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On the Chemistry of Pyrrole Pigments, LXXXIX [1]: Vinylogous Linear Di- and Tetrapyrroles

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Summary. A vinylogous dipyrrinone, its Ehrlich aldehyde condensate, and the vinylogous bilindione derived from the vinylogous dipyrrinone were prepared. Their structural aspects of tautomerism, configuration and conformation were derived by analysis of their ^{1}H-NMR data. Selected physical properties were determined and are discussed.

Keywords. Vinylogous dipyrrinone; Vinylogous bilindione; Synthesis; Structural Aspects; Spectroscopic properties.

Zur Chemie von Pyrrolpigmenten, 89. Mitt. [1]: Vinyloge Lineare Di- und Tetrapyrrole

Zusammenfassung. Ein vinyloges Dipyrrinon, sein Ehrlich-Aldehyd-Kondensat und ein vom vinylogen Dipyrrin abgeleitetes vinyloges Bilindion wurden dargestellt. Ihre strukturellen Aspekte der Tautomerie, Konfiguration und Konformation wurden durch Analyse ihrer ^{1}H-NMR-Daten abgeleitet. Ausgewählte physikalische Eigenschaften wurden gemessen und diskutiert.

Introduction

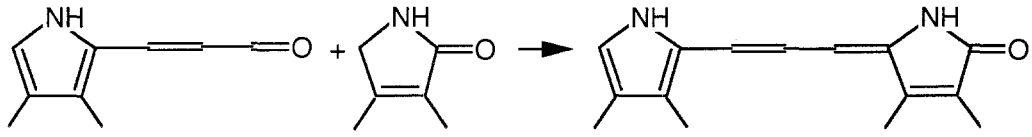
In the recent years we studied a series of artificially modified compounds which were derived from the linear dipyrroles and the natural linear tetrapyrroles [2 – 8]. The modifications introduced used either an elongation of the conjugated system, attaching further pyrrolic units [2, 3, 7], or they were constructed shortening the system by directly linking pyrrole rings [4 – 6]. Such derivatives are of interest with respect to their unique structural features and their function as potential ligands in the transport of cations through membranes [6, 7]. Moreover, such modified linear oligopyrroles are also of interest with respect to their potential non-linear optical properties [1]. Vinylogous systems in the cyclic tetrapyrrole, i. e., porphyrin, series have been communicated [9 – 11], and they exhibit remarkable structural features. We now will report on our investigation of linear oligopyrroles modified by means of a vinylogous elongation of the conjugation path.

Results and Discussion

Synthesis

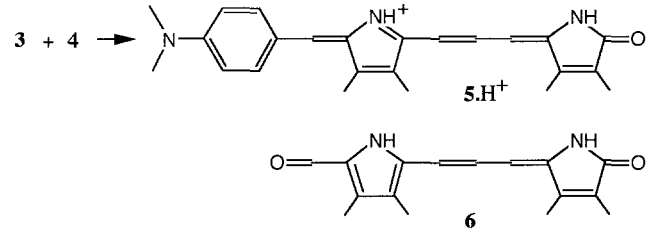
The vinylogous pyrrolecarbaldehyde **1** was prepared in analogy to the corresponding 3,4-diethylpyrrole derivative [12] by means of a Vilsmeier formylation of 3,4-

dimethylpyrrole with dimethylaminoacroleine. Base catalyzed condensation of **1** with the well-known pyrrolinone **2** afforded the vinylogous dipyrrinone **3** with good yield.



