14	9.10	125.95	H12
14a		135.35	H11, H13, H14
14b		134.93	H9, H15
14c		124.03	H7
15	10.12	116.62	
15a		129.48	H1, H6, H7
15b		130.17	H1, H2, H4, H5, H15

couples to C6a and the H6 leads to the assignment of C13c. Orientation of H14 and H15 relative to the H5-H6 spin system is accomplished through the three-bond couplings of H5 and H15 to C13d whereas H6 and H14 both couple to C4b. These correlation pathways are illustrated in **14**.

The final set of correlations that must be considered to complete the assignment hinges on C4a and C15a. Thus, H1, H3, and H15 each exhibit strong long-range coupling to C4a while H2, H4 and H14 all exhibit long-range coupling to C15a. This final set of correlation pathways is shown in **15**.

**15**

The spectral assignment of **5** was analyzed and assigned in a fashion similar to that described in the assignment of the spectra of **4** and their assignments are summarized in Table 2. It is worth noting that H15 of **5** resonates at 10.12 ppm, further downfield than any other proton observed, as anticipated and this observation is ascribed to its unique position in the bay region similar to structural analogs of polycyclic aromatic hydrocarbons (Figure 2) [10].

In conclusion, we have synthesized two novel heterocyclic ring systems. Total assignments of their ¹H- and ¹³C-nmr spectra were accomplished by utilizing inverse-detected HMQC and HMBC two-dimensional nmr methods.

EXPERIMENTAL

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. The ir spectra of the intermediates were recorded on a Beckman FT1100 spectrometer as potassium bromide pellets and frequencies are expressed in cm⁻¹. The ¹H nmr spectra of the intermediates were obtained on a JEOL FX-90Q spectrometer in the solvent indicated with TMS as the internal standard and chemical shifts are reported in ppm (δ) and J values in Hz. Column chromatography was performed utilizing Aldrich silica gel, 70-230 mesh. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona. The electron impact mass spectra were acquired by the Midwest Center for Mass Spectrometry at the University of Nebraska-Lincoln, using a Kratos MS-50 mass spectrometer which has Nier-Johnson geometry.

