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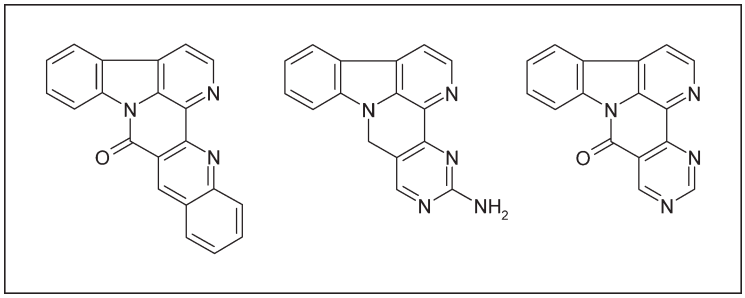

Starting from 5,6-dihydrocanthin-4-one, new penta- and hexacyclic ring systems (1,7b,14-triazadibenzo[e,k]acephenanthrylenes, 1,7b,10,12-tetraazabenzo[e]acephenanthrylenes) were built up using ring annelation reactions. The new compounds represent hybrids between the canthinones and several bioactive aromatic alkaloids

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INTRODUCTION

Polycyclic aromatic compounds, especially alkaloids from terrestric and marine sources [1], have been shown to exhibit significant biological activities. Some prominent examples are the marine pyridoacridone type alkaloids [2], e.g., the cytotoxic metabolites ascididemine (**1a**) [3] and 2-bromoleptoclinidinone (**1b**) [4] from tunicates, the antifungal alkaloid sampangine (**2**) [5] from Annonaceae, the cytotoxic alkaloid camptothecin (**3**) [6], and the antileishmanial β-carboline annomontine (**4**) [7] (Scheme 1).

Very recently, we reported on the first efficient entry to the canthin-4-one ring system starting from 1-acyl-β-carbolines, including total syntheses of the alkaloids tuboflavine and norisotuboflavine [8]. In continuation of our concept on the synthesis of hybrids between biologically active natural products and established drugs [9], we intended to attach additional heterocyclic rings to the canthin-4-one ring system, to combine the said tetracyclic ring system with structural elements of the alkaloids **1**–**4**. Of special interest were polycyclic aromatic compounds containing quinoneimine partial structures, as can be found in the alkaloids **1a/b** and **2**. This structural element seems to be of importance for the biological activities of the alkaloids, even though hetero analogues missing the carbonyl group have been described to exhibit significant antimicrobial activities as well [10]. The new polycyclic compounds might act as DNA intercalators in cancer and microbial cells.

The target compounds were envisaged to contain either an anellated quinoline ring, to gain similarity to ascididemine (**1a**), related pyridoacridones, and camptothecin (**3**), or a pyrimidine ring, to obtain rigid analogues of the aminopyrimidyl-β-carboline alkaloid annomontine (**4**).

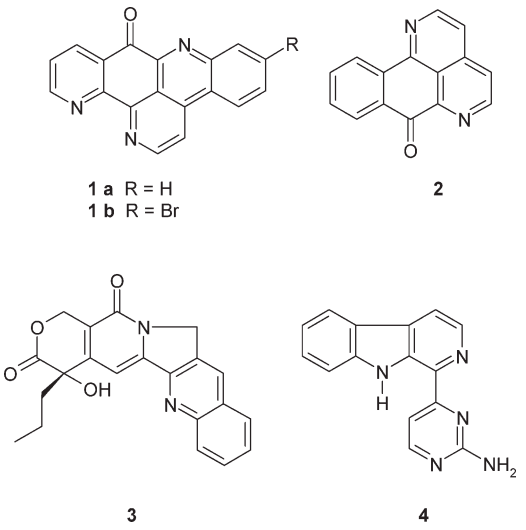
We intended to prepare the target compounds starting from 5,6-dihydrocanthin-4-one (**7**) [11] using established methods for the synthesis of fused heterocyclic ring systems.

RESULTS AND DISCUSSION

So the first objective of this project was to work out an efficient synthesis of the central building block **7**. For this purpose different strategies were tackled.

