The Synthesis of Novel Polycyclic Heterocyclic Ring Systems *via* Photocyclization. 17 [1,2]. Thieno[3',2':4,5]thieno[2,3-c]naphtho-[2,1-f]quinoline and Thieno[3',2':4,5]thieno[2,3-c]-naphtho[1,2-g]quinoline

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The synthesis of two previously unknown novel polycyclic heterocyclic ring systems *via* photocyclization is described. The structural assignment of the isomeric ring systems, **4** and **5**, was achieved by the total assignment of their ^{1}H and ^{13}C nmr spectra by the concerted usage of two-dimensional nmr methods.

In our recent reports, we demonstrated that photocyclization of both 3-chloro-*N*-(2-phenanthryl)benzo[*b*]thiophene-2-carboxamide (**1**) [2e] and its structural isomer, 3-chloro-*N*-(3-phenanthryl)benzo[*b*]thiophene-2-carboxamide (**2**) [2k], yielded the corresponding isomeric mixture of lactams, whereas photocyclization of 3-chloro-*N*-(3-phenanthryl)[1]benzothieno[3,2-*b*]thiophene-2-carboxamide (**3**) [2p] afforded only one of the two possible isomers as illustrated in Scheme 1. This unusual reactivity prompted us to launch serial studies of photocyclization of isomeric phenanthryl anilides. To this end, we wish to report in this paper the synthesis of two previously unknown heterocyclic ring systems, thieno[3',2':4,5]thieno[2,3-*c*]naphtho[2,1-*f*]quinoline (**4**) and thieno[3',2':4,5]thieno[2,3-*c*]naphtho[1,2-*g*]quinoline (**5**).

When 3-chlorothieno[2,3-*b*]thiophene-2-carbonyl chloride (**6**) [2a,4,5] was allowed to react with 2-aminophenanthrene [6] in refluxing benzene, 3-chloro-*N*-(2-phenanthryl)thieno[2,3-*b*]thiophene-2-carboxamide (**7**) was obtained in 72% yield. The oxidative photocyclization of **7** in benzene solution containing triethylamine afforded an isomeric mixture of thieno[3',2':4,5]thieno[2,3-*c*]naphtho[2,1-*f*]quinolin-8(7*H*)-one (**8**) and thieno[3',2':4,5]thieno[2,3-*c*]naphtho[1,2-*g*]quinolin-9(8*H*)-one (**9**) in a combined yield of 95%. Although the mixture was not separated because of its low solubility, chlorination of the mixture of **8** and **9** with phosphorus oxychloride gave the corresponding 8-chlorothieno[3',2':4,5]thieno[2,3-*c*]naphtho[2,1-*f*]quinoline (**10**) in 34% yield and 9-chloro-thieno[3',2':4,5]thieno[2,3-*c*]naphtho[1,2-*g*]quinoline (**11**) in 16% yield upon separation by fractional crystallization. The structural confirmation of **10** and **11** was accomplished by the usage of two-dimensional nmr methods (*vide infra*) after transforming them to the corresponding unsubstituted ring systems. Thus, hydrazination of **10** with anhydrous hydrazine in a refluxing mixture of benzene and ethanol provided 8-hydrazinothieno[3',2':4,5]thieno[2,3-*c*]naphtho-