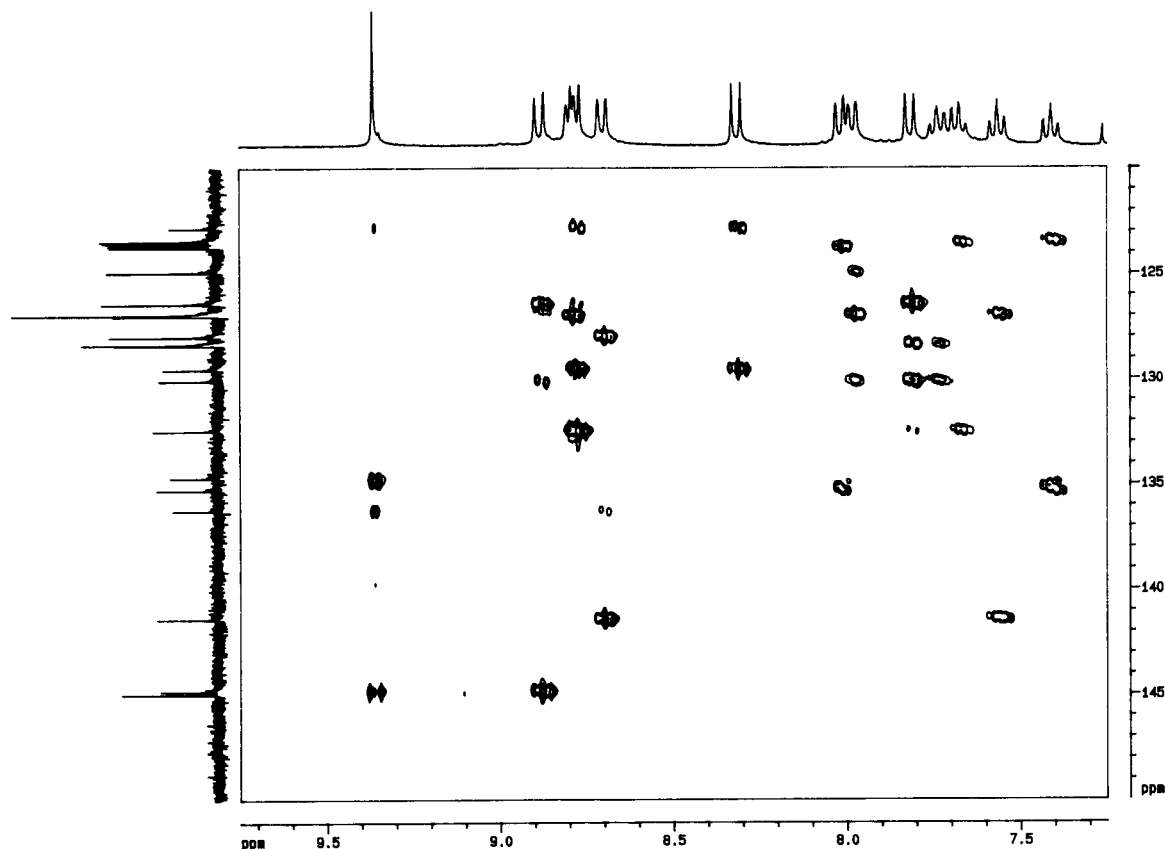


Figure 1. Long-range heteronuclear chemical shift correlation spectrum of **4** recorded in deuteriochloroform at observed frequencies of 360.13/90.56 MHz for ^1H and ^{13}C , respectively.

Proton and carbon nmr spectra of the final products **4** and **5** were acquired using a Bruker AMX360 spectrometer operating at a proton frequency of 360.13 MHz and a carbon frequency of 90.56 MHz. The proton spectra were obtained using a $5\ \mu\text{s}$ (48.6°) pulse and 5 seconds between transients to insure accurate integrals. All two-dimensional experiments were acquired using a Bruker inverse-geometry probe. Spectral width for all proton and proton correlation experiments was 992.06 Hz. A one-dimensional carbon spectrum was obtained with a spectral width of 15001.5 Hz and 2 seconds between transients. A phase-sensitive double quantum filtered (DQCOSY) experiment was acquired [8] with 512 t_1 increments of $504\ \mu\text{s}$ used to encode a second dimension of 992.06 Hz. Proton-carbon correlation experiments were acquired using the inverse-detected techniques of Bax [7,9]. Fixed delay times of 3.0 m seconds and 47.0 m seconds (165 and 10 Hz, respectively) were used for direct and long-range methods, respectively. For the phase sensitive direct correlation techniques, 256 t_1 increments of $156\ \mu\text{s}$ were used to encode an f_1 spectral width of 3205.13 Hz. For the long-range correlation experiment 256 t_1 increments of $312\ \mu\text{s}$ were used to encode an f_1 spectral width of 3205.13 Hz.

3-Chloro-*N*-(2'-phenanthryl)benzo[*b*]thiophene-2-carboxamide (**8**).

A mixture of 1.93 g (8.35 mmoles) of 3-chlorobenzo[*b*]thiophene-2-carbonyl chloride (**6**) [3-5], 1.62 g (8.38 mmoles) of 2-aminophenanthrene (**7**) [6] and 70 ml of benzene was heated under reflux for 4 hours. After cooling to room temperature the precipitate was collected by filtration and recrystallized from benzene to afford 2.46 g (6.34 mmoles, 76%) of **8** as fine colorless needles, mp 236-238°; tlc (benzene) R_f 0.67; ir (potassium bromide): 3389 (NH stretching), 3057 (aromatic CH stretching), 1653 (C=O stretching); ^1H nmr (deuteriochloroform): δ 7.47-7.99 (m, 10H, ArH), 8.37 (d, $J_{1,3'} = 2.2\ \text{Hz}$, 1H, H1'), 8.57-8.72 (m, 2H, ArH), 9.26 (br s, 1H, NH).

Anal. Calcd. for $\text{C}_{23}\text{H}_{14}\text{ClNOS}$: C, 71.22; H, 3.64; N, 3.61; S, 8.27. Found: C, 71.08; H, 3.76; N, 3.67; S, 8.41.

[1]Benzothieno[2,3-*c*]naphtho[2,1-*f*]quinolin-8(7*H*)-one (**9**) and [1]Benzothieno[2,3-*c*]naphtho[1,2-*g*]quinolin-9(8*H*)-one (**10**).

