Synthesis of Benzo[*b*]thieno- and Benzo[*b*]furano-[2,3-*a*]pyrrolo[3,4-*c*]carbazole-5-, -7- and -5,7-dione

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Benzo[*b*]thieno[2,3-*a*]pyrrolo[3,4-*c*]carbazoles and benzo[*b*]furano[2,3-*a*]pyrrolo[3,4-*c*]carbazoles were prepared from 2-(2-benzo[*b*]thieno)- (**8**) and 2-(2-benzo[*b*]furano)-3-[3-(2,5-dioxo-1*H*-pyrrolidinyl)]indole (**9**) by a palladium(II)acetate/tetrachloro-1,4-benzoquinone oxidative A-E ring closure.

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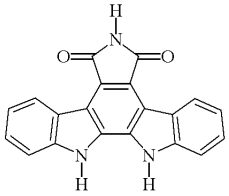
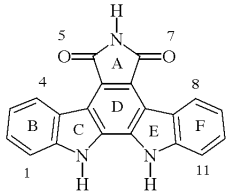
Introduction.

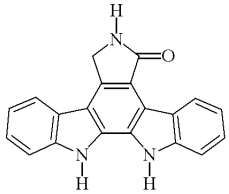
In the course of our investigations we have focused our attention on strategies for the synthesis of new heterocycles structurally related to the indolocarbazoles. Interest in the indolocarbazole class of natural products, exemplified by arcyriaflavin A (**1**), isolated from the slime mold *Arcyria denudata* [1], indolo[2,3-*a*]pyrrolo[3,4-*c*]-carbazole-5-one (K-252c **2**), isolated from the *Nocardiopsis* strain K-290 [2], and the glycosylated derivatives staurosporine [3], K-252a [4], and rebeccamycin [5] results from the discovery of their potent anticancer, antitumor, antifungal and antibiotic properties [6]. Members of this class of natural products have been identified as inhibitors of numerous protein tyrosine and serine-threonine kinases involved in signal transduction pathways critical to cell growth, differentiation and survival. This paper describes an efficient synthesis and the characterization of novel fused benzo[*b*]thieno[2,3-*a*]-pyrrolo[3,4-*c*]carbazoles and benzo[*b*]furano[2,3-*a*]-pyrrolo[3,4-*c*]carbazoles **10**-**13** utilizing a one pot palladium(II)acetate/tetrachloro-1,4-benzoquinone oxidation step to close the A-E rings last in the sequence.



1 Arcyriaflavin A



X = O, S

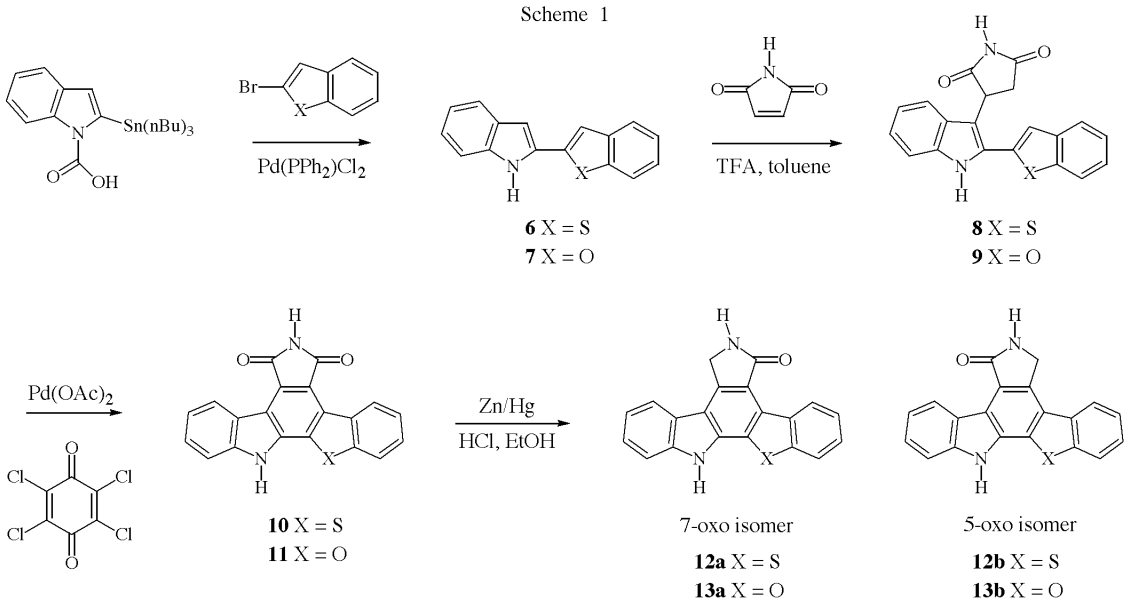


2 Indolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-5-one

Synthesis and Discussion.

