The Synthesis of Novel Polycyclic Heterocyclic Ring Systems *via* Photocyclization. **15** [1]. [1]Benzothieno[3',2':4,5]thieno[2,3-*c*]quinoline, [1]Benzothieno[3',2':4,5]thieno[2,3-*c*][1,2,4]triazolo[4,3-*a*]quinoline, [1]Benzothieno[3',2':4,5]thieno[2,3-*c*]tetrazolo[1,5-*a*]quinoline, Thieno[3',2':4,5]thieno[2,3-*c*][1,2,4]triazolo[4,3-*a*]quinoline, and Thieno[3',2':4,5]thieno[2,3-*c*]tetrazolo[1,5-*a*]quinoline

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The synthesis of five novel polycyclic heterocyclic ring systems *via* photocyclization is reported. These are [1]benzothieno[3',2':4,5]thieno[2,3-*c*]quinoline (**1**), [1]benzothieno[3',2':4,5]thieno[2,3-*c*][1,2,4]triazolo[4,3-*a*]quinoline (**2**), [1]benzothieno[3',2':4,5]thieno[2,3-*c*]tetrazolo[1,5-*a*]quinoline (**3**), thieno[3',2':4,5]thieno[2,3-*c*][1,2,4]triazolo[4,3-*a*]quinoline (**4**), and thieno[3',2':4,5]thieno[2,3-*c*]tetrazolo[1,5-*a*]quinoline (**5**). The total assignments of the ^1H and ^{13}C nmr spectra of **1**, **4**, **5**, and **15** were determined by utilizing two-dimensional nmr methods.

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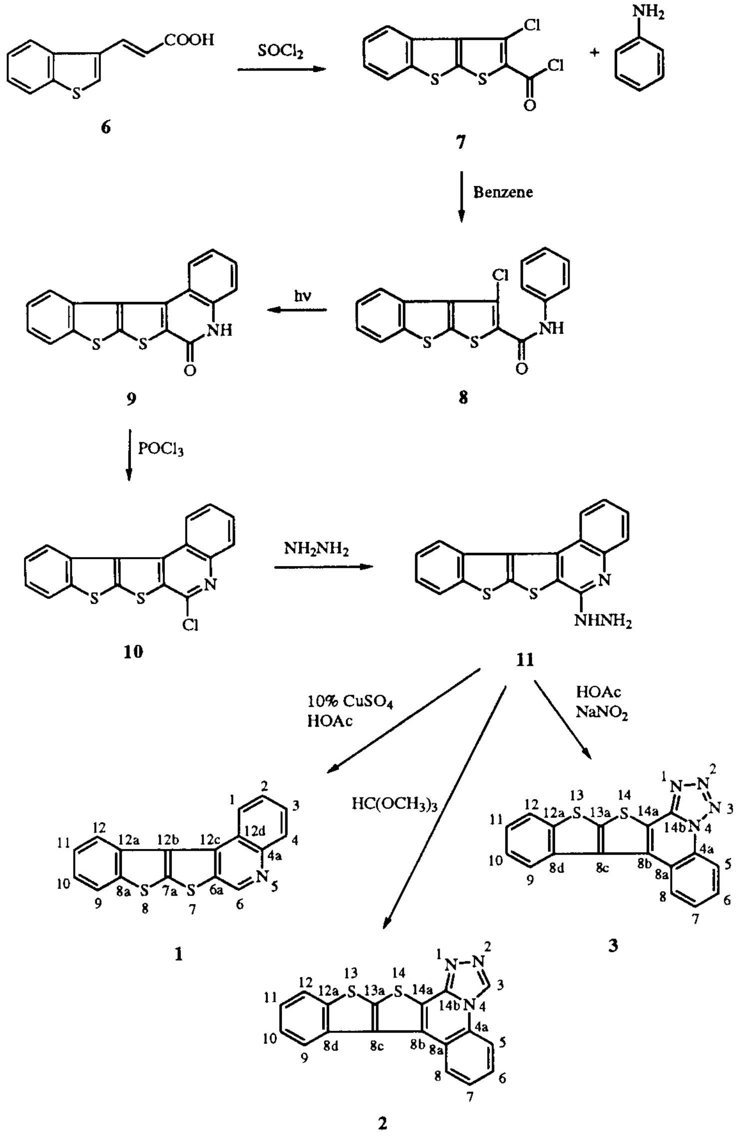
The utilization of oxidative photocyclization of stilbenes, anilides and their analogs for the synthesis of polycyclic aromatic hydrocarbons and heterocycles has been demonstrated to be extremely useful [1,3]. As a continuing study of novel polycyclic heterocyclic ring systems [1] we now present the synthesis of five previously unknown ring systems, [1]benzothieno[3',2':4,5]thieno[2,3-*c*]quinoline (**1**), [1]benzothieno[3',2':4,5]thieno[2,3-*c*][1,2,4]triazolo[4,3-*a*]quinoline (**2**), [1]benzothieno[3',2':4,5]thieno[2,3-*c*]tetrazolo[1,5-*a*]quinoline (**3**), thieno[3',2':4,5]thieno[2,3-*c*][1,2,4]triazolo[4,3-*a*]quinoline (**4**), and thieno[3',2':4,5]thieno[2,3-*c*]tetrazolo[1,5-*a*]quinoline (**5**) *via* photocyclization.