A mixture of 0.5 g (1.29 mmoles) of **8**, 0.13 g (1.29 mmoles) of triethylamine and 500 ml of benzene was irradiated with a 450 watt Hanovia medium pressure mercury lamp for 4 hours. A slow stream of air was passed through the solution during the course

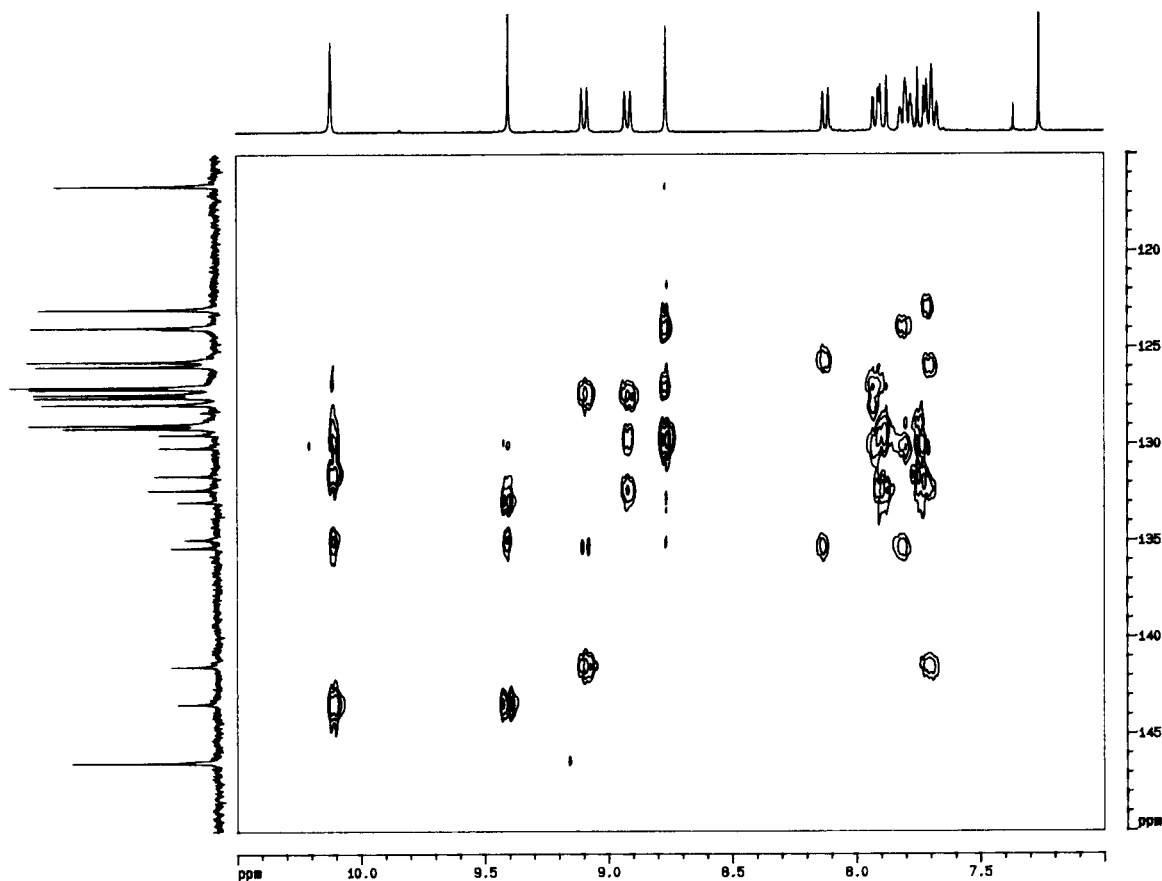


Figure 2. Long-range heteronuclear chemical shift correlation spectrum of **5** recorded in deuteriochloroform at observed frequencies of 360.13/90.56 MHz for ^1H and ^{13}C , respectively.

of the irradiation. The precipitate was collected by filtration and was washed with water to afford a 0.41 g (1.17 mmoles, 91%) of a mixture of **9** and **10** as a brownish product, mp $>250^\circ$. These two compounds were used as a mixture in the next reaction without further purification and characterization due to low solubility.