Scheme 1 outlines the route to prepare a heteroaryl fused pyrrolo[3,4-*c*]carbazoles. The indole intermediates 2-(2-benzofuranyl)indole (**7**) and 2-(2-benzothienyl)indole (**6**)

Scheme 1



6 X = S
7 X = O

8 X = S
9 X = O

10 X = S
11 X = O

7-oxo isomer
12a X = S
13a X = O

5-oxo isomer
12b X = S
13b X = O

were prepared in high yield using a Stille coupling reaction with 1-carboxy-2-(tributylstannyl)indole and the 2-bromo-heteroaryl [7,8]. It was felt the pyrrole moiety could be incorporated by a Michael reaction with maleimide [9]. Previously we reported the reaction of 2,2'-biindole with maleimide under acidic conditions and high temperature resulted in formation of the staurosporinone 6-oxo lactam regioisomer (indolo[2,3-*a*]pyrrolo[2,3-*c*]carbazole-6-one). The proposed mechanism was a tandem Michael-acid catalyzed condensation sequence [8]. Similar conditions using indoles **6** and **7** also underwent this reaction sequence to produce the 6-oxo carbazoles [10]. While investigating a number of reaction conditions it was determined that Michael adducts **8** and **9** could be isolated in good yield (70-90%) by treating **6** or **7**, respectively with a 1.1 equivalents of maleimide and catalytic trifluoro-acetic acid at toluene reflux.

The key step in the route was to develop an efficient process for the A-E ring-closure of 2-(2-benzo[*b*]thieno)-(**8**) and 2-(2-benzo[*b*]furano)-3-[3-(2,5-dioxo-1*H*-pyrrol-idinyl)]indole (**9**) to the pyrrolocarbazole. This approach has not been described for the synthesis of the natural prod-uct, however, Pindur *et al.* [11] reported the ring closure of 3-(2,5-dioxo-1-phenylpyrrolidinyl)-1-methyl-2-(1-methylindol-2-yl)indole and 3-(2,5-dioxo-1-methyl-pyrrolidinyl)-1-methyl-2-(1-methylindol-2-yl)indole using palladium on carbon at xylene reflux in 20% and 10% yield, respectively. Palladium(II)acetate has been used successfully for arylation reactions of small heterocycles [12,13] and was extensively investigated for ring-closure of two-step process: introduction of the A-ring 3,4-double bond, then palladium mediated coupling of the A-E rings. Based on the initial results it was felt facilitating the dehydrogenation step to the maleimide intermediate would enhance yields of the ring-closed products. Treatment of **8** or **9** with 1.1 equivalent of tetrachloro-1,4-benzoquinone and 10-20 mole percent of palladium(II)acetate in dichloroethane increased the yields of carbazole products to 40-45%. Using dichlorobenzene as the solvent further improved the yields of **10** and **11** to 60-70% (Table 1). The use of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone as the oxidizing agent resulted in decomposition of the starting material.

Since the palladium(II)acetate in acetic acid conditions were sufficient for ring closure (entries 1 and 4), the role of tetrachloro-1,4-benzoquinone was investigated. Tetrachloro-1,4-benzoquinone may function to enhance the reaction by oxidation to the A-ring double bond but may also facilitate the reaction by recycling palladium(0) to palladium(II). Palladium(II)acetate in dichlorobenzene in the absence of tetrachloro-1,4-benzoquinone gave primarily starting material and decomposition products (entries 10 and 11). The use of one molar equivalent of palladium(II)acetate and one equivalent of tetrachloro-1,4-benzoquinone in dichlorobenzene reduced the reaction time to 12 hours but did not show improvement in the yields of **11** over the catalytic method (compared entry 6 to 8). Increasing the ratio of tetrachloro-1,4-benzo-quinone:palladium(II)acetate to 2:1 did not further improve the yield of **11** (entry 9).