In the first approach, canthin-4-one (**5**), which is conveniently accessible from 1-acetyl-β-carboline and Bredereck's reagent (*tert*-butoxy-bis(dimethylamino)-methane) [8] in a 1-pot reaction, was submitted to catalytic hydrogenation. Using Pd on charcoal as catalyst we observed only very poor (<5%) conversion, with the secondary alcohol **6** being produced in traces, accompanied by products of over-reduction. Hydrogenation with PtO_2 (Adams catalyst), however gave the alcohol **6** in 70% yield. Subsequent oxidation with manganese dioxide gave the desired 5,6-dihydrocanthin-4-one (**7**) in good yield (71%) (Scheme 2).

Scheme 1



We investigated an alternative approach to the ketone **7** via a Parham cyclization [12]. This reaction represents a convenient, but poorly applied method for the preparation of cyclic aryl ketones starting from an aryl bromide containing a neighboring alkoxycarbonylalkyl chain *via* intermediate bromo-lithium exchange, followed by intramolecular nucleophilic attack of the organolithium species at the ester group. A suitable precursor **9** for our purpose was obtained by Michael-type nucleophilic addition of 1-bromo-β-carboline (**8**) [13] to methyl acrylate. Bromo-lithium exchange of **9** was performed with *n*-butyllithium in THF at –100°C; upon warming to room temperature cyclization took place to give 5,6-dihydrocanthin-4-one (**7**) in 29% yield.

In conclusion, the first approach starting from canthin-4-one (**5**) remains the more effective one for the preparation of ketone **7**.

Friedländer-type condensation [14] of the ketone **7** with 2-aminobenzaldehyde, freshly prepared from 2-nitrobenzaldehyde [15], and ethanolic KOH gave the quinoline derivative **10** in 87% yield. This hexacyclic 1,7b,14-triazadibenzo[e,k]acephenanthrylene ring system has not yet been described in literature. To achieve a quinoneimine-like partial structure (compare the alkaloids **1a/b**, **2**) the methylene group in **10** had to be oxidized. This reaction proceeded with ease using manganese dioxide in chloroform [16], and the carbonyl compound **11** was obtained in 54% yield (Scheme 3).

The anellation of an aminopyrimidine ring to give a rigid analogue of annomontine (**4**) was performed in close analogy to our total synthesis of annomontine [14b]. Thus, 5,6-dihydrocanthin-4-one (**7**) was heated with Bredereck's reagent in DMF to give the enaminoketone **12**, which was further heated with guanidinium carbonate to give the aminopyrimidine **13** in 78% overall yield. Again, the resulting 1,7b,10,12-tetraazabenzo[e]acephenanthrylene ring system has not been described in literature before.

By treating the intermediate enaminoketone **12** with ammonium formate and formamide in formic acid [17] the pyrimidine **14** was obtained in 40% yield. Once again oxidation with manganese dioxide gave the corresponding carbonyl compound **15** containing a quinoneimine partial structure in high yield.

In conclusion, an effective approach towards 5,6-dihydrocanthin-4-one (**7**) has been developed. This ketone served as a versatile building block for the synthesis of hitherto unknown penta- and hexacyclic ring systems.

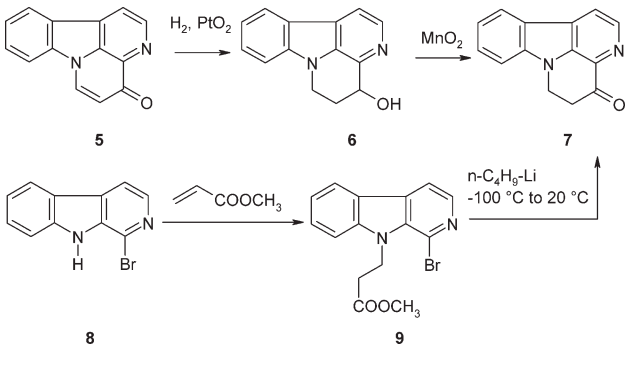
Presently, the new compounds undergo screenings for cytotoxic and antimicrobial activities, the results will be presented elsewhere in due time.