The synthetic pathway to compounds **1**, **2**, and **3** is illustrated in Scheme 1. The carbonyl chloride **7** was obtained by treatment of benzo[b]thiophene-3-acrylic acid (**6**) [4] with thionyl chloride in chlorobenzene in the presence of pyridine and piperidine [5]. The reaction of aniline with **7** in benzene solution afforded 3-chloro-*N*-phenyl[1]benzothieno[2,3-*c*]thiophene-2-carboxamide (**8**) in 92% yield. Photocyclization of **8** in benzene solution containing triethylamine provided [1]benzothieno[3',2':4,5]thieno[2,3-*c*]quinolin-6(5*H*)-one (**9**) in 82% yield. Chlorination of **9** was achieved by refluxing in phosphorus oxychloride to give 6-chloro[1]benzothieno[3',2':4,5]thieno[2,3-*c*]quinoline (**10**) in 81% yield. Attempts of catalytic dechlorination of **10** with 10% Pd-C under various reaction conditions met with failure as reported previously for the synthesis of the unsubstituted ring system, thieno[3',2':4,5]thieno[2,3-*c*]quinoline (**15**) [1a].

In view of our previous reports [1a-f,1i-l,1n], catalytic dechlorination of the chlorides often resulted in incomplete reaction which was attributed to the low solubility of the chlorides in the reaction media and thus gave low yields after laborious separation. Although a one-step dechlorination for chloronitropyridines was reported by Smith, [6], it was found that when 6-chloro[1]benzothieno[2,3-*c*]quinoline [7] was allowed to react with benzoic acid and copper powder at 150-170°, only a trace of [1]benzothieno[2,3-*c*]quinoline [7] and the unreacted starting material were obtained as indicated by tlc analysis. Therefore, an indirect two-step dechlorination *via* hydrazination/dehydrazination of the chloride was adapted [1g-h,1m,8] to complete the synthesis of the unsubstituted ring systems. The advantage of this process is that, in addition to the unsubstituted ring systems, one may utilize the hydrazino intermediates to synthesize triazoles [1g-h,7] and tetrazoles [7]. Thus, when 6-hydrazino[1]benzothieno[2,3-*c*]quinoline (**12**) [7] and 6-hydrazinothieno[3',2':4,5]thieno[2,3-*c*]quinoline (**13**) were treated with 10% copper sulfate solution in aqueous acetic acid, the unsubstituted [1]benzothieno[2,3-*c*]quinoline (**14**) and thieno[3',2':4,5]thieno[2,3-*c*]quinoline (**15**) were obtained in 69 and 65% yields, respectively. The hydrazino derivative **13** in refluxing triethyl orthoformate and ethanol afforded thieno[3',2':4,5]thieno[2,3-*c*][1,2,4]triazolo[4,3-*a*]quinoline (**4**) in 58% yield, whereas the addition of sodium nitrite to a mixture of **13** and 50% aqueous acetic acid resulted in a 60% yield of thieno[3',2':4,5]thieno[2,3-*c*]tetrazolo[1,5-*a*]quinoline (**5**) (Scheme 2).

Likewise, the hydrazino derivative **11**, obtained in 81% yield by refluxing **10** with anhydrous hydrazine, was refluxed with aqueous acetic acid in the presence of 10% copper sulfate to yield the unsubstituted ring system **1** in 74% yield (Scheme 1). The triazole **2** was obtained in 66% yield when the hydrazino derivative **11** was allowed to react with trimethyl orthoformate in refluxing ethanol. Upon treatment of **11** with sodium nitrite in 50% acetic acid the tetrazole **3** was obtained in 50% yield.