Table 1

Reaction Conditions for the Palladium(II)acetate Cyclization

Entry	Palladium(II)acetate[a]	Chloranil[b]	Solvent[c]	Substrate	Product	% Yield[d]
1	0.1	0	HOAc	8	10	25
2	0.2	1.1	$C_2H_4Cl_2$	8	10	40
3	1.5	1.5	$C_6H_4Cl_2$	8	10	61
4	0.1	0	HOAc	9	11	25
5	0.1	1.1	$C_2H_4Cl_2$	9	11	45
6	0.2	1.1	$C_6H_4Cl_2$	9	11	68
7	0.2	2.0	$C_6H_4Cl_2$	9	11	58
8	1.0	1.0	$C_6H_4Cl_2$	9	11	58[e]
9	1.0	2.0	$C_6H_4Cl_2$	9	11	60[e]
10	1.0	0	$C_6H_4Cl_2$	9	11	0
11	2.0	0	$C_6H_4Cl_2$	9	11	0

[a] Values for palladium(II)acetate and chloranil are mole equivalents based on the starting substrate; [b] Chloranil = tetrachloro-1,4-benzoquinone; [c] Reaction solvents: HOAc = acetic acid; $C_2H_4Cl_2$ = 1,2 dichloroethane; $C_6H_4Cl_2$ = 1,2-dichlorobenzene; [d] Yields based on 24-hour reaction times; [e] Reaction complete after 12 hours.

8 and **9** to the pyrrolo[3,4-*c*]carbazoles. Initial experiments established that treatment of **8** or **9** with 10 mole percent of palladium(II)acetate in acetic acid at reflux produced the ring closed products **10** and **11**, respectively in approxi-mately 25% yield (Table 1). Palladium(II)chloride was ineffective in this reaction. The mechanism is uncertain but it is reasonable that carbazole formation proceeds through a

Imides **10** and **11** were reduced to the 5-oxo and 7-oxo lactam regioisomers using a Clemmensen reduction (zinc·mercury amalgam, ethanol, hydrochloric acid) [14]. The lactam isomers were formed in approximately 60-65% yield as a mixture of 7-oxo:5-oxo isomers in a ratio of 2:1 for **12a**:**12b** and 3:1 for **13a**:**13b**. The regiosiomers were separated using reverse phase HPLC and the

regiochemistry was assigned from the proton nmr spectra with correlation spectra from the natural indolo[2,3-*a*]-pyrrolo[3,4-*c*]carbazole. The proton nmr spectra (300 MHz, dimethylsulfoxide-d_6) of **2** revealed a characteristic deshielding effect from the lactam carbonyl on the C-4 aryl proton. The chemical shift of the proton on C-4 is δ 9.22 (d, *J* = 7.85 Hz) as opposed to the C-8 proton, which is at δ 8.05 (d, *J* = 7.43 Hz). The 5-oxo analogs **12b** and **13b** displayed the H-4 chemical shifts at δ 9.23 and 9.24 respectively. The 7-oxo analogs **12a** and **13a** displayed the H-4 chemical shift at δ 8.14 and 8.10, whereas the H-8 chemical shift for **12a** and **13a** were at δ 10.24 and 9.00, respectively.

In summary, this paper reports the first synthesis and the characterization of the benzofurano[2,3-*a*]pyrrolo[3,4-*c*]-carbazole and benzothieno[2,3-*a*]pyrrolo[3,4-*c*]carbazole ring systems using a palladium(II)acetate/tetrachloro-1,4-benzoquinone oxidative cyclization procedure.

EXPERIMENTAL

The proton and carbon nmr spectra were recorded at 300 MHz and 75 MHz respectively, in the solvent indicated with tetramethylsilane as an internal standard. High-resolution mass spectra were performed by M-Scan Inc., West Chester, PA. Column chromatography was performed on silica gel 60 (230-400 mesh). Quantitative Technologies Inc., performed elemental analyses. All reagents were purchased from commercial sources and used as received. 2-(2-Benzo[*b*]-thienyl)indole **6** and 2-(2-benzo[*b*]furanyl)indole **7** were prepared using the literature procedure [7].