EXPERIMENTAL

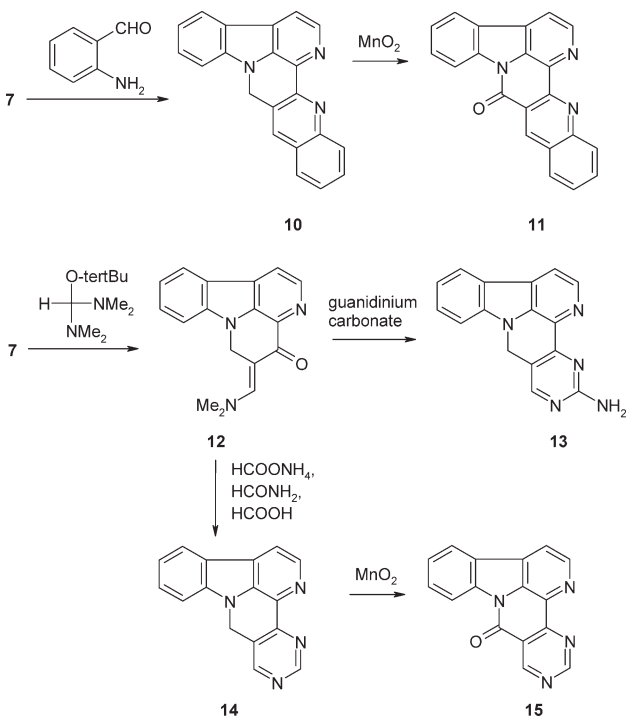
General. Elementar analysis: Heraeus CHN Rapid; MS: Hewlett Packard MS-Engine, electron ionization (EI) 70 eV, chemical ionization (CI) with CH_4 (300 eV); NMR: Jeol GSX 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz); Melting points were determined on a Büchi Melting Point B-540 apparatus and are uncorrected, flash column chromatography (FCC): silica gel 60 (230–400 mesh, E. Merck, Darmstadt).

(±)-5,6-Dihydro-4*H*-indolo[3,2,1-de][1,5]naphthyridin-4-ol (6). A suspension of canthin-4-one (**5**) [8] (100 mg, 0.454 mmol) and PtO_2 (25 mg) in 35 mL ethanol was stirred under a hydrogen atmosphere at atmospheric pressure for 30 min. After filtration and evaporating the solvent, the residual solid was purified by FCC (dichloromethane:ethanol, 14:1, v/v) to give 71 mg (70%) **6** as a light yellow solid. mp 171°C; ^{1}H nmr (deuterochloroform): δ 8.26 (d, J = 5.5 Hz, 1H, 2-H), 8.12 (ddd, J = 8.0 Hz, J = 1.7 Hz, J = 0.7 Hz, 1H, 11-H), 7.82 (d, J = 5.5 Hz, 1H, 1-H), 7.61 (ddd, J = 8.3 Hz, J = 7.2 Hz, J = 1.2 Hz, 1H, 9-H), 7.48 (d, J = 8.3 Hz, 1H, 8-H), 7.29 (ddd, J = 8.0 Hz, J = 7.2 Hz, J = 1.0 Hz, 1H, 10-H), 5.35 (m, 1H, 4-H), 4.38 (m, 3H, 6-H, OH), 2.57 (m, 2H, 5-H); ^{13}C nmr (deuterochloroform): 143.6 (C-3a), 141.0 (C-7a), 137.5 (C-2), 132.9 (C-11c), 128.5 (C-9), 126.8 (C-11b), 122.7 (C-11), 121.4

Scheme 2



Scheme 3



(C-11a), 119.8 (C-10), 114.7 (C-1), 109.6 (C-8), 64.9 (C-4), 37.8 (C-6), 30.8 (C-5); ms: *m/z* 224 (61, M^+), 205 (22), 168 (100), 140 (12); *Anal*. Calcd. for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.39; N, 12,49. Found: C, 74,42; H, 5,30; N, 12,33.

5,6-Dihydroindolo[3,2,1-de][1,5]naphthyridin-4-one (7). (a) MnO_2 (856 mg, 9.85 mmol) was added to a solution of **6** (170 mg, 0.758 mmol) in 7 mL chloroform, and the mixture was stirred for 5 h at room temperature. After filtration the solution was evaporated in vacuo, and the residue was purifieed by FCC (dichloromethane:ethanol, 14:1, v/v) to give 119 mg (71%) **7** as a yellow solid.

