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THE SYNTHESIS OF *TRANS*-A_2B-CORROLES BEARING ACRIDINE MOIETY

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Abstract – Three new acridine-corroles were synthesized. For the synthesis of dyad with acridine directly attached at position 10 of corrole core the new procedure has been developed which can be used for other sterically hindered aldehydes bearing basic nitrogen atoms.

INTRODUCTION

Corroles, one carbon short analogues of porphyrins, recently emerged as an independent area of research.[1] Their coordination chemistry,[2] synthesis,[3] chemical transformations,[4] electrochemistry[5] and other properties[6] have recently been studied in great detail. In contrast to porphyrins, photophysics of corroles is scarcely studied field.[7] In fact only very recently information regarding basic photophysical properties of corroles began to be available[8] and stable dyads comprising of corrole and other units were investigated.[9] As a part of a broader program in the chemistry of corrole containing dyads, we have created covalently linked corrole-acridine assemblies.

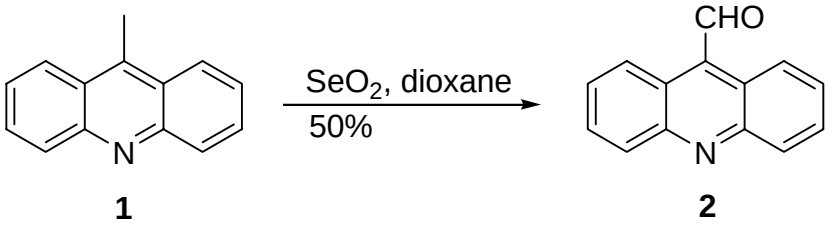
One may expect that combination of these two pigments (corroles and acridines) will lead to chromophores involving the physical properties derived from the original molecules as well as an acquired property from a combination of the two. Acridine derivatives draw recently further attention due to the extremely long charge separation state claimed by Fukuzumi and coworkers for mesitylacridinium cations.[10,11]

Herein we report the results of synthetic studies on dyads comprising of corrole and acridine units.

RESULTS AND DISCUSSION

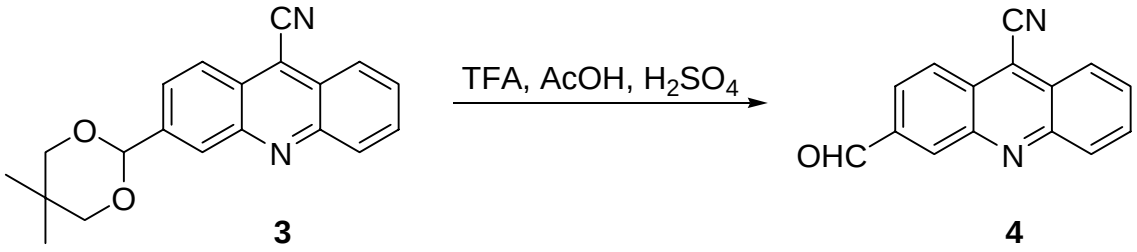
Given the moderate stability of corroles it is desirable to gain significant relief from the corrole manipulations. Consequently we resolved to start with the preparation of an elaborated acridine-derived aldehydes which would then be used in the corrole forming reactions. We decided to build up on our experience in the synthesis of *meso*-substituted *trans*-A_2B-corroles from dipyrromethanes and aldehydes.[12]

This methodology allows to introduce the desired substituent at the 10 position of the macrocycle core. The two remaining identical substituents at the positions 5 and 15 allow to control other properties of the system like: solubility, stability and redox properties. The flux of energy along molecular array shows an exquisite dependence on the chemical nature of the bridge and spatial orientation. Consequently we decided to design three dyads with various orientation of corrole ring versus acridine moiety.