1 **2** **3**

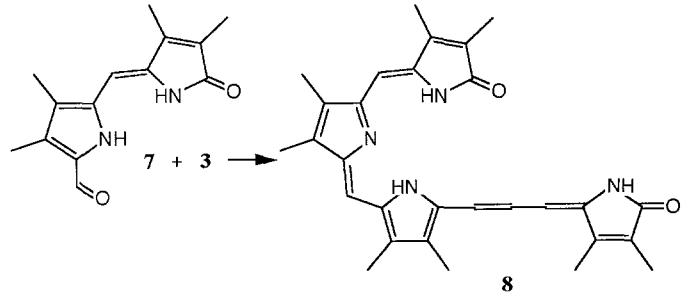
Acid catalyzed condensation of **3** with Ehrlich's aldehyde (**4**) resulted in the formation of the protonated derivative **5** · H^+. Deprotonation of this salt by means of the polymeric base dimethylaminomethyl polystyrene afforded the rather instable free base **5**, which obviously is extremely prone to attack by nucleophiles. This behavior is well known from several examples in which there is no stabilization of the pyrroleninic nitrogen by means of an intramolecular hydrogen bond available [13–16]. Vilsmeier formylation of **3** by means of dimethylaminoformaldehyde yielded the corresponding extended dipyrrinone-11-carbaldehyde **6**.



5.H^+

6

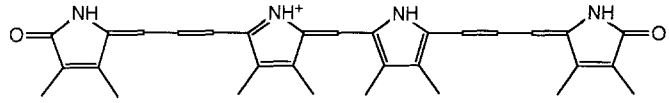
To prepare the mono-vinylogous verdin **8**, the vinylogous dipyrrinone **3** was condensated with the dipyrrinone carbaldehyde **7** under acid catalysis. In contrast to **5** · H^+, deprotonation of the resulting **8** · H^+ proved to proceed without any problem. In this case the pyrroleninic ring of **8** can be easily stabilized by an intramolecular hydrogen bridge system which is comparable to the one in common verdinoid systems [8]. Of course, it was checked that acid catalyzed condensation of the carbaldehyde **6** with the tetramethyldipyrrinone **9**, derived from **7**, also yields **8**.



8

Acid catalyzed condensation of the carbaldehyde **6** with its corresponding vinylogous dipyrrinone **3** resulted in the formation of the protonated bis-vinylogous verdin **10** · H^+. Due to its insolubility, only its ^{1}H-NMR and UV-Vis spectra in trifluoroacetic acid could be recorded. Compared to **5** · H^+, deprotonation of

10 · H^+ resulted in a too rapid decomposition to allow the characterization of **10** free base. At least, its UV-Vis spectrum could be recorded with pyridine as the solvent.



10.H+

Structural Aspects

The structural aspect of tautomerism posed no problem in the vinylogous dipyrrinones like **3** as no indication of the presence of a lactim tautomer was found in the NMR data, and the protonation pK_a value of this compound was estimated to amount to -0.3, thus providing the necessary pK_a gap to the corresponding lactim form (compare [8]). On the contrary, the configurational and conformational aspects of the vinylogous dipyrrinones are quite formidable. Fig. 1 shows the interconversion graph (which is isomorphous to the one found for linear tripyrroles [8]), where *ZZ...EE* and *ss...aa* denote the configurations at the two exocyclic double bonds and the *synperiplanar* and *antiperiplanar* conformations at the two

