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This paper is dedicated to the memory of Prof. Raymond N. Castle

A previously unknown heterocyclic ring system, naphtho[2',1':4,5]thieno[2,3-*c*]naphtho[2,1-*f*]quinoline (**14**), was synthesized *via* oxidative photocyclization of 3-chloro-*N*-(2-phenanthryl)naphtho[1,2-*b*]thiophene-2-carboxamide (**9**). Further elaboration of the lactam **10** yielded the unsubstituted ring system **14**. Structural confirmation of compound **14** was accomplished by a total assignment of its ¹H and ¹³C nmr spectra utilizing the concerted two-dimensional nmr spectroscopic methods.

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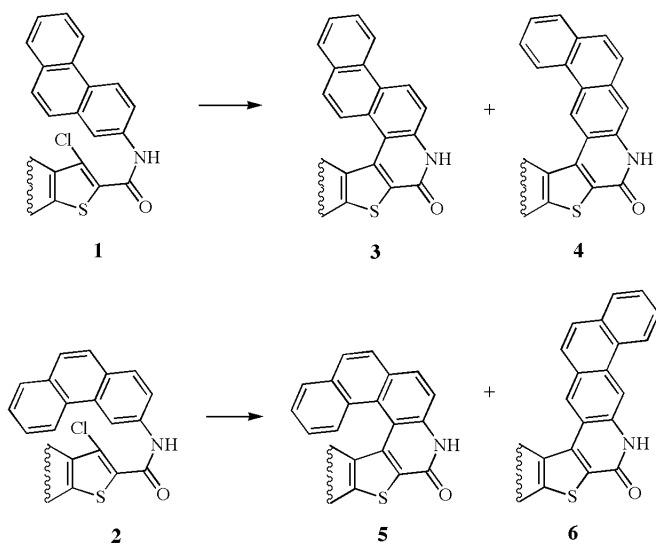
In the course of our studies concerned with nitrogen/sulfur-containing polycyclic heterocycles which occur or are suspected of occurring in coal liquids, coal-derived products and shale oils, we have synthesized a few novel polycyclic heterocyclic ring systems [1]. The crucial step in the synthesis of those ring systems is the oxidative photocyclization of carboxamides such as **1** and **2**. Theoretically **1** and **2** upon photocyclization should yield mixtures of lactams **3/4** and **5/6**, respectively (Scheme 1). In our recent reports [1e,k,p,r,t,v], we have demonstrated that photocyclization of **1** consistently affords a mixture of **3** and **4** with **3** as the major product. On the other hand, the photocyclization of **2** is less predictable, but the angular product **5** is always obtained if not both **5** and **6**. This unusual reactivity prompted us to study a series of photo-

naphtho[2',1':4,5]thieno[2,3-*c*]naphtho[2,1-*f*]quinoline (**14**) and the confirmation of its structure through two-dimensional nmr spectroscopy.

The synthesis of the requisite intermediate, 3-chloro-naphtho[1,2-*b*]thiophene-2-carbonyl chloride (**7**), has been reported [4,5] by refluxing 3-(2-naphthyl)propenoic acid [6] and thionyl chloride in the presence of pyridine [7,8]. When **7** was allowed to react with 2-aminophenanthrene (**8**) [9] in refluxing benzene 3-chloro-*N*-(2-phenanthryl)naphtho[1,2-*b*]thiophene-2-carboxamide (**9**) was obtained in 78% yield. Irradiation of **9** in benzene solution containing triethylamine with a 450 watt medium pressure mercury vapor lamp afforded naphtho[2',1':4,5]thieno[2,3-*c*]naphtho[2,1-*f*]quinolin-8(*7H*)-one (**10**) in 87% yield. A trace of impurity contaminated in **10** was suspected as naphtho[2',1':4,5]thieno[2,3-*c*]naphtho[1,2-*g*]quinolin-9(*8H*)-one (**11**), but it was never realized and detected even after transformation of the lactam **10** into its chloride. Chlorination of **10** with phosphorus oxychloride gave 8-chloro-naphtho[2',1':4,5]thieno[2,3-*c*]naphtho[2,1-*f*]quinoline (**12**) in 50% yield. The structure proof of **10** was achieved by the use of two-dimensional nmr methods after converting it to the corresponding unsubstituted ring system. Thus, upon hydrazination of **12** with anhydrous hydrazine in a refluxing mixture of benzene and ethanol 8-hydrazinonaphtho[2',1':4,5]thieno[2,3-*c*]naphtho[2,1-*f*]quinoline (**13**) was obtained in 99% yield. Treatment of **13** with a 10% copper sulfate solution in refluxing aqueous acetic acid yielded the unsubstituted novel ring system, naphtho[2',1':4,5]thieno[2,3-*c*]naphtho[2,1-*f*]quinoline (**14**) in 55% yield. The synthetic pathway is illustrated in Scheme 2.