8-Chloro[1]benzothieno[2,3-c]naphtho[2,1-f]quinoline (**11**) and 9-Chloro[1]benzothieno[2,3-c]naphtho[1,2-g]quinoline (**12**).

A mixture of 1.81 g (5.15 mmoles) of **9** and **10**, and 100 ml of phosphorus oxychloride was heated at $100\text{--}110^\circ$ for 4 hours. After cooling in an ice bath, the mixture was poured into 600 ml of ice water very slowly with vigorous stirring. The precipitate was collected by filtration and recrystallized from benzene to give 0.30 g (0.81 mmole, 16%) of **12** as fine yellow needles, mp $266\text{--}268^\circ$; tlc (benzene) R_f 0.77; ir (potassium bromide): 3055, 3034 (aromatic CH stretching); ^1H nmr (deuteriochloroform): 55° δ 7.55-8.08 (m, 8H, ArH), 8.53 (s, 1H, H7), 8.64-8.92 (m, 2H, ArH), 9.84 (s, 1H, H15).

Anal. Calcd. for $\text{C}_{23}\text{H}_{12}\text{ClNS}$: C, 74.69; H, 3.27; N, 3.79; S, 8.67. Found: C, 74.80; H, 3.34; N, 3.83; S, 8.81.

The filtrate from the above crystallization was evaporated to dryness *in vacuo* and the solid was recrystallized from cyclohexane to give 1.15 g (3.11 mmoles, 60%) of **11** as yellow granules,

mp $242\text{--}244^\circ$; tlc (benzene) R_f 0.77; ir (potassium bromide): 3052 (aromatic CH stretching); ^1H nmr (deuteriochloroform): 50° δ 7.46-8.27 (m, 8H, ArH), 8.57-8.93 (m, 4H, ArH).

Anal. Calcd. for $\text{C}_{23}\text{H}_{12}\text{ClNS}$: C, 74.69; H, 3.27; N, 3.79. Found: C, 74.83; H, 3.30; N, 3.73.

[1]Benzothieno[2,3-c]naphtho[2,1-f]quinoline (**4**).

A mixture of 0.54 g (1.46 mmoles) of **11**, 0.082 g (1.46 mmoles) of potassium hydroxide, 0.1 g of 10% palladium on carbon, 120 ml of benzene and 120 ml of methanol was hydrogenated at 45 psi at room temperature in a Parr hydrogenation apparatus until the uptake of hydrogen ceased. The catalyst was removed by filtration and the filtrate was evaporated to dryness *in vacuo*. The solid was taken up in 20 ml of methylene chloride and chromatographed on a silica gel column eluting with methylene chloride to remove 0.13 g of starting material and yield 0.23 g (0.69 mmole, 62% based on the reacted starting material) of **4** after recrystallization from cyclohexane, mp $225\text{--}227^\circ$; tlc (benzene) R_f 0.14; ir (potassium bromide): 3052 (aromatic CH stretching).

Anal. Calcd. for $\text{C}_{23}\text{H}_{13}\text{NS}$: C, 82.36; H, 3.91; N, 4.18. Found: C, 82.39; H, 4.12; N, 4.14.

[1]Benzothieno[2,3-c]naphtho[1,2-g]quinoline (**5**).

A mixture of 0.19 g (0.51 mmole) of **12**, 0.03 g (0.53 mmole) of potassium hydroxide, 0.1 g of 10% palladium on carbon, 90 ml of

benzene and 90 ml of methanol was hydrogenated at 45 psi at 50-55° in a Parr hydrogenation apparatus until the uptake of hydrogen ceased. The catalyst was removed by filtration and the filtrate was evaporated to dryness *in vacuo*. The solid was taken up in 5 ml of methylene chloride and chromatographed on a silica gel column eluting with cyclohexane-methylene chloride (1:4) to remove 50 mg of starting material and yield 72 mg (0.21 mmole, 57% based on the reacted starting material) of **5** after recrystallization from cyclohexane-benzene, mp 247-250°; tlc (benzene) R_f 0.17; ms: m/z (% relative intensity) 337 (M + 2)⁺ (5), 336 (M + 1)⁺ (30), 335 (M)⁺ (100), 167 (14); hrms: m/z measured 335.0774 (C₂₃H₁₃NS requires 335.0769) [11].

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