Scheme 1

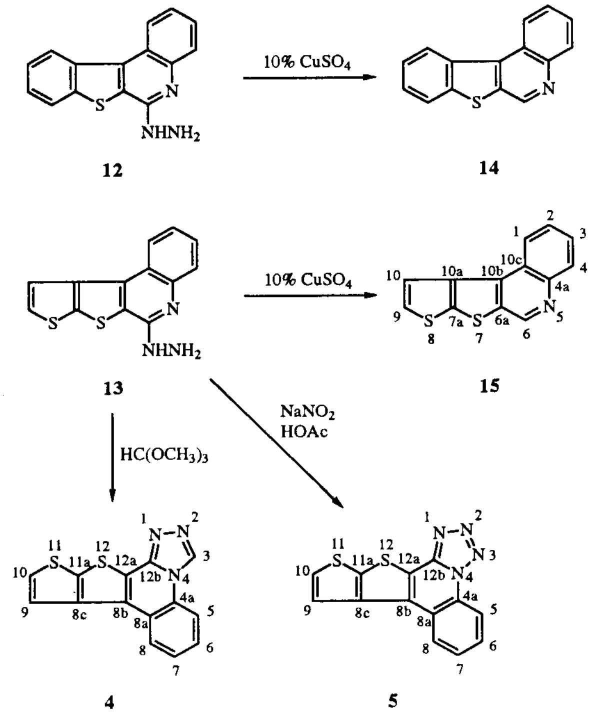


NMR Spectroscopy.

The unequivocal assignments of ^{1}H and ^{13}C spectra of **1** were achieved by concerted usage of HMQC [9], HMBC [10], and NOESY [11]. Although direct (one bond, $^1J_{CH}$) heteronuclear correlations were established for **1** utilizing the HMQC pulse sequence [9], it was necessary to orient the two four-spin systems relative to each other and to assign the quaternary carbon resonances.

The isolated spin, H6, serves as a convenient entry point and leads to the assignment of the four-spin system of H1, H2, H3, and H4 (Figure 1) with the assistance of the NOESY spectrum [11] (Figure 2), which provides very useful connectivities among H1, H2, H3, and H4. Thus, the assignment of the quinoline moiety can be accomplished by concerted usage of HMQC, HMBC, and NOESY experiments.

Scheme 2



The connectivity of the four-spin system in the benzo[*b*]thiophene moiety may be readily identified, but its orientation can only be established by the observation of the nuclear Overhauser effect shown in the NOESY spectrum (Figure 2), which is attributed to the proximity of H1/H12 on the opposite sides of the helical bay region of **1**. Thus, the assignment of H12 orients the four-spin system in the benzo[*b*]thiophene moiety (Figure 3) and thereby completes the spectral assignment of **1** (Table 1).

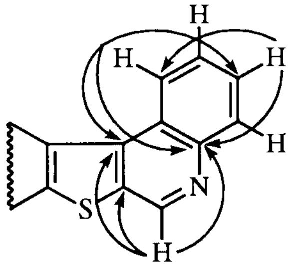


Figure 1. Diagram of long-range correlations observed on the HMBC spectrum for the quinoline moiety of **1**.

Likewise, the complete assignments of ^{1}H and ^{13}C spectra of **15** were achieved by the concerted usage of COSY [12], NOESY, HMQC and HMBC experiments (Table 2). Both differential nuclear Overhauser effect and NOESY experiments indicated a strong nOe between the proton resonating at 8.59 and 8.04 ppm accounting for the close proximity of H1 and H10, respectively. The COSY

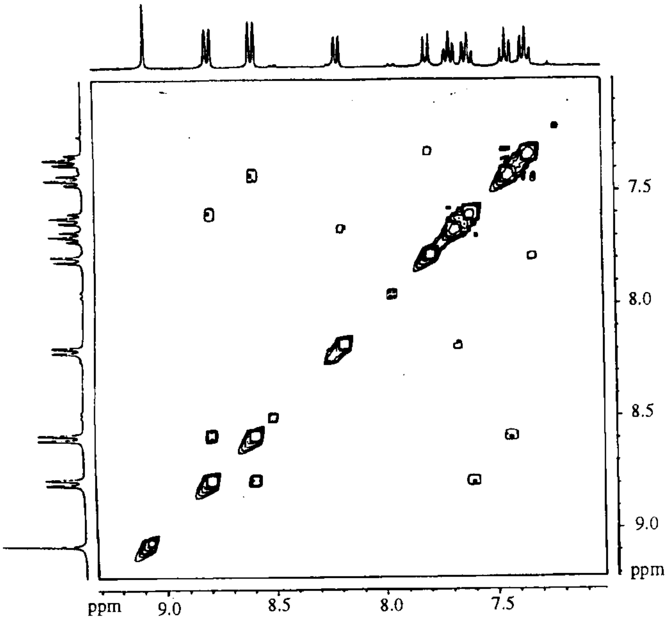


Figure 2. The NOSEY spectrum of **1** recorded in deuteriochloroform at an observation frequency of 360.13 MHz.