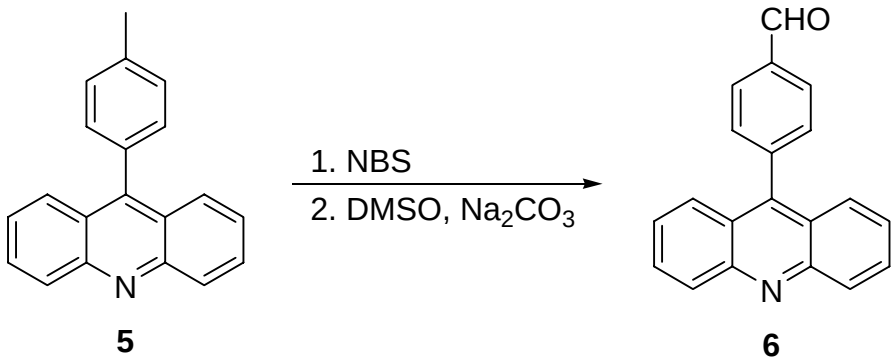


Scheme 1

The most obvious idea is the one with acridine ring directly attached at *meso* position of corrole. From the synthetic point of view the position 9 in acridine is the easiest to functionalize due to the fact that substituent in this position can be easily introduced in the Bernthsen reaction.[13] 9-Methylacridine (**1**) is well-known compound and could be transformed into respective 9-formylacridine (**2**) using selenium oxide (Scheme 1). Since it would be interesting to study the difference in absorption spectrum depending on the place of attachment of acridine ring to corrole moiety we designed aldehyde **4** possessing formyl group at position 2. In order to synthesize aldehyde **4** we took advantage of newly available Wróbel procedure for the synthesis of diversely substituted acridines.[14] Acetal of 4-nitrobenzaldehyde has been transformed into acridine **3**. Deprotection under acidic conditions gave desired aldehyde **4** in 85 % yield (Scheme 2). Yet, another interesting geometry is the one with corrole and acridine moieties being able to achieve perfect coplanarity. To reach this goal we designed aldehyde **6**. 9-(4-Methylphenyl)acridine (**5**) (prepared from *p*-toluic acid and diphenylamine)[15] was brominated with NBS and oxidized with DMSO according to general method to give aldehyde **6** in good overall yield (Scheme 3).



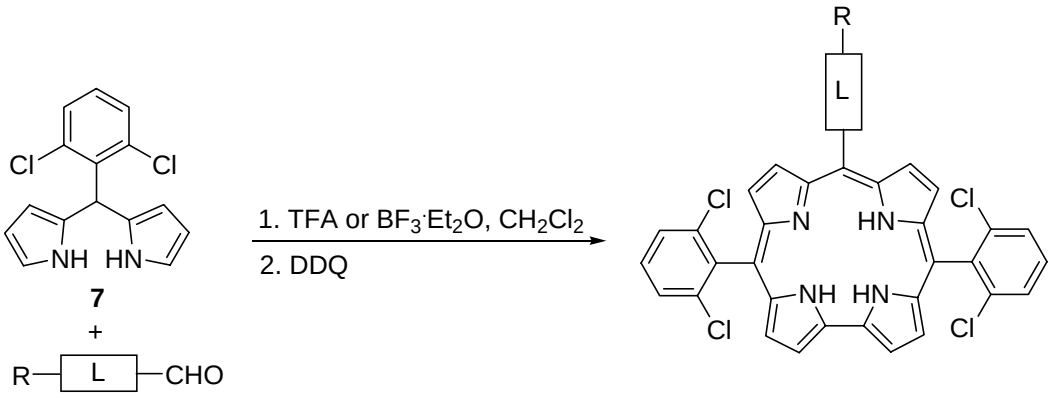
Scheme 2



Scheme 3

Having in hand these three aldehydes we started the synthesis of respective *trans*-A_2B-corroles. The general procedure for the synthesis of *trans*-A_2B-corroles from aldehydes bearing basic nitrogen atom has been developed a few years ago and consists of condensation of dipyrromethanes with aldehydes in the presence of TFA and subsequent oxidation of bilanes with DDQ.[12a] We have chosen 5-(2,6-dichlorophenyl)dipyrromethane (**7**) as a substrate since it gives corroles with high yields and reasonable stability. We found however that this general procedure does not work for 9-formylacridine (**2**). Regardless the reaction time and concentration of TFA we did not obtained corrole **8**. While studying this reaction in-depth we found that reaction stops on the level of first acidic condensation and subsequent elimination to give probably substituted dipyrrine (its presence has been confirmed by MS). This compound does not react further with second molecule of dipyrromethane **7**. We resolved to use $BF_3 \cdot Et_2O$ as an alternative acidic catalyst often employed in porphyrinoid forming reactions and recently employed in corrole synthesis.[16] We found that reaction performed in the presence of 1.35 equivalents of $BF_3 \cdot Et_2O$ followed by addition of DDQ gave desired corrole **8** in the 6% yield. The synthesis of corroles **9** and **10** was less troublesome. We found that they formed easily under previously described conditions[12a] with yields 20% and 34% respectively. One has to note that purification of corroles **9** and **10** had to be done via size exclusion chromatography because the unreactive aldehydes **4** and **6** could not be separated from respective corroles using SiO_2-column chromatography.