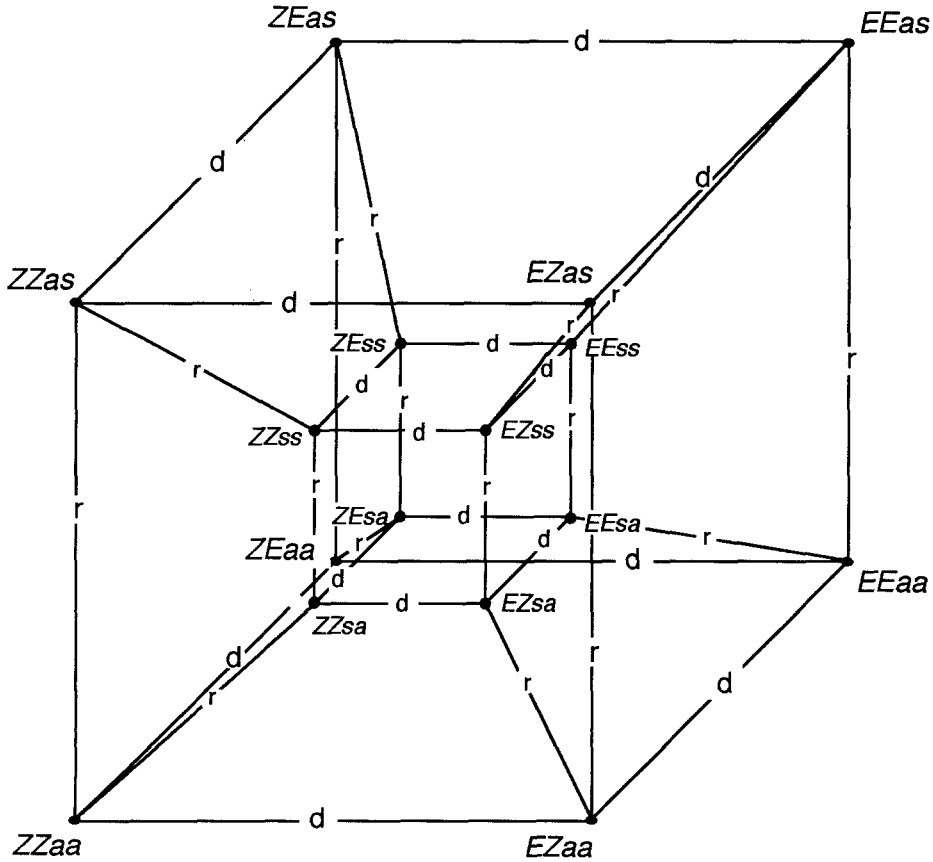


Fig. 1. Interconversion graph for the stereoisomers of a vinylogous dipyrrinone like **3** (d...diastereomerizations, r...rotational modes)

exocyclic single bonds. The latter approximation, to restrict the discussion to the *periplanar* arrangements, seemed to be justified because of the conjugative planarization of such conjugated molecules. Accordingly, in principle one has to take into account sixteen species.

The coupling constants in the ^{1}H-NMR spectrum of the vinylic protons H-6 and H-7 of **3** were found to be 15.4 Hz. Thus the configuration (*E*) at the double bond in position **6** was assigned. A significant NOE between the 3-methyl group and the 5-H led to the assignment of the (*Z*) configuration to the exocyclic double bond in position 4. From the coupling constant of 11.1 Hz between H-5 and H-6, which is typical of protons situated *antiperiplanar* in conjugated systems, together with NOEs between the 9-methyl group and both, H-6 and H-7, we derived an equilibrium between the about equipopulated 5*ap*, 7*sp* and the 5*ap*, 7*ap* conformers (Fig. 2). The torsional angles at the two single bonds were estimated to be $<30°$

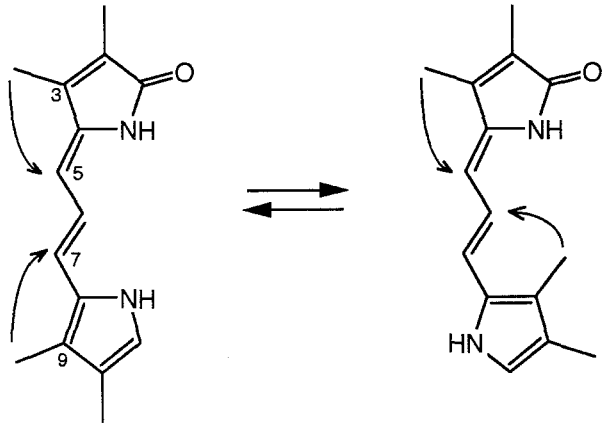


Fig. 2. Strategic NOEs and equilibrium between (4*Z*,6*E*,5*ap*,7*sp*)-**3** and (4*Z*,6*E*,5*ap*,7*ap*)-**3**