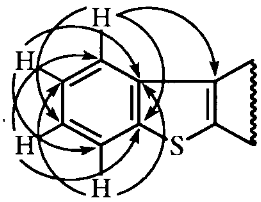


Figure 3. Diagram of long-range correlations observed on the HMBC spectrum for the benzo[*b*]thiophene moiety of **1**.

Table 1

^{1}H and ^{13}C Chemical Shifts of [1]Benzothieno[3',2':4,5]thieno[2,3-*c*]quinoline (**1**)

Position	δH	δC	Long-range Correlation
1	8.79	125.3	H3
2	7.61	125.9	H4
3	7.70	128.0	H1
4	8.20	130.2	H2
4a		145.7	H1, H3, H6
6	9.07	144.7	
6a		136.4	H6
7a		126.9	
8a		143.8	H10, H12
9	7.80	123.5	H11
10	7.36	124.5	H12
11	7.45	124.8	H9
12	8.59	123.2	H10
12a		132.8	H9, H11
12b		136.6	H12
12c		135.8	H1, H6
12d		123.9	H2, H4

Table 2

^{1}H and ^{13}C Chemical Shifts of Thieno[3',2':4,5]thieno[2,3-*c*]quinoline (**15**)

Position	δH	δC	Long-range Correlation
1	8.59	122.9	H3
2	7.73	126.6	H4
3	7.78	127.8	H1
4	8.28	129.8	H2
4a		144.7	H1, H3, H6
6	9.28	144.8	
6a		136.7	H6
7a		142.6	H9, H10
9	7.66	129.3	H10
10	8.04	121.1	H9
10a		140.8	H9, H10
10b		133.4	H1, H6
10c		123.5	H2, H4

Table 3

^{1}H and ^{13}C Chemical Shifts of Thieno[3',2':4,5]thieno[2,3-*c*][1,2,4]triazolo[4,3-*a*]quinoline (**4**)

Position	δH	δC	Long-range Correlation
3	9.93	136.2	
4a		128.6	H1, H3
5	8.48	116.8	H7
6	7.76	128.2	H8
7	7.69	126.2	H5
8	8.64	124.5	H6
8a		119.5	H5, H7
8b		126.9	H8
8c		139.7	H9, H10
9	8.15	120.2	H10
10	7.92	131.1	H9
11a		141.1	H9, H10
12a		125.5	
12b		143.8	H3

Table 4

^{1}H and ^{13}C Chemical Shifts of Thieno[3',2':4,5]thieno[2,3-*c*]tetrazolo[1,5-*a*]quinoline (**5**)

Position	δH	δC	Long-range Correlation
4a		129.1	H6, H8
5	8.75	117.8	H7
6	7.85	129.6	H8
7	7.79	128.1	H5
8	8.56	124.6	H6
8a		120.7	H7
8b		130.6	H8, H9
8c		141.5	H9, H10
9	7.93	120.3	H10
10	7.69	130.7	H9
11a		143.2	H9, H10
12a		124.1	
12b		144.7	

spectrum of **15** provides further support of the assignment of H1 and H10 by exhibiting a minor long-range correlation between H1 and H10. The only ambiguous assignment is C7a and C10a since both quaternary carbons exhibit correlations with H9 and H10. However, in consideration of the structure of **15** we expect C10a is more shielded than C7a because C10a is situated in the helical bay region. Thus, we temporarily assign the carbon resonating at 142.6 ppm as C7a and 140.8 ppm as C10a.

The total assignments of ^{1}H and ^{13}C spectra of **4** and **5** were carried out in a manner as described above (Tables 3 and 4, respectively).

In conclusion, we have synthesized five novel heterocyclic ring systems **1-5**. The total assignments of the ^{1}H and ^{13}C spectra of **1**, **3**, **4** and **15** were accomplished by concerted utilization of COSY, HMQC, HMBC, NOESY and differential nOe techniques.

EXPERIMENTAL

Melting points were determined on a Thomas-Hoover melting point 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 ^{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. Analysis (tlc) were performed on Sigma precoated silica gel plates containing a fluorescent indicator. The mass spectra were determined on a Hewlett-Packard model 5980A mass spectrometer. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona.