Corroles **8**-**10** prepared in such a way were studied for their UV-Vis absorption spectra. The spectra of the dyads are essentially the sum of the spectra of the component parts which indicates weak interaction between chromophores.



2 L = --- R = acridyn-9-yl
4 L = --- R = 9-cyano-acridyn-2-yl
6 L = 1,4-phenylene R = acridyn-9-yl

8 L = --- R = acridyn-9-yl
9 L = --- R = 9-cyano-acridyn-2-yl
10 L = 1,4-phenylene R = acridyn-9-yl

Scheme 4

We proved that covalent assemblies of acridine and *meso*-substituted corrole can be efficiently synthesized via divergent approach with corrole forming step as the last one. The synthesis from the most sterically hindered 9-formylacridine can be performed in acceptable yield when $BF_3 \cdot Et_2O$ is used as catalyst of bilane formation. Interaction between these chromophores is rather small.

EXPERIMENTAL

All chemicals were used as received unless otherwise noted. Reagent grade solvents (CH_2Cl_2, hexanes, cyclohexane) were distilled prior to use. All reported ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AM 500 MHz or Varian 400 MHz spectrometer. Chemical shifts (δ ppm) were determined with TMS as the internal reference; *J* values are given in Hz. Chromatography was performed on silica (Kieselgel 60, 200-400 mesh), or dry column vacuum chromatography (DCVC)[17] was performed on preparative thin layer chromatography silica (Merck 107747). Preparative scale size exclusion chromatography (SEC) was performed using BioRad Bio-Beads SX-1 with THF as eluent. Mass spectra were obtained *via* electrospray MS (ESI-MS). The purity of new corroles was established based on ^{1}H NMR spectra and elemental analysis. The following compounds were obtained according to literature procedures: **3**,[14b] **5**,[18] **7**.[19]

9-Formylacridine (2). Selenium dioxide (1.3 g, 11.7 mmol) was dissolved in dioxane (20 mL) containing 4 % of water. Then 9-methylacridine **1** (1.53 g, 8 mmol), dissolved in 100 mL of dioxane was added and the whole mixture was refluxed for 2 h. After filtration through a pad of Celite, solvent was removed to the ¼ of initial volume and water (100 mL) was added. The resulting mixture was extracted with CH_2Cl_2 (3×20 mL), organic extracts were washed with water (20 mL), dried (Na_2SO_4), evaporated with silica and chromatographed (EtOAc/hexane 3:2) to afford 800 mg (50%) of pure **2**. All analytical data are consistent with literature values.[20]

9-Cyano-4-formylacridine (4). The sample of acetal **3** (318 mg, 1 mmol) was dissolved in the mixture of AcOH (5 ml), TFA (2.5 mL) and 5% aq H_2SO_4 (1.25 mL). After stirring for 4 h at 100 °C, acids were neutralized by addition of Na_2CO_3 aq sat. The resulting suspension was extracted with CH_2Cl_2 (3×10 mL), organic extracts were evaporated and chromatographed (silica, acetone:CH_2Cl_2 5:95) to afford pure aldehyde, which was subsequently crystallized ($CHCl_3$/hexane), 197 mg, 85%. Mp = 217-218 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83-7.87 (m 1H, acridine), 7.97-8.01 (m, 1H, acridine), 8.32-8.38 (m, 2H, acridine), 8.39-8.44 (m, 2H, acridine), 8.83-8.85 (m, 1H, acridine). ^{13}C NMR δ 114.5, 177.6, 125.2, 125.5, 126.5, 126.8, 129.9, 130.7, 131.9, 132.2, 132.5, 135.9, 149.8, 150.0, 190.7. EI-HR obsd 232.0642 [$M^{\cdot+}$], calcd exact mass 232.0636 ($C_{15}H_8N_2O$). Anal. Calcd for $C_{15}H_8N_2O\cdot 1/5H_2O$: C, 76.39; H, 3.59; N, 11.88. Found: C, 76.53; H, 3.63; N, 11.70.