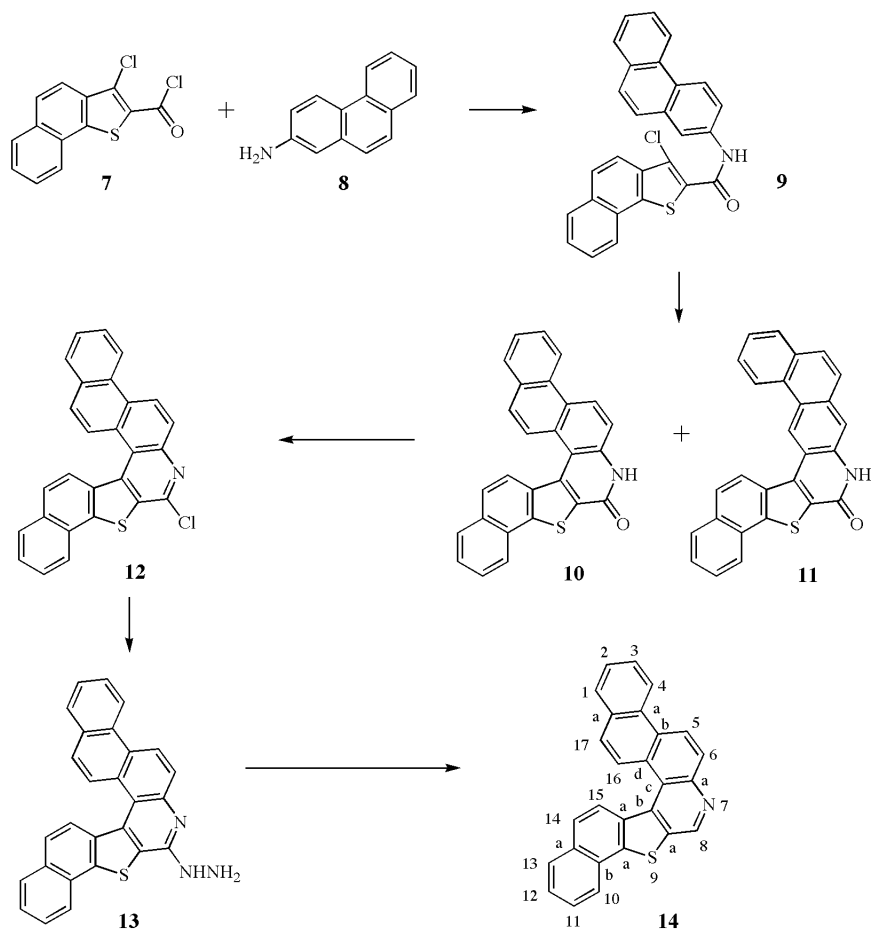
The structure of **14** has been confirmed and achieved by the total assignment of the proton and carbon-13 nmr spectra through the concerted utilization of two-dimensional nmr techniques [10]. The ¹H and ¹³C chemical shifts of **14** are summarized in Table 1.