Scheme 1
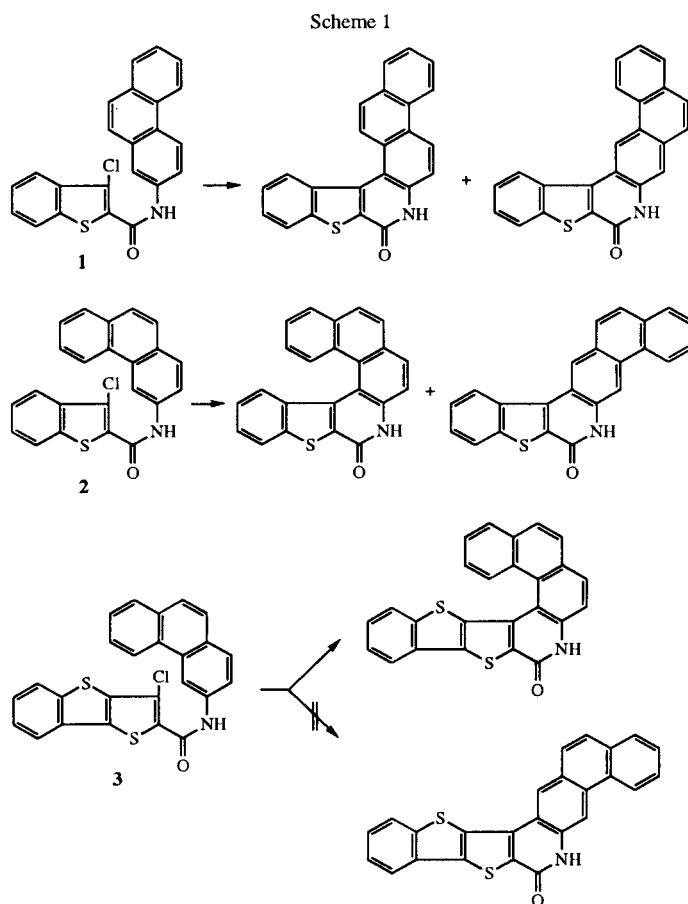
[2,1-*f*]quinoline (**12**) in 80% yield. Dehydrazination was carried out with 10% copper sulfate in refluxing aqueous acetic acid to give the unsubstituted novel ring system, thieno[3',2':4,5]thieno[2,3-*c*]naphtho[2,1-*f*]quinoline (**4**), in 60% yield. Likewise, the unsubstituted novel ring system, thieno[3',2':4,5]thieno[2,3-*c*]naphtho[1,2-*g*]quinoline (**5**), was obtained by hydrazination/dehydrazination

Scheme 2

10, R = Cl
12, R = NHNH$_2$
4, R = H

11, R = Cl
13, R = NHNH$_2$
5, R = H
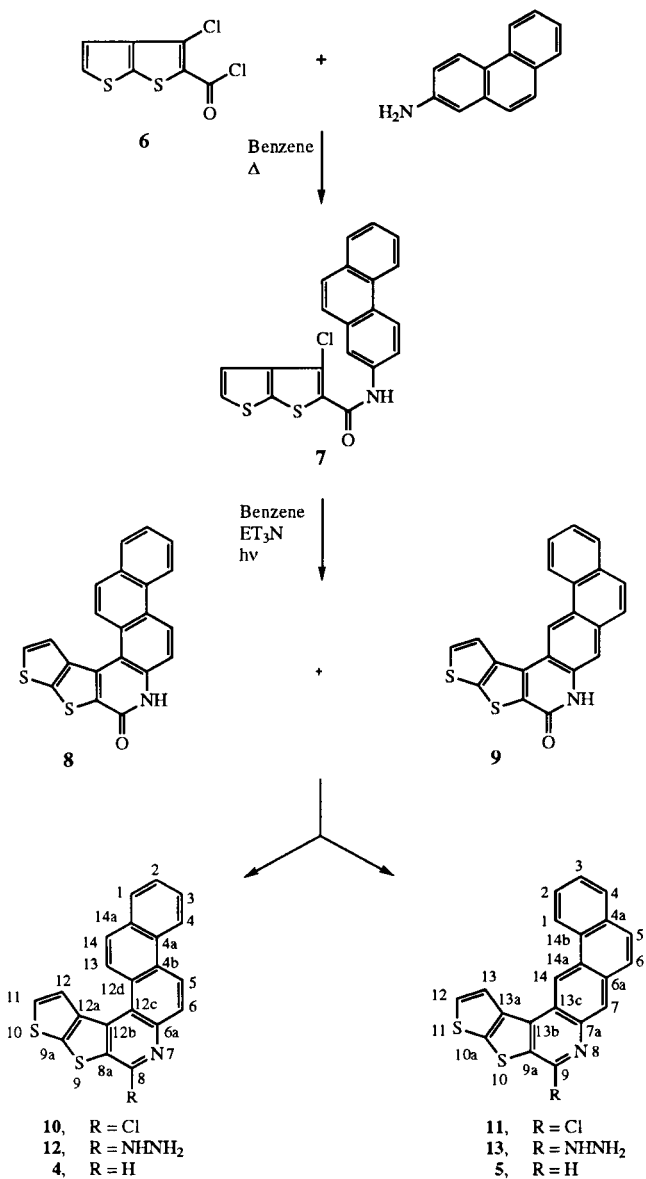
of chloride **11** in 91% and 63% yield, respectively (Scheme 2).