9-(4-Formylphenyl)-acridine (6). Bromide prepared from derivative **5**[15] (2.6 g, 7.5 mmol) was dissolved in DMSO (50 mL) and Na_2CO_3 (4.86 g, 45 mmol) was added. The resulting mixture was stirred at 100 °C for 20 min. Solvent was removed under high vacuum, the yellow residue was chromatographed (alumina, AcOEt:hexane 1:4) to afford crude aldehyde (1.69 g, 80%, contaminated with bromide) which was used in the next step without further purification.

10-Acridinyl-5,15-bis(2,6-dichlorophenyl)corrole (8). Dipyrromethane **7** (1.16 g, 4 mmol) and aldehyde **2** (414 mg, 2 mmol) were dissolved in CH_2Cl_2 (160 mL). This mixture was bubbled with argon for 20 min. and $BF_3\cdot Et_2O$ (340 μL, 2.68 mmol) was added dropwise. After stirring for 4 h, Et_3N (373 μL, 2.68 mmol) was added. DDQ (1.18 g, 5.2 mmol) was dissolved in toluene:CH_2Cl_2 (1:1, 40 mL) and both mixtures were added simultaneously to the vigorously stirred CH_2Cl_2 (50 mL). After 15 min. the reaction mixture was concentrated to ¼ of initial volume and filtered through silica pad (CH_2Cl_2). The fluorescent band was collected and chromatographed (DCVC, silica, CH_2Cl_2). After evaporation the residue was crystallized from $CHCl_3$/hexanes to afford corrole **8** (92 mg, 6%). R_f = 0.55 (silica, acetone/CH_2Cl_2, 5:95). ^{1}H NMR (500 MHz, $CDCl_3$) δ (–2.5) – (–0.5) (br s, 3H, NH), 7.10-7.20 (m, 2H, acridine), 7.30 (d, 2H, 9 Hz, acridine), 7.63 (t, 2H, 8 Hz, $C_6H_3Cl_2$), 7.75 (d, 8 Hz, 4H, $C_6H_3Cl_2$), 7.78 (t, 8 Hz, 2H, acridine), 7.90 (d, 4Hz, 2H, β-H), 8.36 (d, 4 Hz, 2H, β-H), 8.43 (br d, 4 Hz, 2H, β-H), 8.49 (d, 8 Hz, 2H, acridine), 9.01 (d, 2H, 4 Hz, β-H). ESI-HR obsd 764.0973 [M + H^+], calcd exact mass 764.0937 ($C_{44}H_{25}Cl_4N_5$). Anal. Calcd for $C_{47}H_{26}F_9N_5O_2$: C, 69.03; H, 3.39; Cl, 18.53; N, 9.15. Found: C, 69.01; H, 3.61; Cl, 18.38; N, 8.90. λ_{abs} (toluene, $\varepsilon \times 10^{-3}$) 410 (114), 426 (102), 568 (20.9), 6.8 (13.1), 640 (3.9) nm.

10-[9-Cyano-2-acridinyl]-5,15-bis(2,6-dichlorophenyl)corrole (9). Dipyrromethane **7** (580 mg, 2 mmol) and aldehyde **4** (232 mg, 1 mmol) were dissolved in CH_2Cl_2 (60 mL). Then TFA (230 μL, 3 mmol) was added dropwise and the whole mixture was stirred for 1 h at rt followed by addition of Et_3N (420 μL, 3 mmol). DDQ (590 mg, 2.6 mmol) was dissolved in toluene:CH_2Cl_2 (1:1, 60 mL) and both mixtures were added simultaneously to the vigorously stirred 50 mL of CH_2Cl_2. After 15 min. the reaction mixture was