Scheme 1



cyclization of isomeric phenanthryl anilides **1** and **2**. To this end, we report in this paper the synthesis of a previously unknown heterocyclic ring system, namely,

Scheme 2



In conclusion, we have synthesized and identified the novel polycyclic heterocyclic ring system, naphtho[2',1':4,5]thieno[2,3-*c*]naphtho[2,1-*f*]quinoline (**14**). However, more research is required to shed the light on the predictability of the photocyclization of anilides with structural moiety like **1** or **2**.

EXPERIMENTAL

Melting points were determined on a Thomas-Hoover melting apparatus and are uncorrected. The ir spectra 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 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. Analysis (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 ^1H and ^{13}C spectra of **1** were acquired on a Bruker AMX360 MHz NMR spectrometer operating at an observation frequency of 360.13 MHz for ^1H and 90.56 MHz for ^{13}C . All experiments were

performed using an inverse-geometry 5 mm broad band probe. Pulse widths (90°) for ^1H and ^{13}C were 7.2 and 14.4 μs . The COSY spectra were recorded using the Bruker pulse program (COSY90) [11]. The NOESY experiments were performed using the Bruker pulse program (noesytp) [12]. The HMQC experiments were performed using the Bruker pulse program (invbdgtp) [13] with the BIRD sequence optimized for direct couplings ($165 \text{ Hz } ^1J_{\text{CH}}$). The HMBC spectra were obtained using the Bruker pulse program (inv4plmnd) [14] optimized for $10 \text{ Hz } ^3J_{\text{CH}}$ couplings. The HMQC-TOCSY experiment was acquired using the standard Bruker pulse program (invbmltp) [15].

3-Chloro-*N*-(2-phenanthryl)naphtho[1,2-*b*]thiophene-2-carboxamide (**9**).

A mixture of 2.40 g (8.54 mmoles) of carbonyl chloride **7** [4,5] and 1.65 g (8.54 mmoles) of 2-aminophenanthrene (**8**) [9] in 80 ml of benzene was heated under reflux for 4 hours. After cooling to room temperature, the solid was collected by filtration and recrystallized from *N,N*-dimethylformamide to afford 2.92 g (6.67 mmoles, 78%) of amide **9** as colorless fine needles, mp 284–286°; ir (potassium bromide): 1635 (C=O stretching); ^1H nmr (DMSO- d_6): 150°, δ 7.55–8.25 (m, 12H, ArH), 8.35 (d, $J_{1',3'} = 2.3 \text{ Hz}$, 1H, H1'), 8.65 (m, 2H, ArH), 10.18 (br s, 1H, NH).

Anal. Calcd. for $\text{C}_{27}\text{H}_{16}\text{ClNOS}$: C, 74.05; H, 3.68; N, 3.20; S, 7.32. Found: C, 74.31; H, 3.79; N, 3.28; S, 7.13.

Table 1

¹H and ¹³C NMR Chemical Shift Assignments and Observed Proton-Carbon Multiple-Bond Correlations for Compound **14** in Deuteriochloroform at 298 K at Observation Frequencies of 360.13 and 90.56 MHz, Respectively

Position	δ H	δ C	Two-Bond Correlation	Three-Bond Correlation
1	8.12	128.8		H3, H17
2	7.87	128.6		H4
3	7.90	128.4		H1
4	8.88	123.8		H2
4a		129.5		H1, H3, H5, H17
4b		130.8		H4, H6, H16
5	9.26	129.2		
6	8.51	118.4		
6a		135.0		H5, H8
8	9.80	137.5		
8a		143.7	H8	
9a		148.24		H10, H15
9b		128.1		H11, H13, H14
10	8.41	125.5		H12
11	7.87	128.7		H13
12	7.87	130.5		H10
13	8.12	129.2		H11, H14
13a		133.6		H10, H12, H15
14	7.93	126.6		
15	8.62	123.7		
15a		131.5		H14
15b		132.9		H8, H15
15c		123.1		H6, H16
15d		125.8		H5, H17
16	8.84	125.0		
17	8.10	128.0		H1
17a		133.1		H2, H4, H16

Naphtho[2',1':4,5]thieno[2,3-*c*]naphtho[2,1-*f*]quinolin-8(7*H*)-one (**10**).