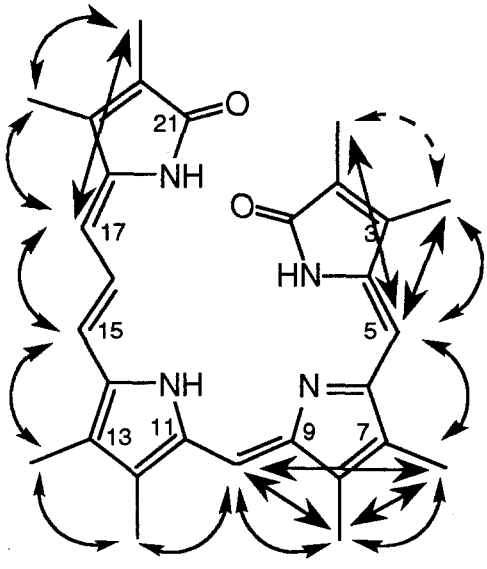


Fig. 3. Geometry, COSY (straight arrows), and NOESY (bent arrows) ^{1}H-correlations; chloroform-d_1 solution of **8**

from the characteristic one double bond extension shift of 28 nm between the long wavelength absorption bands of **3** and **9**.

The principal structural possibilities for the extended verdin **8** are impressive indeed: the 1 240 species of bilindiones [8] become expanded by the configurational and conformational modes of the vinylogous fragment to yield 4 960 species. Concerning tautomerism, **8** was thought to exhibit the bis-lactam form in analogy to the bilindiones (only the protonation pK_a at the pyrrolenine nitrogen atom of 5.0, could be established). Accordingly, a strong hydrogen bonding system stabilizes this arrangement (compare [8] for tripyrrins and bilindiones). With respect to the position of the third mobile proton, the couplings between CH_3-7 and CH_3-8 as well as between them and H-10, which were derived from the COSY experiment (see Fig. 3), pointed to a linear conjugation path along C-7 to C-10 (for examples of this phenomenon see [8]). Accordingly, the acidic proton was found to be localized at N-24.

The configuration of (4*Z*,9*Z*,15*E*,17*Z*) immediately followed from the NOEs as shown in Fig. 3, and from the magnitude of the coupling constant $J_{H15-H16}$ for chloroform as the solvent. By the same means and from the coupling constant $J_{H16-H17}$ a preferred (5 *syn*, 10 *syn*, 14 *syn*, 16 *anti*) conformation was deduced.

This resulted in a circular helical arrangement, which has been found also for a variety of bilindiones [8]. However, inspection of the absorption spectrum of **8**, recorded with chloroform as the solvent, revealed a second smaller short wavelength transition (Fig. 4). It turned out that the relative intensities of these two absorption bands changed with the polarity of the solvent used. Moreover, this second band became the prominent one in hexamethylphosphoric triamide (*HMPT*; Fig. 4).

The COSY and NOESY data of **8** (Fig. 5) together with the coupling constants of the AMX system for the latter solvent suggested a deformed, but still helical arrangement of the 24-H tautomer, which was of (4*Z*,9*Z*,15*E*,17*Z*) configuration,