concentrated to ¼ of initial volume and filtered through silica pad (CH_2Cl_2, then CH_2Cl_2 + acetone). The fluorescent band was collected and chromatographed (DCVC, silica, CH_2Cl_2 then CH_2Cl_2 + 1% of acetone) to afford corrole **9** contaminated with aldehyde **4**. After evaporation, the residue was dissolved in THF and loaded on SEC column (THF). The violet fraction was collected, evaporated and crystallized from $CHCl_3$/hexane to afford 268 mg (34%) of corrole **9**. R_f = 0.55 (silica, acetone/CH_2Cl_2, 1:99).^{1}H NMR (500 MHz, $CDCl_3$) δ (–3) – (–1) (br s, 3H, NH), 7.63 (t, 2H, 8 Hz, $C_6H_3Cl_2$), 7.73-7.79 (t, 8 Hz, 4H, $C_6H_3Cl_2$), 7.85 (m, 1H, acridine), 7.98 (m, 1H, acridine), 8.42 (br d, 3 Hz, 2H, β-H), 8.50 (d, 2H, acridine), 8.56-8.59 (2×d, 4H, β-H), 8.61 (d, 9 Hz, 1H, acridine), 8.78 (d, 8 Hz, 1H, acridine) 9.01 (d, 4 Hz, 2H, β-H), 9.14 (s, 1H acridine). ESI-HR obsd 789.0926 [M + H^+], calcd exact mass 789.0889 ($C_{45}H_{25}Cl_4N_6$). Anal. Calcd for $C_{45}H_{25}Cl_4N_6$: C, 68.37; H, 3.06; N, 10.63. Found: C, 68.32; H, 3.29; N, 10.43. λ_{abs} (toluene, $\varepsilon \times 10^{-3}$) 408 (103), 425 (96.5), 531 (18.6), 571 (18.0), 610 (13.0) nm.

10-[4-(9-Acridinyl)-phenyl]-5,15-bis(2,6-dichlorophenyl)corrole (10). Dipyrromethane **7** (580 mg, 2 mmol) and crude aldehyde **6** (283 mg, 1 mmol) were dissolved in CH_2Cl_2 (60 mL). Then TFA (230 μL, 3 mmol) was added drop wise and the whole mixture was stirred for 1 h at r.t. followed by addition of Et_3N (420 μL, 3 mmol). DDQ (590 mg, 2.6 mmol) was dissolved in toluene:CH_2Cl_2 (1:1, 60 mL) and both mixtures were added simultaneously to the vigorous stirred 50 mL of CH_2Cl_2. After 15 min. the reaction mixture was concentrated to ¼ of initial volume and filtered through silica pad (CH_2Cl_2, then CH_2Cl_2 + acetone). The fluorescent band was collected and chromatographed (DCVC, silica, CH_2Cl_2 then CH_2Cl_2 + 1% of acetone) to afford corrole **10** contaminated with aldehyde **7**. After evaporation, the residue was dissolved in THF and loaded on SEC column (THF). The violet fraction was collected, evaporated and crystallized from $CHCl_3$/hexane to afford 168 mg (20%) of corrole **10**. R_f = 0.52 (silica, acetone/CH_2Cl_2, 1:99). ^{1}H NMR (500 MHz, $CDCl_3$) δ (–2.5) – (–1) (br s, 3H, NH), 7.69 (t, 2H, 8 Hz, $C_6H_3Cl_2$), 7.80 (d, 8 Hz, 4H, $C_6H_3Cl_2$), 7.86 (d, 7.5 Hz, 4H, C_6H_4), 7.95 (br s, 2H, acridine), 8.20 (br s, 3H, acridine), 8.45 (br d, 4 Hz, 2H, β-H), 8.50 (br m, 3H, acridine), 8.64 (d, 4Hz, 2H, β-H), 8.79 (d, 4 Hz, 2H, β-H), 9.03 (d, 4 Hz, 2H β-H). ESI-MS obsd 840.1 [M + H^+]. λ_{abs} (toluene, $\varepsilon \times 10^{-3}$) 413 (105), 430 (95.8), 569 (17.1), 610 (10.7) nm.

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