(b) A solution of **9** (259 mg, 0.777 mmol) in 7 mL anhydrous THF under nitrogen atmosphere was cooled to –100°C, then a solution of *n*-butyllithium (1.6*M* in hexane; 0.49 mL, 0.77 mmol) was added slowly. The mixture was stirred at –100°C for 1 h, and then at ambient temperature for 15 h. After addition of 40 mL water the mixture was extracted with dichloromethane (2 × 30 mL). The combined organic layers were dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by FCC (ethyl acetate) to give 50 mg (29%) of **7**.

mp 189°C; ^{1}H nmr (deuterochloroform): δ 8.63 (d, J = 5.0 Hz, 1H, 2-H), 8.17 (ddd, J = 7.9 Hz, J = 1.8 Hz, J = 0.8 Hz, 1H, 11-H), 8.02 (d, J = 5.0 Hz, 1H, 1-H), 7.68 (ddd, J = 8.3 Hz, J = 7.3 Hz, J = 1.2 Hz, 1H, 9-H), 7.50 (d, J = 8.3 Hz, 1H, 8-H), 7.38 (ddd, J = 7.9 Hz, J = 7.3 Hz, J = 0.9 Hz, 1H, 10-H), 4.56 (t, J = 6.9 Hz, 2H, 6-H), 3.31 (t, J = 6.9 Hz, 2H, 5-H); ^{13}C nmr (deuterochloroform): δ 191.5 (C=O), 141.5 (C-7a), 141.4 (C-11c), 140.9 (C-2), 133.9 (C-3a), 129.9 (C-11b), 129.6 (C-9), 123.0 (C-11), 121.7 (C-11a), 120.9 (C-10), 119.2 (C-1), 110.0 (C-8), 41.0 (C-6), 38.3 (C-5); ms: *m/z* 222 (49, M^+), 193 (14), 166 (24), 149 (35), 111 (40); *Anal*. Calcd. for $C_{14}H_{10}N_2O$: C, 75.66; H, 4.54; N, 12.60. Found: C, 75.78; H, 4.78; N, 12.50.

Methyl 3-(1-bromopyrido[3,4-b]indol-9-yl)-propanoate (9). To a solution of 1-bromo-β-carboline (**8**) [13] (200 mg, 0.809 mmol) in 5 mL anhydrous DMF under a nitrogen atmosphere, anhydrous potassium carbonate (250 mg, 1.81 mmol) and methyl acrylate (2.0 mL, 2.2 mmol) were added, and the mixture was stirred at 50°C for 24 h. After adding 80 mL water, the mixture was extracted with dichloromethane (2 × 60 mL), and the combined organic layers were dried over Na_2SO_4 and evaporated. The residue was purified by FCC (dichlormethane:ethanol, 14:1, v/v) to yield 71 mg (63%) **9** as a colorless solid. mp 86°C; ^{1}H nmr (deuterochloroform): δ 8.20 (d, J = 5.0 Hz, 1H, 3-H), 8.10 (ddd, J = 7.9 Hz, J = 1.0 Hz, J = 0.8 Hz, 1H, 5-H), 7.92 (d, J = 5.0 Hz, 1H, 4-H), 7.64 (ddd, J = 8.4 Hz, J = 7.1 Hz, J = 1.1 Hz, 1H, 7-H), 7.57 (d, J = 8.4 Hz, 1H, 8-H), 7.33 (ddd, J = 7.9 Hz, J = 7.1 Hz, J = 0.9 Hz, 1H, 6-H), 5.11 (m, 2H, 3′-H), 3.67 (s, 3H, CH_3), 2.93 (m, 2H, 2′-H), ^{13}C nmr (deuterochloroform): δ 171.5 (C=O), 141.6 (C-8a), 138.9 (C-3), 133.7 (C-9a), 132.1 (C-4a), 129.3 (C-7), 122.6 (C-1), 121.7 (C-5), 120.9 (C-6), 120.8 (C-4b), 114.5 (C-4), 110.1 (C-8), 52.0 (CH_3), 39.7 (C-3′), 35.3 (C-2′); ms: *m/z* 334 (27, M^+), 332 (29, M^+), 261 (100), 259 (92), 179 (38); *Anal*. Calcd. for $C_{15}H_{13}BrN_2O_2$ C, 54.07; H, 3.93; N, 8.41. Found: C, 54.99; H, 4.28; N, 8.15.