The ^{1}H and ^{13}C spectra of **1**, **4**, **5** and **15** were acquired on a Bruker AMX 360 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 6.8 and 13.6 µsec, respectively. The COSY spectra were recorded using the Bruker pulse program (*cosy90*) [12]. The HMQC experiments were performed using the Bruker pulse program (*invbdgtp*) with the BIRD sequence optimized for direct couplings (165 Hz $^1J_{CH}$) [9]. The HMBC spectra were obtained using the Bruker pulse program (*inv4lplrnd*) [10] optimized for 10 Hz $^3J_{CH}$ couplings. The NOESY experiments were performed using the Bruker pulse program (*noesytp*) [11].

3-Chloro[1]benzothieno[2,3-*b*]thiophene-2-carbonyl Chloride (**7**).

To a mixture of 15.0 g (73.4 mmoles) of benzo[*b*]thiophene-3-acrylic acid (**6**) [4], 0.6 ml of pyridine, and 70 ml of chlorobenzene in an ice bath was added dropwise 26 ml of thionyl chloride [5]. The resulting mixture was heated at 120-125° for 72 hours. The solvent and thionyl chloride were removed by distillation under reduced pressure. The residue was triturated with hexane and filtered. The solid was recrystallized from benzene to afford 11.2 g (39.0 mmoles, 53%) of chloride **7** as fine yellow needles, mp 174-175°; ^{1}H nmr (deuteriochloroform): δ 7.50 (m, 2H, H-5 and H-6), 7.83 (m, 1H, H-7), 8.49 (m, 1H, H-4); ms: m/z 291.9 (M$^+$ + 6, 0.3), 290.9 (M$^+$ + 5, 0.5), 289.9 (M$^+$ + 4, 4.3), 288.9 (M$^+$ + 3, 2.6), 287.9 (M$^+$ + 2, 19), 286.9 (M$^+$ + 1, 4.0), 285.9 (M$^+$, 25.0), 252.9 (41.4), 250.9 (M$^+$ - Cl, 100). This compound was converted to its methyl ester for elemental analysis. Thus, a mixture of 1.0 g (3.48 mmoles) of **7** and 50 ml of methanol was refluxed for an hour. Upon removal of solvent the residue was recrystallized from methanol to yield 0.8 g (2.83 mmoles, 81%) of yellowish crystals, mp 137-138°; ir (potassium bromide): 3044 (aromatic CH stretching), 2960 (aliphatic CH stretching), 1725 (C=O stretching), 1381 (CH bending of CH_3), 1245, 1077 (C-O stretching); ^{1}H nmr (deuteriochloroform): δ 3.90 (s, 3H, CH_3), 7.35 (m, 2H, H-5 and H-6) 7.70 (m, 1H, H-7), 8.48 (m, 1H, H-4); ms: m/z 286.0 (M$^+$ + 4, 3.2), 284.9 (M$^+$ + 3, 5.7), 283.9 (M$^+$ + 2, 41.1), 282.9 (M$^+$ + 1, 14.1), 281.9 (M$^+$, 100), 252.9 (35.7), 250.9 (M$^+$ - OCH_3, 86.7).

Anal. Calcd. for $C_{12}H_7ClO_2S_2$: C, 50.97; H, 2.50; S, 22.68. Found: C, 50.81; H, 2.66; S, 22.78.

3-Chloro-*N*-phenyl[1]benzothieno[2,3-*b*]thiophene-2-carboxamide (**8**).

A mixture of 2.87 g (10.0 mmoles) of **7** and 0.93 g (10.0 mmoles) of aniline in 50 ml of benzene was heated under reflux for four hours. After cooling to room temperature the precipitate was collected by filtration and recrystallized from benzene to afford 3.16 g (9.19 mmoles, 92%) of **8** as colorless needles, mp 171-172°; ir (potassium bromide): 3317 (NH stretching), 3057, 3037 (aromatic CH stretching), 1635 (C=O stretching); ^{1}H nmr (deuteriochloroform/DMSO-d$_6$): δ 7.15 (t, J = 7.1 Hz, 1H, H-4'), 7.38 (t, J = 7.7 Hz, 2H, H-3' and H-5'), 7.48-7.57 (m, 2H, H-5 and H-6), 7.72 (d, J = 8.3 Hz, 2H, H-2' and H-6'), 8.12 (d, $J_{6,7}$ = 7.9 Hz, 1H, H-7), 8.44 (d, $J_{4,5}$ = 8.0 Hz, 1H, H-4), 10.31 (s, 1H, NH); ms: m/z 345.0 (M$^+$ + 2, 16.3), 344.0 (M$^+$ + 1, 6.9), 343.0 (M$^+$, 38.7), 252.9 (45.1), 250.9 (M$^+$ - NHC_6H_5, 100), 44.0 (52.5).