A mixture of 0.50 g (1.14 mmoles) of amide **9** and 0.115 g (1.14 mmoles) of triethylamine in 480 ml of benzene was irradiated with a 450 watt Hanovia medium pressure mercury vapor lamp for 4 hours. A slow stream of air was passed through the solution during the course of the reaction. The precipitate was collected by filtration and washed with water to afford 0.40 g (1.0 mmole, 87%) of lactam **10**, mp >300°; ir (potassium bromide): 1653 (C=O stretching); ¹H nmr (DMSO-*d*₆): δ 7.70-9.13 (m, ArH). This compound was used in the next step without further purification because of its low solubility.

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

A mixture of 1.98 g (4.93 mmoles) of lactam **10** and 80 ml of phosphorus oxychloride was heated at 100-110° for 4 hours. After cooling to room temperature, the mixture was poured into 500 ml of ice water with vigorous stirring. The precipitate was collected by filtration, washed with water, and then dried. The solid was recrystallized from benzene to obtain 1.04 g (2.47 mmoles, 50%) of chloride **12** as colorless granules, mp 314-316°; tlc (dichloromethane) R_f 0.73; ir (potassium bromide): 3047 (aromatic CH stretching); ¹H nmr (deuteriochloroform): 50°, δ 7.63-8.06 (m, 8H, ArH), 8.24-8.39 (m, 2H, ArH), 8.57 (d, J = 9.0 Hz, 1H, ArH), 8.74-9.02 (m, 3H, ArH).

Anal. Calcd. for C₂₇H₁₄CINS: C, 77.22; H, 3.36; N, 3.34; S, 7.64. Found: C, 76.95; H, 3.54; N, 3.19; S, 7.46.

8-Hydrazinonaphtho[2',1':4,5]thieno[2,3-*c*]naphtho[2,1-*f*]quinoline (**13**).

To a mixture of 0.50 g (1.19 mmoles) of chloride **12** in 30 ml of boiling ethanol and 15 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 15 hours. After cooling to room temperature, the solid was collected by filtration, washed with ethanol, and dried to give 0.49 g (1.18 mmoles, 99%) of hydrazine derivative **13** as yellow crystals, mp > 280° dec; tlc (dichloromethane/ethyl acetate 4:1) R_f 0.63; ¹H nmr (deuteriochloroform and two drops of deuterated trifluoroacetic acid): δ 7.36 (m, 10H, ArH), 8.34 (d, J = 9.1 Hz, 1H, ArH), 8.49 (d, J = 9.1 Hz, 1H, ArH), 8.77 (d, J = 8.1 Hz, 1H, ArH), 9.03 (d, J = 9.0 Hz, 1H, ArH). This compound was used in the next reaction without further purification due to its low solubility and thermal instability.

Naphtho[2',1':4,5]thieno[2,3-*c*]naphtho[2,1-*f*]quinoline (**14**).

To a boiling mixture of 0.15 g (0.36 mmole) of hydrazine derivative **13** in 5 ml of water and 15 ml of glacial acetic acid was added dropwise 10 ml of 10% copper solution and the mixture was heated under reflux for 20 hours. After cooling to room temperature, the mixture was neutralized with a 2 *N* sodium hydroxide solution. The solid was collected by filtration and washed with water. The dried solid was dissolved in 10 ml of chloroform and was chromatographed over silica gel eluting with a dichloromethane/ethyl acetate (4:1) mixture to give 0.076 g (0.20 mmole, 55%) of **14** as yellowish needles, mp > 280°; tlc (dichloromethane/ethyl acetate 4:1) R_f 0.78; ir (potassium bromide): 3044 (aromatic CH stretching).

Anal. Calcd. for C₂₇H₁₅NS: C, 84.13; H, 3.92; N, 3.63. Found: C, 83.93; H, 3.97; N, 3.50.

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