2-(2-Benzo[*b*]thieno)-3-[3-(2,5-dioxo-1-pyrrolidinyl)]indole (**8**).

A solution of 2-(2-benzo[*b*]thieno)indole **6** (2.6 g, 10.2 mmole), maleimide (1.2 g, 12.3 mmole) and trifluoroacetic acid (1 ml) in dry toluene (200 ml) was stirred at reflux for 12 hours. The solution was cooled to room temperature then concentrated at reduced pressure to give a crude solid. The solid was purified by flash column chromatography (ethyl acetate:hexane 1:1, Rf = 0.4) to give 2.1 g (82%) of **8** as a white solid: mp > 300 °C; ^{1}H nmr (dimethylsulfoxide-d_6): δ 2.80 (dd, 1H, *J* = 18.1, 5.5 Hz), 3.30 (dd, 1H, *J* = 18.1, 9.8 Hz), 4.75 (dd, 1H, *J* = 9.8, 5.5 Hz), 7.06 (t, 1H, *J* = 7.4 Hz), 7.23 (dd, 2H, *J* = 11.5, 8.0 Hz), 7.46 (m, 3H), 7.80 (s, 1H), 7.90 (d, 1H, *J* = 8.2 Hz), 8.10 (d, 1H, *J* = 7.1 Hz), 11.5 (s, 1H), 11.7 (s, 1H); ^{13}C nmr (dimethylsulfoxide-d_6) δ 37.5, 41.8, 110.0, 112.5, 119.0, 120.6, 122.7, 123.0, 124.7, 125.6, 126.3, 131.5, 132.6, 134.0, 136.3, 137.0, 139.7, 140.1, 178.2, 180.6; hrms (calcd. for $C_{20}H_{14}N_2O_2S$) 346.0776, found 346.0780.

Anal. Calcd. for $C_{20}H_{14}N_2O_2S$: C, 69.35; H, 4.47; N, 8.09. Found: C, 69.42; H, 4.52; N, 7.81.

2-(2-Benzo[*b*]furano)-3-[3-(2,5-dioxo-1-pyrrolidinyl)]indole (**9**).

A solution of 2-(2-benzo[*b*]furano)indole **7** (2.2 g, 9.4 mmole), maleimide (1.0 g, 10.4 mmole) and trifluoroacetic acid (2.5 ml) in dry toluene (100 ml) was stirred at reflux 12 hour. The solution was cooled to room temperature, concentrated to approximately 25 ml then cooled to -20 °C. The product, which precipitated, was collected by filtration, washed with cold toluene and dried under vacuum (80 °C, 1 mm) to give a tan solid (2.3 g, 74%). The combined toluene mother liquors and washings were concentrated at reduced pressure. The resulting solid was purified by chromatography on silica gel (ethyl acetate:hexane, 2:1, Rf = 0.6) to give an additional 400 mg of product for a total yield of 2.7 g (87 %): mp (toluene) 234-235 °C (dec.). ^{1}H nmr (dimethylsulfoxide-d6): δ 2.74 (dd, 1H, *J* = 18.1, 5.8 Hz), 3.28 (dd, 1H, *J* = 18.1, 9.8 Hz), 4.94 (dd, 1H, *J* = 9.6, 5.8 Hz), 7.08 (t, 1H, *J* = 7.4 Hz), 7.22 (t, 1H, *J* = 7.7 Hz), 7.28-7.39 (m, 3H), 7.44-7.53 (m, 3H), 7.73 (d, 1H, *J* = 7.6 Hz), 11.52 (s, 1H), 11.85 (s, 1H); ^{13}C nmr (dimethylsulfoxide-d6): δ 103.3, 111.1, 111.4, 112.1, 118.9, 120.2, 121.8, 123.7, 124.0, 125.2, 125.8, 128.0, 128.7, 136.9, 149.6, 154.4, 178.7, 180.8; ms(es$^-$): m/z = 329 (M - 1). hrms (calcd. for $C_{20}H_{14}N_2O_3$) 330.1005, found 330.0990.

Anal. Calcd. for $C_{20}H_{14}N_2O_3$: C, 72.72; H, 4.27; N, 8.48. Found: C, 72.63; H, 4.16, N, 8.63.