NMR Spectroscopy.

The structural confirmation of **4** was established by the unequivocal assignment of its ^{1}H and ^{13}C spectra through the concerted use of COSY [7], HMQC [8], and HMBC [9] spectra. The COSY spectrum of **4** revealed one four-spin and three two-spin systems. The long-range couplings in the COSY spectrum of **4** provided not only the orientation of those spin systems, but also the means of differentiating the three two-spin systems. For instance, the long-range couplings between H4/H5 and H4/H14 not only distinguish the two-spin system of H13/H14 from H5/H6, but also establish the orientation of the four-spin system of H1 to H4 and

two-spin systems of H5/H6 and H13/H14. Interestingly, a weak but very distinct response was observed and ascribed to the seven-bond long-range coupling across the "bay" between H12 and H13 [10] and facilitates the assignment of H11 and H12. The seven-bond long-range coupling was confirmed by a nOe difference experiment. Further support for the assignment of H12 was afforded by its NOESY spectrum [11], in which a nOe was observed between H12 and H13. Other nOe observed in the NOESY spectrum of **4** were H1/H2, H2/H3, H3/H4, H4/H5, H11/H12, H13/H14, and H1/H14. Thus, an unequivocal assignment of the ^{1}H nmr spectrum of **4** can be achieved with the COSY spectrum in conjuction with the NOESY experiments.

Given every proton being accounted for, the protonated carbons of **4** can be immediately identified with a proton-carbon direct heteronuclear chemical shift correlation (HMQC) spectrum. The assignment of the remaining quaternary carbons, however, needs to employ a long-range heteronuclear chemical shift correlation (HMBC) spectrum of **4**.

The most convenient point of entry into the assignment process is afforded by the H8 singlet resonating at 9.64 ppm. Long-range couplings to H8 are observed to four quaternary carbons resonating at 134.7, 137.4, 139.4, and 142.0 ppm. The quaternary carbon resonating furthest upfield of this group has a long-range coupling to H5 and is attributed to C6a. The carbon resonating furthest downfield of this group exhibits two more responses correlating to H11 and H12, respectively and is assigned as C12a. The weak but distinct long-range coupling arising from H8/C12a is attributed to a

Table 1

^{1}H and ^{13}C-NMR Chemical Shift Assignments and Observed Proton-Carbon Multiple-Bond Correlations for Compound **4** in Deuterio-chloroform in the Presence of Deuterated Trifluoroacetic Acid at 298°K at Observation Frequencies of 360.13 and 90.6 MHz, Respectively

Position	δH	δC	Two-Bond Correlation	Three-Bond Correlation	Four-Bond Correlation
1	8.13	128.8		H3, H14	
2	7.84	128.7		H4	
3	7.90	128.4		H1	
4	8.86	123.6		H2	
4a		129.6		H1, H3, H5, H14	
4b		130.5		H4, H6, H13	
5	9.26	129.3			
6	8.41	118.1			
6a		134.7		H5, H8	
8	9.64	137.1			
8a		137.4	H8		
9a		154.2		H11, H12	
11	7.76	130.7	H12		
12	8.20	124.1	H11		
12a		142.0	H12	H11	H8
12b		139.4		H8	
12c		122.1		H6, H13	
12d		126.2		H5, H14	
13	8.93	124.2			
14	8.20	128.7		H1	
14a		132.9		H2, H4, H1	

four-bond coupling [2d,2k] observed previously. The remaining two quaternary carbons show no other long-range couplings, although a three-bond coupling is anticipated to arise from H12/C12b. Upon consideration of the chemical shift, the intensity of the responses and our past experience [2d,2m,12], the quaternary carbon resonating at 137.4 ppm may be assigned as C8a, whereas the resonance at 139.4 ppm was assigned as C12b. The remaining quaternary carbons can be easily assigned with every proton and protonated carbon being accounted for (Table 1). It is worth noting that the chemical shift of C9a is significantly shifted downfield by approximately 10 ppm when the spectra of **4** are measured in the presence of deuterated trifluoroacetic acid in deuteriochloroform. This phenomenon also is exhibited in the experiments of **5** (*vide infra*).