8*H*-1,7b,14-Triazadibenzo[e,k]acephenanthrylene (10). A solution of dihydrocanthin-4-one (**7**) (116 mg, 0.52 mmol) and 2-aminobenzaldehyde (63 mg, 0.520 mmol) in 7 mL ethanol (96%) was treated with a solution of potassium hydroxide (29 mg, 0.52 mmol) in 0.5 mL ethanol (96%), and then the mixture was refluxed for 18 h. The solvent was evaporated in vacuo and the residue purified by FCC (dichloromethane:ethanol, 19:1, v/v) to yield 139 mg (87%) **10** as a yellow solid. mp 189°C; ^{1}H nmr ([D$_6$]DMSO): δ 8.48 (d, J = 5.0 Hz, 1H, 2-H), 8.32 (s, 1H, 9-H), 8.27 (d, J = 7.9 Hz, 1H, 4-H), 8.11 (d, J = 8.5 Hz, 1H, 13-H), 8.04 (d, J = 5.0 Hz, 1H, 3-H), 7.93 (d, J = 8.0 Hz, 1H, 10-H), 7.75 (ddd, J = 8.5 Hz, J = 8.0 Hz, J = 1.1 Hz, 1H, 12-H), 7.67 (m, 2H, 7-H, 6-H), 7.59 (dd, J = 8.0 Hz, J = 8.0 Hz, J = 1.0 Hz, 1H, 11-H), 7.36 (ddd, J = 7.9 Hz, J = 6.8 Hz, J = 1.5 Hz, 1H, 5-H), 5.87 (s, 2H, 8-H); ^{13}C nmr ([D$_6$]DMSO): δ 148.2 (C-14a), 147.3 (C-13a), 140.4 (C-7a), 139.8 (C-2), 136.8 (C-14b), 136.1 (C-14c), 134.4 (C-9), 129.8 (C-12), 129.2 (C-13), 128.4 (C-6), 127.5 (C-10), 127.4 (C-9a), 127.2 (C-11), 126.5 (C-8a), 126.4 (C-3a), 122.5 (C-4), 121.1 (C-3b), 120.2 (C-5), 116.2 (C-3), 110.4 (C-7), 45.1 (C-8); ms: *m/z* 307 (69, M^+), 306 (100), 153 (27), 139 (8); HRMS Calcd. for $C_{21}H_{13}N_3$: 321.0904. Found: 321.0902.

1,7b,14-Triazadibenzo[e,k]acephenanthrylen-8-one (11). To a solution of **10** (222 mg, 0.723 mmol) in 25 mL chloroform was added MnO_2 (1.10 g, 12.7 mmol), and the mixture was stirred at room temperature for 12 h. The inorganic precipitates were filtered off and the filtrate was evaporated in vacuo. The residue was purified by FCC (dichloromethane: ethanol, 14:1, v/v), and the main fraction was crystallized from dichloromethane/heptane to give 126 mg (54%) **11** as a colorless solid. mp 313°C; ^{1}H nmr (CF_3COOD): δ 9.28 (s, 1H, 9-H), 8.98 (d, J = 6.2 Hz, 1H, 2-H), 8.77 (d, J = 8.0 Hz, 1H, 7-H), 8.70 (d, J = 6.2 Hz, 1H, 3-H), 8.46 (d, J = 7.9 Hz, 1H, 4-H), 8.42 (d, J = 8.2 Hz, 1H, 13-H), 8.38 (d, J = 8.0 Hz, 1H, 10-H), 8.12 (dd, J = 8.2 Hz, J = 7.5 Hz, 1H, 12-H), 8.00 (dd, J = 8.0 Hz, J = 7.7 Hz, 1H, 6-H), 7.90 (dd, J = 8.0 Hz, J = 7.5 Hz, 1H, 11-H), 7.75 (dd, J = 7.9 Hz, J = 7.7 Hz, 1H, 5-H);

^{13}C nmr (CF_3COOD): δ 156.4 (C=O), 147.1 (C-13a), 140.3 (C-14a), 139.8 (C-7a), 139.6 (C-9), 135.9 (C-3a), 135.5 (C-2), 133.1 (C-12), 132.8 (C-6), 131.6 (C-14c), 128.4 (C-11), 128.3 (C-10), 127.2 (C-14b), 126.9 (C-13), 126.6 (C-9a), 125.2 (C-5), 122.9 (C-4), 121.6 (C-8a), 121.2 (C-3b), 116.6 (C-3), 115.2 (C-7); ms: *m/z* 321 (100, M^+), 293 (18), 265 (10), 149 (62), 133 (19); HRMS Calcd. for $C_{21}H_{11}N_3O$: 321.0899. Found: 321.0902.