6*H*,12*H*-Benzo[*b*]thieno[2,3-*a*]pyrrolo[3,4-*c*]carbazole-5,7-dione (**10**).

A stirred solution of 2-(2-benzo[*b*]thieno)-3-[3-(2,5-dioxo-1-pyrrolidinyl)]indole **8** (1.3 g, 3.7 mmole), palladium(II)acetate (1.3 g, 5.6 mmole) and tetrachloro-1,4-benzoquinone (1.4 g, 5.6 mmole) in 1,2-dichlorobenzene (100 ml) was heated to 170 °C in an oil bath. After 24 hours the starting material was consumed based on tlc (ethyl acetate: methanol; 9:1) analysis. The mixture was allowed to cool to room temperature then concentrated under vacuum. The resulting material was dissolved in 1,4-dioxane, filtered through a pad of celite and concentrated. The resulting material was triturated with methanol/ether (1:1) to a solid and collected to give 786 mg (2.25 mmole, 61%) of product **10**: mp 239 °C (dec.); ^{1}H nmr (dimethylsulfoxide-d_6, 300 MHz): δ 7.40 (m, 2H), 7.62 (m, 3H), 8.22 (dd, 1H, *J* = 7.2, 0.7 Hz), 9.03 (d, 1H, *J* = 7.2 Hz), 9.81 (dd, 1H, *J* = 9.0, 0.7 Hz), 11.38 (s, 1H), 12.80 (s, 1H); ^{13}C nmr (dimethylsulfoxide-d_6, 75 MHz): δ 112.1, 115.7, 119.9, 121.0, 121.3, 123.3, 125.4, 125.5, 126.7, 127.0, 127.5, 128.0, 128.0, 130.1, 134.7, 137.2, 138.5, 141.7, 170.7, 171.1; hrms (calcd. for $C_{20}H_{10}N_2O_2S$) 342.0449, found 342.0462.

Anal. Calcd. for $C_{20}H_{10}N_2O_2S$: C, 70.16; H, 2.94; N, 8.18. Found: C, 70.50; H, 3.07; N, 8.23.

6*H*,12*H*-Benzo[*b*]thieno[2,3-*a*]pyrrolo[3,4-*c*]carbazole-5-one (**12a**) and 6*H*,12-*H*-Benzo[*b*]thieno[2,3-*a*]pyrrolo[3,4-*c*]-carbazole-7-one (**12b**).

To a stirred suspension of zinc dust (500 mg) and mercuric chloride (150 mg) in water (3 ml) was added concentrated hydrochloric acid (0.5 ml) dropwise. After stirring for 10 minutes, the aqueous layer was decanted from the amalgam. The zinc mercury amalgam was washed followed by decanting first with water, then repeatedly with ethanol. The amalgam was then suspended in ethanol (10 ml), and solid 6*H*,12*H*-benzo-[*b*]thieno[2,3-*a*]pyrrolo[3,4-c]carbazole-5,7-dione **10** (40 mg, 0.12 mmole) was added. Three drops of concentrated hydrochloric acid were added then the reaction was brought to reflux. The yellow suspension slowly became a clear, greenish solution. After 3 hours at reflux the reaction was allowed to cool to room temperature and the solvent was removed at reduced pressure. The residue was dissolved in a tetrahydrofuran:ethyl acetate mixture (1:1, 50 ml) and extracted with a saturated sodium

carbonate solution (2 x 25 ml), brine (2 x 25 ml), then dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solvent was concentrated at reduced pressure to give a yellow solid. The product was initially purified by column chromatography (silica gel, 2:1 ethyl acetate:hexanes) to give the 5-oxo and 7-oxo regioisomers (**12b**:**12a**) as a 1:2 mixture (based on ^{1}H nmr). The 5-oxo **12b** and 7-oxo **12a** regioisomers were separated by reverse-phase hplc (C-8 column) and the solvents concentrated by lyophilization, to give 24 mg (62%) of **12a** and 12 mg (31%) of **12b**.