The spectral assignment of **5** was analyzed and assigned in a manner similar to that described in the assignment of the spectra of **4** and their assignments are summarized in Table 2. In the NOESY spectrum of **5** the furthest downfield singlet resonating at 9.96 ppm revealing two responses at 8.86 and 8.41 ppm is assigned as H14 due to its unique position in the bay region similar to a structural analogs reported previously [2e]. In contrast to **4** the HMBC spectrum of **5** does not show the four-bond correlation of H9/C13a. Thus, the assignment of C13a and C10a is derived from the chemical shift consideration demonstrated in the prior assignment of **4** (*vide supra*).

It is interesting to note that while **5** is flat, **4** assumes a helically distorted conformation. The MM2 [13] and

MOPAC (using PM3 parameters [14]) calculations of **5** predicts internuclear distances between H-13 and H-14 of 2.0 Å, H-13 and H-1 of 2.9 Å and H-14 and H-1 of 2.0 Å. For **4** the internuclear distance predicted between H-12 and H-13 is 2.4 Å for the MM2 calculations and 2.3 Å for the MOPAC calculation. The structures generated by MOPAC are shown in Figures 1 and 2.
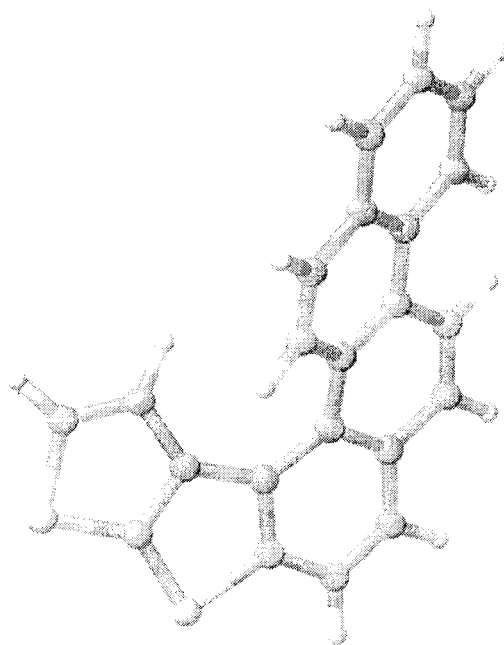

Figure 1. MOPAC generated structure of **4** showing the helically distorted conformation.

Table 2

¹H and ¹³C-NMR Chemical Shift Assignments and Observed Proton-Carbon Multiple-Bond Correlations for Compound **5** in Deuteriochloroform in the Presence of Deuterated Trifluoroacetic Acid at 298°K at Observation Frequencies of 360.13 and 90.6 MHz, Respectively