Anal. Calcd. for $C_{17}H_{10}ClNOS_2$: C, 59.38; H, 2.93; N, 4.07; S, 18.65. Found: C, 59.63; H, 3.18; N, 4.17; S, 18.53.

[1]Benzothieno[3',2':4,5]thieno[2,3-*c*]quinolin-6(5*H*)-one (**9**).

A solution of 0.5 g (1.45 mmoles) of **8** and 0.15 g of triethylamine in 480 ml of benzene was irradiated with a 450 watt Hanovia medium pressure mercury vapor lamp for four hours. During the course of the reaction, a slow stream of air was passed through the solution. The solid was collected by filtration and washed with water to give 0.37 g (1.20 mmoles, 82%) of **9**, mp >280°; ir (potassium bromide): 3129 (NH stretching), 3050 (aromatic CH stretching), 1653 (C=O stretching); ^{1}H nmr (deuteriochloroform/DMSO-d$_6$): δ 7.41-7.63 (m, 5H, H-2, H-3, H-9, H-10 and H-11), 8.05 (d, $J_{3,4}$ = 8.0 Hz, 1H, H-4), 8.71 (d, $J_{11,12}$ = 8.1 Hz, 1H, H-12), 8.73 (d, $J_{1,2}$ = 7.8 Hz, 1H, H-1), 11.94 (br s, 1H, NH); ms: m/z 309.7 (M$^+$ + 3, 1.7), 308.7 (M$^+$ + 2, 12.2), 307.7 (M$^+$ + 1, 22.5), 306.7 (M$^+$, 100), 277.7 (16.9). This compound was used in the next step without further purification because of low solubility.

6-Chloro[1]benzothieno[3',2':4,5]thieno[2,3-*c*]quinoline (**10**).

A mixture of 2.0 g (6.51 mmoles) of **9** and 100 ml of phosphorus oxychloride was heated under reflux for four hours. After cooling in an ice bath, the mixture was poured into 800 ml of ice water very slowly with vigorous stirring. The precipitate was collected by filtration and washed with water, and then recrystallized from benzene to yield 1.72 g (5.28 mmoles, 81%) of **10** as colorless crystals, mp 187-189°; tlc (benzene) R_f 0.62; ir (potassium bromide): 3062 (aromatic CH stretching); ^{1}H nmr (deuteriochloroform/DMSO-d$_6$): δ 7.43-7.48 (m, 1H, H-10), 7.53-7.57 (m, 1H, H-11), 7.69-7.79 (m, 2H, H-2 and H-3), 7.91 (d, $J_{9,10}$ = 7.9 Hz, 1H, H-9), 8.17 (dd, $J_{3,4}$ = 8.4 Hz, $J_{2,4}$ = 1.0 Hz, 1H, H-4), 8.70 (d, $J_{11,12}$ = 8.1 Hz, 1H, H-12), 8.93 (d, $J_{1,2}$ = 8.0 Hz, 1H, H-1).

Anal. Calcd. for $C_{17}H_8ClNS_2$: C, 62.66; H, 2.48; N, 4.30; S, 19.68. Found: C, 62.78; H, 2.47; N, 4.36; S, 19.55.

6-Hydrazino[1]benzothieno[3',2':4,5]thieno[2,3-*c*]quinoline (**11**).

To a boiling mixture of 1.54 g (4.73 mmoles) of **10** in 100 ml of absolute ethanol and 50 ml of benzene was added dropwise 30 ml of anhydrous hydrazine over a period of one hour. The mixture was heated at 100-110° for 24 hours. After cooling to room temperature the solid was collected by filtration, washed with ethanol and recrystallized from ethanol to obtain 1.37 g (4.26 mmoles, 90%) of **11** as pinkish needles, mp 222-225°; tlc (methylene chloride:ethyl acetate, 4:1) R_f 0.48; ir (potassium bromide): 3343, 3201 (NH_2 stretching), 3029 (aromatic CH stretching), 1630 (NH bending); ^1H nmr (deuteriochloroform/DMSO-d_6): δ 4.88 (s, 2H, NH_2), 7.42 (t, $J_{9,10} = J_{10,11} = 8.0$ Hz, 1H, H-10), 7.50 (t, $J_{10,11} = J_{11,12} = 8.0$ Hz, 1H, H-11), 7.56-7.64 (m, 2H, H-2 and H-3), 7.71 (d, $J_{9,10} = 8.0$ Hz, 1H, H-9), 8.17 (d, $J_{3,4} = 8.1$ Hz, 1H, H-4), 8.52 (s, 1H, NH), 8.75 (d, $J_{11,12} = 8.0$ Hz, 1H, H-12), 8.76 (d, $J_{1,2} = 8.0$ Hz, 1H, H-1).