5-(Dimethylaminomethylene)-5,6-dihydroindolo[3, 2,1-de]-[1,5]naphthyridin-4-one (12). To a solution of dihydrochanthin-4-one (**7**) (176 mg, 0.792 mmol) in 10 mL anhydrous THF, *tert*-butoxy-bis(dimethylamino)methane (Bredereck's reagent; 0.18 mL, 0.84 mmol) was added dropwise. The mixture was stirred under a nitrogen atmosphere for 3 h at 50°C. The volatile components were evaporated in vacuo, and the residue was purified by FCC (dichloromethane: ethanol:triethylamine, 13:1:1, v/v) to give 166 mg (80%) **12** as a yellow solid. Due to partial hydrolysis of the enamine in the course of silica gel chromatography this compound could not be obtained in absolutely pure form. mp 223–225°C; ^{1}H nmr ([D_6]DMSO): δ 8.42 (d, J = 5.1 Hz, 1H, 1-H), 8.31 (d, J = 7.9 Hz, 1H, 11-H), 8.14 (d, J = 5.1 Hz, 1H, 2-H), 7.80 (d, J = 8.2 Hz, 1H, 8-H), 7.77 (s, 1H, 1′-H), 7.67 (dd, J = 8.2 Hz, J = 7.1 Hz, 1H, 9-H), 7.36 (dd, J = 7.9 Hz, J = 7.1 Hz, 1H, 10-H), 5.67 (s, 2H, 6-H), 2.51 (s, 6H, $N(CH_3)_2$); ^{13}C nmr ([D_6]DMSO): δ 178.4 (C=O), 151.7 (C-1′), 140.4 (C-7a), 139.2 (C-2), 138.9 (C-11c), 135.6 (C-3a), 128.5 (C-9), 126.6 (C-11b), 122.7 (C-11), 120.6 (C-11a), 120.1 (C-10), 117.6 (C-1), 110.8 (C-8), 98.6 (C-5), 43.7 (CH_3), 42.7 (C-6); ms: *m/z* 277 (22, M^+), 234 (20), 205 (12), 169 (8), 94 (100); HRMS Calcd. for $C_{17}H_{15}N_3O$: 277.1215. Found: 277.1218.

11-Amino-8*H*-1,7b,10,12-tetraazabenzo[e]acephenanthrylene (13). A solution of dihydrocanthin-4-one (**7**) (120 mg, 0.540 mmol) and *tert*-butoxy-bis(dimethylamino)methane (0.15 mL, 0.70 mmol) in 12 mL anhydrous DMF was refluxed under a nitrogen atmosphere for 1 h. Then guanidinium carbonate (283 mg, 2.02 mmol) was added and the mixture was refluxed for further 5 h. After cooling to ambient temperature 20 mL saturated sodium carbonate solution were added and the mixture was extracted with ethyl acetate (2 × 30 mL). The combined organic layers were dried over Na_2SO_4 and evaporated in vacuo, the residue was purified by FCC (dichlormethane:ethanol, 9:1, v/v) to give 115 mg (78%) **13** as a yellow solid. mp >300°C (dec.); ^{1}H nmr ([D_6]DMSO): δ 8.40 (d, J = 5.3 Hz, 1H, 2-H), 8.39 (s, 1H, 9-H), 8.30 (d, J = 7.9 Hz, 1H, 4-H), 8.09 (d, J = 5.3 Hz, 1H, 3-H), 7.66 (m, 2H, 7-H, 6-H), 7.36 (ddd, J = 7.9 Hz, J = 6.7 Hz, J = 1.5 Hz, 1H, 5-H), 6.88 (s, 2H, NH_2), 5.57 (s, 2H, 8-H); ^{13}C nmr ([D_6]DMSO): δ 163.5 (C-11), 157.6 (C-9), 155.1 (C-12a), 140.2 (C-7a), 139.3 (C-2), 136.3 (C-12c), 135.9 (C-12b), 128.5 (C-6), 125.8 (C-3a), 122.7 (C-4), 120.8 (C-3b), 120.2 (C-5), 117.0 (C-3), 113.6 (C-8a), 110.4 (C-7), 42.8 (C-8); ms: *m/z* 273 (16, M^+), 272 (32, M^+-H), 169 (100), 147 (44), 119 (60); HRMS Calcd. for $C_{16}H_{11}N_5$: 272.0935 [M^+-H]. Found: 272.0918.