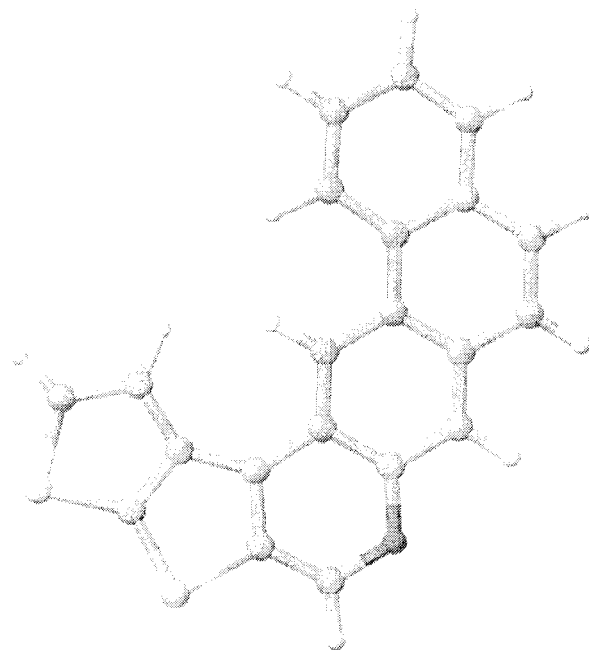| Position	δH	δC	Two-Bond Correlation	Three-Bond Correlation
1	8.86	123.1		H3
2	7.86	128.5		H4
3	7.82	129.7		H1
4	7.99	129.9		H2, H5
4a		132.7		H1, H3, H6
5	7.93	132.1		H4
6	7.90	125.8		H7
6a		135.2		H5, H14
7	8.75	119.4		H6
7a		140.0		H9, H14
9	9.53	140.1		
9a		133.3	H9	
10a		154.7		H12, H13
12	8.04	133.8	H13	
13	8.41	121.5	H12	
13a		141.1	H13	H12
13b		131.8		H9, H14
13c		120.8		H7
14	9.96	118.6		
14a		131.8		H6, H7
14b		129.1	H2, H4, H5, H14	

Figure 2. MOPAC generated structure of **5** showing the essentially planar conformation.

In conclusion, we have synthesized two previously unknown isomeric heterocyclic ring systems. Their structures have been determined and the proton and carbon nmr spectra unequivocally and totally assigned.

EXPERIMENTAL

Melting points were determined on a Thomas-Hoover melting apparatus and are uncorrected. The ir spectra were recorded on a Beckman FT1100 spectrometer or a Nicolet Magna-IR Spectrometer 550 as potassium bromide pellets and frequencies are expressed in cm^{-1}. The ^{1}H nmr spectra of the intermediates were obtained on a JEOL FX-90Q or on a Bruker AMX360 MHz NMR spectrometer in the solvent indicated with TMS as the internal standard and chemical shifts are reported in ppm (δ) and J values in Hz. Analyses (tlc) were performed on Sigma precoated silica gel plates containing a fluorescent indicator. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona.

The ^{1}H and ^{13}C spectra of 4 and 5 were acquired on a Bruker AMX360 MHz NMR spectrometer operating at an observation frequency of 360.13 MHz for ^{1}H and 90.56 for ^{13}C. All experiments were performed using an inverse-geometry 5 mm broad band probe. Pulse widths (90°) for ^{1}H and ^{13}C were 7.8 and 15.6 μsec. The COSY spectra were recorded using the Bruker pulse program (COSY90) [7]. The HMQC experiments were performed using the Bruker pulse program (invbdgtp) with the BIRD sequence optimized for direct couplings (165 Hz $^1J_{CH}$) [8]. The HMBC spectra were obtained using the Bruker pulse program (inv4lplrnd) [9] optimized for 10 Hz $^3J_{CH}$ couplings. The nOe experiments were carried out using the Bruker pulse program (zgh2pr). The NOESY experiment was performed using the Bruker pulse program (noesytp) [11].

3-Chloro-N-(2-phenanthryl)thieno[2,3-b]thiophene-2-carboxamide (7).

A mixture of 2.0 g (8.43 mmoles) of 6 [2a,4,5] and 1.63 g (8.43 mmoles) of 2-aminophenanthrene in 80 ml of benzene was heated under reflux for 4 hours. After cooling to room temperature the mixture was evaporated to dryness in vacuo and the solid was recrystallized from benzene to give 2.40 g (6.09 mmoles, 72%) of amide 7 as off-white granules, mp 220-222°; ir (potassium bromide): 3376 (NH stretching), 1643 (C=O stretching); ^{1}H nmr (deuteriochloroform): δ 7.17-7.89 (m, 8H, ArH), 7.88 (d, $J_{1',\ 3'}$ = 2.2 Hz, 1H, H-1'), 8.56-8.66 (m, 2H, H-4' and H-5'), 8.92 (br s, 1H, NH).