Anal. Calcd. for $C_{17}H_{11}N_3S_2$: C, 63.53; H, 3.45; N, 13.07. Found: C, 63.52; H, 3.50; N, 12.89.

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

To a boiling mixture of 0.3 g (0.93 mmole) of **11** in 10 ml of water and 15 ml of glacial acetic acid was added dropwise 15 ml of 10% copper sulfate solution. The mixture was heated under reflux for 24 hours. After cooling to room temperature the mixture was basified with 2*N* sodium hydroxide solution. The solid was collected by filtration, washed with water, dried, and recrystallized from benzene/cyclohexane mixture to give 0.2 g (0.69 mmole, 74%) of **1** as off-white granules, mp 180-182°; tlc (methylene chloride:ethyl acetate, 4:1) R_f 0.79; ir (potassium bromide): 3060 (aromatic CH stretching).

Anal. Calcd. for $C_{17}H_9NS_2$: C, 70.07; H, 3.11; N, 4.81. Found: C, 70.27; H, 3.01; N, 5.02.

[1]Benzothieno[3',2':4,5]thieno[2,3-*c*][1,2,4]triazolo[4,3-*a*]quinoline (**2**).

A mixture of 0.25 g (0.78 mmole) of **11** in 40 ml of absolute ethanol and 15 ml of trimethyl orthoformate was heated under reflux for 24 hours. After cooling the mixture was evaporated to dryness *in vacuo* and the solid was recrystallized from benzene to afford 0.17 g (0.51 mmole, 66%) of **2** as off-white crystals, mp >310°; tlc (methylene chloride:ethyl acetate, 4:1) R_f 0.19; ir (potassium bromide): 3073 (aromatic CH stretching); ^1H nmr (deuteriochloroform): δ 7.47 (m, 1H, H-11), 7.56 (m, 1H, H-10), 7.71-7.76 (m, 2H, H-6 and H-7), 7.96 (d, $J_{11,12} = 8.2$ Hz, 1H, H-12), 8.08 (m, 1H, H-9), 8.68 (d, $J_{7,8} = 8.0$ Hz, 1H, H-8), 9.05 (m, 1H, H-5), 9.23 (s, 1H, H-3).

Anal. Calcd. for $C_{18}H_9N_3S_2$: C, 65.23; H, 2.74; N, 12.68. Found: C, 65.42; H, 2.80; N, 12.47.

[1]Benzothieno[3',2':4,5]thieno[2,3-*c*]tetrazolo[1,5-*a*]quinoline (**3**).

To a mixture of 0.25 g (0.78 mmole) of **11** in 16 ml of 50% glacial acetic acid in an ice bath was added dropwise a solution of 0.16 g (2.32 mmoles) of sodium nitrite in 8 ml of water with vigorous stirring. The mixture was allowed to warm up to room temperature and stirred for 12 hours. The solid was collected by filtration, washed with water, and recrystallized from benzene to afford 0.13 g (0.39 mmole, 50%) of **3** as brownish cubic crystals, mp 247-250° dec; tlc (methylene chloride) R_f 0.48; ir (potassium bromide): 3057 (aromatic CH stretching); ^1H nmr (deuteriochloroform): δ 7.46 (m, 1H, H-11), 7.52 (m, 1H, H-10), 7.79 (m, 1H, H-7), 7.85 (m, 1H, H-6), 7.90 (dd, $J_{11,12} = 7.5$ Hz, $J_{10,12} = 1.2$ Hz, 1H, H-12), 8.53 (d, $J_{9,10} = 8.0$ Hz, 1H, H-9), 8.74 (dd, $J_{7,8} = 8.2$ Hz, $J_{6,8} = 1.2$ Hz, 1H, H-8), 8.93 (d, $J_{5,6} = 8.1$ Hz, 1H, H-5).

Anal. Calcd. for $C_{17}H_8N_4S_2$: C, 61.43; H, 2.43; N, 16.86. Found: C, 61.55; H, 2.28; N, 16.98.

[1]Benzothieno[2,3-*c*]quinoline (**14**).