12a: mp 263-265 °C (dec.); ^{1}H nmr (dimethylsulfoxide-d_6, 300 MHz): δ 5.01 (s, 2H), 7.29 (t, 1H, *J* = 7.3 Hz), 7.35 (m, 1H), 7.53 (m, 1H), 7.68 (t, 2H, *J* = 8.8 Hz), 8.14 (dd, 2H, *J* = 8.8, 5.6 Hz), 8.74 (s, 1H), 10.24 (m, 1H), 12.43 (s, 1H); ^{13}C nmr (dimethylsulfoxide-d_6, 75 MHz): δ 45.2, 110.6, 114.7, 120.7, 121.0, 121.5, 122.1, 122.6, 125.1, 126.5, 127.0, 128.7, 129.4, 131.6, 135.7, 138.4, 140.2, 142.0, 172.0; ms (es$^+$): m/z 329.18 (M + 1); hrms (calcd. for $C_{20}H_{12}N_2OS$) 329.0749, found 329.0743.

Anal. Calcd. for $C_{20}H_{12}N_2O_2S$: C, 73.15; H, 3.68; N, 8.53. Found: C, 72.72; H, 4.05; N, 8.67.

Compound **12b** has mp >240 °C (dec.); ^{1}H nmr (dimethylsulfoxide-d_6, 300 MHz): δ 5.10 (s, 2H), 7.26 (t, 1H, *J* = 8.1 Hz), 7.39 (dt, 1H, *J* = 6.9, 1.5 Hz), 7.47 (t, 1H, *J* = 7.3 Hz), 7.61 (dt, 2H, *J* = 6.9, 1.5 Hz), 8.21 (dt, 2H, *J* = 7.3, 5.1 Hz), 8.89 (s, 1H), 9.23 (d, 1H, *J* = 8.1 Hz), 12.31 (s, 1H); ^{13}C nmr (dimethylsulfoxide-d_6, 75 MHz): δ 46.4, 111.7, 116.3, 119.9, 120.3, 122.5, 123.9, 124.2, 125.4, 126.0, 126.2, 126.6, 126.9, 128.0, 133.2, 134.5, 135.6, 139.0, 140.7, 170.2; ms (es$^+$) m/z 329.17 (M + 1); hrms (calcd. for $C_{20}H_{12}N_2OS$) 329.0749, found 329.0738.

Anal. Calcd. for $C_{20}H_{12}N_2O_2S$: C, 73.15; H, 3.68; N, 8.53. Found: C, 72.92; H, 3.74; N, 8.61.

6*H*,12*H*-Benzo[*b*]furano[2,3-*a*]pyrrolo[3,4-*c*]carbazole-5,7-dione (**11**).

A well stirred solution of 2-(2-benzo[*b*]furano)-3-(3-2,5-dioxo-1-pyrrolidinyl)indole **9** (2.0 g, 6.1 mmole), palladium(II)acetate (135 mg, 0.6 mmole) and tetrachloro-1,4-benzoquinone (1.7 g, 6.7 mmole) in 1,2-dichlorobenzene (100 ml) was heated to reflux for 24 hours, cooled to room temperature then concentrated to dryness under reduced pressure. The resulting material was triturated with methanol to a solid and collected by filtration to give 1.9 g of a dark solid. The product was purified by column chromatography (silica gel, toluene:tetrahydrofuran; 7:3) to give 1.5 g (68%) of **11** as a yellow solid: mp > 300 °C; ^{1}H nmr (dimethylsulfoxide-d_6): δ 7.40 (t, 1H, *J* = 7.4 Hz), 7.57-7.73 (m, 4H), 7.95 (d, 1H, *J* = 8.2 Hz), 8.80 (d, 1H, *J* = 7.3 Hz), 8.98 (d, 1H, *J* = 7.7 Hz), 11.13 (s, 1H), 12.93 (s, 1H). ^{13}C nmr (dimethylsulfoxide-d_6, 75 MHz): δ 112.5, 117.5, 119.3, 119.3, 121.2, 121.5, 122.8, 123.8, 124.7, 125.1, 128.5, 128.9, 129.1, 129.2, 134.6, 140.0, 142.0, 157.0, 170.7, 171.0. ms: m/z = 325 (M - 1). hrms (calcd. for $C_{20}H_{10}N_2O_3$) 326.0692, found 326.0689.

Anal. Calcd. for $C_{20}H_{10}N_2O_3$•0.5 H_2O: C, 71.64; H, 3.31; N, 8.35. Found C, 71.66; H, 3.16, N, 8.18.