Anal. Calcd. for $C_{21}H_{12}ClNOS_2$: C, 64.03; H, 3.07; N, 3.56; S, 16.28. Found: C, 63.86; H, 3.24; N, 3.29; S, 16.41.

Thieno[3',2':4,5]thieno[2,3-c]naphtho[2,1-f]quinolin-8(7H)-one (8) and Thieno[3',2':4,5]thieno[2,3-c]naphtho[1,2-g]quinolin-9(8H)-one (9).

A mixture of 0.5 g (1.27 mmoles) of 7 and 0.13 g of triethylamine in 500 ml of benzene was irradiated with a 450 watt Hanovia medium pressure mercury vapor lamp for four hours. A slow stream of air was passed through the solution during the course of the reaction. The solid was collected by filtration and washed with water to afford 0.43 g (1.20 mmoles, 95%) of lactams 8 and 9 as a brownish mixture, mp >280°; ^{1}H nmr (DMSO-d$_6$): 150°, δ 7.57-8.09 (m, ArH), 8.39-9.01 (m, ArH),

9.56 (s, 1H, H-14 of 9). The singlet at δ 9.56 indicates that compound 9 is present in the mixture. The ratio of 8:9 is about 2:1 based on the ^{1}H nmr data. This mixture was used in the next step without further purification because of its low solubility.

8-Chlorothieno[3',2':4,5]thieno[2,3-c]naphtho[2,1-f]quinoline (10) and 9-Chlorothieno[3',2':4,5]thieno[2,3-c]naphtho-[1,2-g]quinoline (11).

A mixture of 1.50 g (4.20 mmoles) of lactams 8 and 9 and 80 ml of phosphorus oxychloride was heated under reflux for four hours. After cooling to room temperature, the mixture was poured into 500 ml of ice water with vigorous stirring. The solid was collected by filtration, washed with water, and then dried. The solid was recrystallized from benzene to afford 0.25 g (0.67 mmole, 16%) of chloride 11 as fine golden needles, mp 304-305°dec; ir (potassium bromide): 3050 (aromatic CH stretching); ^{1}H nmr (deuteriochloroform): 50°, δ 7.65-7.95 (m, 6H, ArH), 8.27 (d, $J_{12,13}$ = 5.4 Hz, 1H, H-13), 8.66 (s, 1H, H-7), 8.85 (dd, $J_{1,2}$ = 7.1 Hz, $J_{1,3}$ = 2.4 Hz, 1H, H-1), 9.80 (s, 1H, H-14).

Anal. Calcd. for $C_{21}H_{10}ClNS_2$: C, 67.10; H, 2.68; N, 3.73; S, 17.06. Found: C, 66.85; H, 2.41; N, 3.64; S, 16.81.

The filtrate from the above crystallization was evaporated to dryness in vacuo and the solid was recrystallized from benzene to afford 0.54 g (1.44 mmoles, 34%) of chloride 10 as tan short needles, mp 248-250° dec; ir (potassium bromide): 3091 (aromatic CH stretching); ^{1}H nmr (deuteriochloroform): 50°, δ 7.50 (d, $J_{11,12}$ = 5.4 Hz, 1H, H-11), 7.65-7.78 (m, 2H, ArH), 7.90-8.06 (m, 3H, ArH), 8.19 (d, J = 9.3 Hz, 1H, ArH), 8.78 (m, 3H, ArH).

Anal. Calcd. for $C_{21}H_{10}ClNS_2$: C, 67.10; H, 2.68; N, 3.73; S, 17.06. Found: C, 67.30; H, 2.88; N, 3.53; S, 17.17.

8-Hydrazinothieno[3',2':4,5]thieno[2,3-c]naphtho[2,1-f]-quinoline (12).