A boiling solution of 0.18 g (0.68 mmole) of **12** [7] in 4 ml of water and 2 ml of glacial acetic acid was added dropwise with 3 ml of a 10% copper sulfate solution. The mixture was heated under reflux for two hours. After the mixture was basified with 2*N* sodium hydroxide solution, the mixture was extracted with methylene chloride (50 ml x 3), and dried over anhydrous magnesium sulfate. Upon removal of the solvent *in vacuo* the solid was recrystallized from hexane to give 0.11 g (0.47 mmole, 69%) of **14** as colorless prisms, mp 118-120° (lit [7] mp 118-119°). This compound has identical ir and nmr spectral data to the authentic sample [7].

6-Hydrazinothieno[3',2':4,5]thieno[2,3-*c*]quinoline (**13**).

To a stirred suspension of 1.0 g (3.62 mmoles) of 6-chlorothieno[3',2':4,5]thieno[2,3-*c*]quinoline [1a] in 50 ml of boiling ethanol was added dropwise 8.0 ml of anhydrous hydrazine over a period of 30 minutes. The resulting mixture was heated under reflux for six hours. After cooling to room temperature the solution was evaporated to dryness *in vacuo* and the solid was recrystallized from ethanol to yield 0.86 g (3.17 mmoles, 88%) of **13** as light orange needles, mp 215-218°; tlc (methylene chloride) R_f 0.076; ir (potassium bromide): 3284 (NH stretching), 3037 (aromatic CH stretching), 1630 (NH bending); ^1H nmr (DMSO-d_6): δ 4.87 (br s, 2H, NH_2), 7.28-7.73 (m, 3H, H-2, H-3, and H-4), 7.87 (d, $J_{9,10} = 5.4$ Hz, 1H, H-9), 8.19 (d, $J_{9,10} = 5.4$ Hz, 1H, H-10), 8.46-8.55 (m and br s, 2H, H-1 and NH).

Anal. Calcd. for $C_{13}H_9N_3S_2$: C, 57.54; H, 3.34; N, 15.49. Found: C, 57.37; H, 3.58; N, 15.36.

Thieno[3',2':4,5]thieno[2,3-*c*]quinoline (**15**).

To a refluxing solution of 0.26 g (0.96 mmole) of **13** in 6 ml of water and 3 ml of glacial acetic acid was treated with 4.5 ml of a 10% copper sulfate solution. The mixture was heated under reflux for two hours. After cooling to room temperature, the mixture was basified with 2*N* sodium hydroxide solution. The mixture was extracted with methylene chloride (100 ml x 3), and dried over anhydrous magnesium sulfate. Upon removal of the solvent *in vacuo* the solid was recrystallized from benzene to afford 0.15 g (0.62 mmole, 65%) of **15** as off-white crystals, mp 203-204°; tlc (benzene) R_f 0.087; ir (potassium bromide): 3068 (aromatic CH stretching).

Anal. Calcd. for $C_{13}H_7NS_2$: C, 64.70; H, 2.92; N, 5.80. Found: C, 64.75; H, 2.82; N, 5.73.

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

A mixture of 0.25 g (0.92 mmole) of **13** and 15 ml of triethyl orthoformate was heated at 95-100° for 12 hours. After cooling to room temperature the solid was collected by filtration and recrystallized from benzene to afford 0.15 g (0.53 mmole, 58%) of **4** as yellow prisms, mp >300°; tlc (chloroform:ethyl acetate, 4:1) R_f 0.12; ir (potassium bromide): 3086 (aromatic CH stretching).

Anal. Calcd. for $C_{14}H_7N_3S_2$: C, 59.76; H, 2.51; N, 14.94.

Found: C, 59.79; H, 2.46; N, 14.78.

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

To a solution of 0.27 g (1.0 mmole) of **13** in 10 ml of 50% aqueous acetic acid in an ice-salt bath was added dropwise a solution of 0.1 g (1.45 mmoles) of sodium nitrite in 5 ml of water. The reaction mixture was allowed to warm up to room temperature slowly. The mixture was stirred at room temperature for additional four hours. The solid was collected by filtration, washed with water, dried, and then recrystallized from benzene to yield 0.17 g (0.60 mmole, 60%) of **5** as brownish crystals, mp 254-256° dec; tlc (chloroform) R_f 0.41; ir (potassium bromide): 3098 (aromatic CH stretching).

Anal. Calcd. for $C_{13}H_6N_4S_2$: C, 55.30; H, 2.14; N, 19.85. Found: C, 55.29; H, 2.26; N, 19.57.

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