6*H*,12*H*-Benzo[*b*]furano[2,3-*a*]pyrrolo[3,4-*c*]carbazole-7-one (**13a**) and 6*H*,12*H*-Benzo[*b*]furano[2,3-*a*]pyrrolo[3,4-*c*]-carbazole-5-one (**13b**).

In a 25 ml round bottom flask, to a stirred suspension of zinc dust (2 g) and mercuric chloride (500 mg) in water (3 ml) was added concentrated hydrochloric acid (1.0 ml) dropwise. After 10 minutes of stirring, the aqueous layer was slowly decanted from the amalgam. The zinc-mercury amalgam was washed followed by decanting first with water, then repeatedly with ethanol. The zinc amalgam was pulverized and suspended in ethanol and acetic acid (1:1, 40 ml). Solid 6*H*,12*H*-benzo[*b*]furano[2,3-*a*]pyrrolo[3,4-*c*]carbazole-5,7-dione **11** (200 mg, 0.61 mmole) and concentrated hydrochloric acid (5 ml) were added and the reaction brought to reflux. The solution became homogeneous and light tan in color. After 3 hours at reflux the reaction was allowed to cool to room temperature and the solvent was removed at reduced pressure. The residue was triturated with methanol to a white solid (120 mg, 63%). The ratio of **13b**:**13a** was 1:3 based on ^{1}H nmr. The methanol mother liquor was concentrated, the solid material obtained dissolved in tetrahydrofuran (50 ml) then washed with saturated sodium bicarbonate (2 x 40 ml), saturated sodium chloride solution (2 x 40 ml) and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solvent concentrated to yield an additional 35 mg for a total yield of 155 mg (81%). Isomers **13b**:**13a** were separated by reverse-phase hplc (C-8 column) and pure fractions by analytical hplc were pooled concentrated by lyophilization.

Compound **13a** (dimethylformamide-ethyl ether) has mp > 300 °C; ^{1}H nmr (dimethylsulfoxide-d_6, 300 MHz): δ 5.02 (s, 2H), 7.35 (t, 1H, *J* = 7.3 Hz), 7.47-7.62 (m, 3H), 7.68 (d, 1H, *J* = 8.0 Hz), 7.86 (d, 1H, *J* = 8.1 Hz), 8.10 (d, 1H, *J* = 7.7 Hz), 8.70 (s, 1H), 9.00 (d, 1H, *J* = 7.7 Hz), 12.58 (s 1H); ^{13}C nmr (dimethylsulfoxide-d_6, 75 MHz): δ 46.0, 112.0, 112.4, 117.3, 117.5, 119.1, 120.7, 122.1, 122.5, 123.8, 124.3, 125.9, 126.5, 127.0, 127.7, 136.3, 140.1, 141.9, 156.2, 171.8; ms (es$^+$): m/z = 313 (M + 1); hrms (calcd. for $C_{20}H_{12}N_2O_2$) 312.0899, found 312.0905.

Anal. Calcd. for $C_{20}H_{12}N_2O_3$•H_2O: C, 72.72; H, 4.27; N, 8.48. Found: C, 72.66; H, 4.05; 8.18.

Compound **13b** has mp > 300 °C; ^{1}H nmr (dimethylsulfoxide-d_6, 300 MHz): δ 4.98 (s, 2H), 7.27 (t, 1H, *J* = 7.4 Hz), 7.46-7.64 (m, 4H), 7.90 (d, 1H, *J* = 8.1 Hz), 8.11 (d, 1H, *J* = 7.4 Hz), 8.77 (s, 1H), 9.24 (d, 1H, *J* = 7.8 Hz), 12.40 (s, 1H); ^{13}C nmr (dimethylsulfoxide-d_6, 75 MHz): δ 45.1, 105.3, 111.8, 112.3, 115.9, 119.8, 122.1, 123.9, 124.2, 126.0, 126.4, 126.8, 132.0, 140.8, 144.0, 156.1, 171.9. ms: m/z = 313 (M + 1); hrms (calcd. for $C_{20}H_{12}N_2O_2$) 312.0899, found 312.0905.

Anal. Calcd. for $C_{20}H_{12}N_2O_3$•0.5 H_2O: C, 74.75; H, 4.08; N, 8.71. Found: C, 74.89; H, 3.93; N, 8.99.

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