To a boiling mixture of 0.47 g (1.25 mmoles) of chloride 10 in 40 ml of absolute ethanol and 20 ml of benzene, 10 ml of anhydrous hydrazine was added dropwise over a period of 30 minutes. The mixture was heated under reflux for 20 hours. After cooling to room temperature, the solid was collected by filtration and washed with ethanol to afford 0.37 g (1.0 mmole, 80%) of hydrazine 12 as off-white crystals, mp 236-239°; ir (potassium bromide): 3295 (NH stretching), 3101, 3085 (NH$_2$ stretching); ^{1}H nmr (DMSO-d$_6$): δ 4.95 (br s, 2H, NH$_2$), 7.63-7.89 (m, 5H, ArH), 8.01 (d, $J_{5,6}$ = 9.3 Hz, 1H, H-6), 8.06 (d, $J_{1,2}$ = 7.6 Hz, 1H, H-1), 8.62 (s, 1H, NH), 8.63 (d, $J_{3,4}$ = 8.5 Hz, 1H, H-4), 8.88 (d, $J_{13,14}$ = 8.5 Hz, 1H, H-13), 8.90 (d, $J_{5,6}$ = 9.3 Hz, 1H, H-5). This compound was used in the next step without further purification due to its low solubility and stability [2p].

Thieno[3',2':4,5]thieno[2,3-c]naphtho[2,1-f]quinoline (4).

To a boiling solution of 0.1 g (0.27 mmole) of hydrazine 12 in 11 ml of glacial acetic acid and 2 ml of water was added dropwise 10 ml of 10% aqueous copper sulfate solution. The resulting mixture was heated under reflux for 20 hours. After cooling to room temperature, the mixture was neutralized with 2N sodium hydroxide solution. The solid was collected by filtration, washed with water, and dried. The solid was recrystallized from benzene/cyclohexane mixture to yield 0.055 g (0.16 mmole, 60%) of 4 as colorless crystals, mp 200-203°; tlc (chloroform) R$_f$ 0.10; ir (potassium bromide): 3061, 3047 (aromatic CH stretching).

Anal. Calcd. for $C_{21}H_{11}NS_2$: C, 73.87; H, 3.25; N, 4.10. Found: C, 74.06; H, 3.05; N, 3.90.

9-Hydrazinothieno[3',2':4,5]thieno[2,3-*c*]naphtho[1,2-*g*]-quinoline (**13**).

To a stirred boiling mixture of 0.20 g (0.53 mmole) of chloride **11** in 40 ml of absolute ethanol and 20 ml of benzene was added dropwise 10 ml of anhydrous hydrazine over a period of 30 minutes. The resulting mixture was heated under reflux for 20 hours. After cooling to room temperature, the solid was collected by filtration and washed with ethanol to afford 0.18 g (0.49 mmole, 92%) of hydrazine **13** as a yellowish powder, mp 269-270°; ir (potassium bromide): 3354 (NH stretching); ^{1}H nmr (DMSO-d_6): δ 4.95 (br s, 2H, NH$_2$), 7.60-8.00 (m, 5H, ArH), 8.02 (d, $J_{12,13}$ = 4.7 Hz, 1H, H-12), 8.21 (s, 1H, H-7), 8.56 (d, $J_{12,13}$ = 4.7 Hz, 1H, H-13), 8.75 (s, 1H, NH), 9.29 (d, $J_{1,2}$ = 8.2 Hz, 1H, H-1), 9.70 (s, 1H, H-14). This compound was used in the next step without further purification due to its low solubility and stability [2p].

Thieno[3',2':4,5]thieno[2,3-*c*]naphtho[1,2-*g*]quinoline (**5**).

To a boiling mixture of 0.13 g (0.35 mmole) of hydrazine **13** in 12 ml of glacial acetic acid and 3 ml of water was added dropwise 10 ml of 10% aqueous copper sulfate solution. The resulting mixture was heated under reflux for 20 hours. After cooling to room temperature, the mixture was neutralized with 2*N* sodium hydroxide solution. The solid was collected by filtration and washed with water. The dried solid was recrystallized from benzene to afford 0.075g (0.22 mmole, 63%) of **5** as brownish granules, mp 256-258°; tlc (chloroform:ethyl acetate, 4:1) R_f 0.48; ir (potassium bromide): 3089, 3065 (aromatic CH stretching).

Anal. Calcd. for $C_{21}H_{11}NS$: C, 73.87; H, 3.25; N, 4.10. Found: C, 73.75; H, 3.15; N, 3.96.

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