8*H*-1,7b,10,12-Tetraazabenzo[e]acephenanthrylene (14). A solution of **12** (184 mg, 0.663 mmol), ammonium formate (416 mg, 6.60 mmol), formamide (159 mg, 3.54 mmol) and formic acid (159 mg, 3.46 mmol) was stirred at 160°C (temperature of the oil bath) in an open flask for 1 h. After cooling to ambient temperature 50 mL water were added, the mixture was neutralized with solid sodium carbonate and extracted with dichloromethane (2 × 50 mL). The combined organic layers were dried over Na_2SO_4 and evaporated, the residue was purified by FCC (dichloromethane:ethanol, 14:1, v/v) to give 68 mg (40%) **14** as a yellow solid. mp >237°C (dec.); ^{1}H nmr ([D_6]DMSO): δ 9.23 (s, 1H, 11-H), 8.89 (s, 1H, 9-H), 8.46 (d, J = 5.2 Hz, 1H, 2-H), 8.33 (dd, J = 7.9 Hz, J = 0.9 Hz, 1H, 4-H), 8.15 (d, J = 5.2 Hz, 1H, 3-H), 7.70 (m, 2H, 7-H, 6-H), 7.40 (ddd, J = 7.9 Hz, J = 6.5 Hz, J = 1.5 Hz, 1H, 5-H), 5.84 (s, 2H, 8-H); ^{13}C nmr ([D_6]DMSO): δ 158.0 (C-11); 156.4 (C-9), 154.8 (C-12a), 140.2 (C-7a), 139.8 (C-2), 136.3 (C-12c), 134.9 (C-3a), 128.7 (C-6), 126.1 (C-12b and C-8a), 122.8 (C-5), 120.7 (C-3b), 120.4 (C-4), 117.7 (C-3), 110.4 (C-7), 43.1 (C-8); ms: *m/z* 258 (75, M^+), 257 (100), 203 (18), 115 (21); *Anal*. Calcd. for $C_{16}H_{10}N_4$: C, 74.41; H, 3.90; N, 21.69. Found: C, 73.43; H, 3.84; N, 21.13.

1,7b,10,12-Tetraazabenzo[e]acephenanthrylen-8-one (15). To a solution of **14** (68 mg, 0.26 mmol) in 10 mL chloroform was added MnO_2 (400 mg, 4.60 mmol), and the mixture was stirred at room temperature for 12 h. The inorganic precipitates were filtered off and the filtrate was evaporated in vacuo. The residue was purified by FCC (dichlormethane:ethanol, 14:1, v/v), and the main fraction was crystallized from dichloromethane/heptane to give 89 mg (64%) **15** as a colorless solid. mp 256°C; ^{1}H nmr ([D_6]DMSO): δ 99.82 (s, 1H, 9-H), 9.65 (s, 1H, 11-H), 8.98 (d, J = 4.9 Hz, 1H, 2-H), 8.63 (d, J = 8.3 Hz, 1H, 7-H), 8.33 (d, J = 4.9 Hz, 1H, 3-H), 8.30 (d, J = 8.1 Hz, 4-H), 7.78 (ddd, J = 8.3 Hz, J = 7.5 Hz, J = 1.1 Hz,1H, 6-H), 7.60 (ddd, J = 8.1 Hz, J = 7.5 Hz, J = 1.0 Hz, 1H, 5-H); ^{13}C nmr ([D_6]DMSO): δ 161.1 (C-11), 158.8 (C-9), 156.9 (C-12b), 156.2 (C-12a), 146.0 (C-2), 138.0 (C-7a), 133.6 (C-12c), 133.1 (C-3a), 130.8 (C-6), 125.6 (C-5), 124.0 (C-3b), 122.9 (C-4), 122.1 (C-8a), 118.4 (C-3), 116.4 (C-7); ms: *m/z* 272 (84, M^+), 244 (57), 217 (45), 193 (34), 105 (100); *Anal*. Calcd. for $C_{16}H_8N_4O$: C, 70.58; H, 2.96; N, 20.58. Found: C, 70.16; H, 3.09; N, 19.79.

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