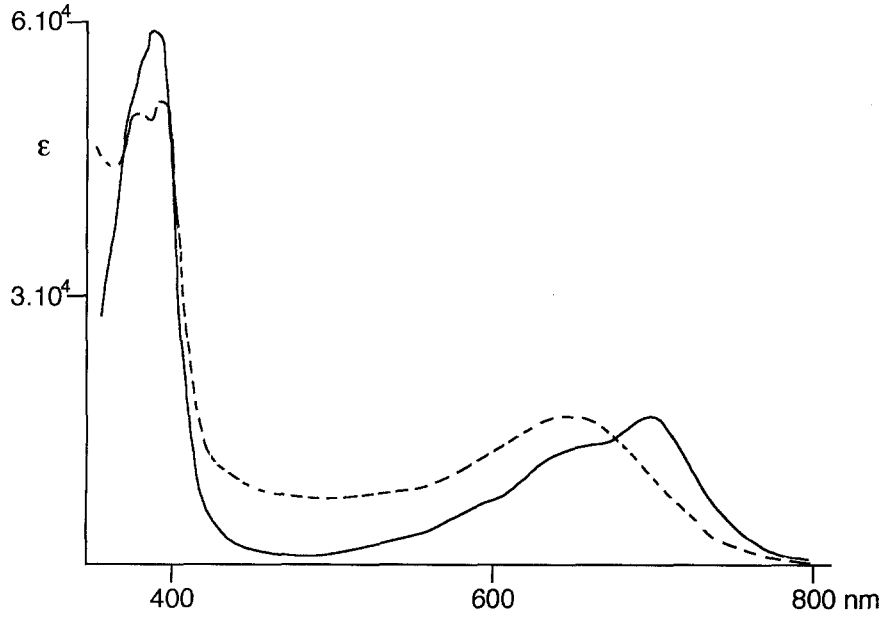


Fig. 4. Absorption spectra of **8** in chloroform (?) and hexamethylphosphoric triamide (– –; x1) solutions

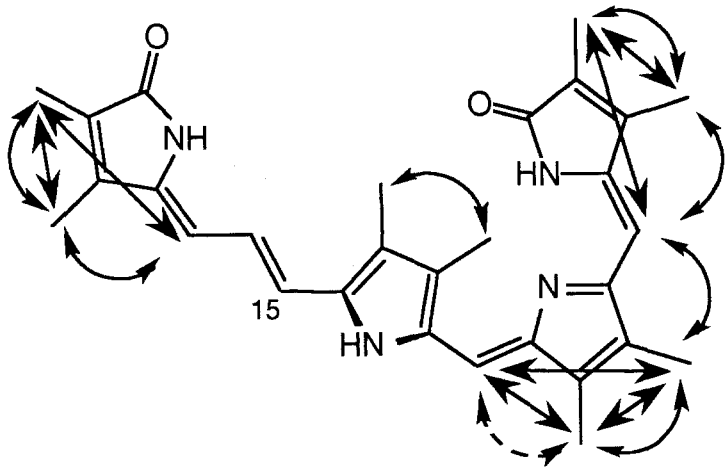


Fig. 5. Geometry, COSY (straight arrows), and NOESY (bent allows) ^{1}H-correlations; hexamethylphosphoric triamide-d_{18} solution of **8**

and (*5 syn*, 10 *anti*, 14 *anti*, 16 *anti*) conformation. It was different from the one observed for corresponding *HMPT* solutions of 2,3-dihydrobilindiones [17], as the tripyrrin moiety still is in a circular conformation. This was also in accord with the observation that the relative intensities of the long wavelength to short wavelength absorption bands did not significantly change on the transition between the two solvents (see Fig. 4). It has been found that an inverted relative intensity is characteristic of arrangements stretched by diastereomerization at the methine position 10 in the bilindione series [8, 17]. The hypsochromic shift of about 50 nm between chloroform and *HMPT* solutions was accounted for by the stronger dihedral distorsions of the single bonds at C-10 and C-14 (Fig. 5) due to a pronounced steric crowding between the 12-methyl group and the pyrrolenine ring. This stronger distorsion would also account for the absence of a NOE between CH_3-13 and H-16.

Obviously, **8** exhibits a conformational equilibrium which is dependent on the solvent used, and which is similar to the one deduced for **3**.

Concerning the structural aspects of **10** the rather "normal" shaped UV-Vis spectrum points to a configurational and conformational situation of a more or less circular helical arrangement which is analogous to that deduced for **8** dissolved in an apolar solvent (compare Fig. 3). Unfortunately, due to the instability of the free base **10** advanced NMR techniques could not be applied to this compound.

Selected Physical Properties

With respect to their non-linear optical properties **3** and **5** presented appropriate examples to compare normal and vinylogous derivatives. The corresponding data were estimated as described in the previous paper by the method of solvatochromic shifts [1]. From ω_{eg} (*DMSO*) = 23 552 cm^{-1}, ω_{eg} (heptane) = 23 496 cm^{-1}, ε = 23 670, $\delta\nu_{1/2}$ = 2 108 cm^{-1}, a mean μ_g = 3.9 D for the equilibrium mixture of the two conformers, a = 8.7 Å, ω_{eg} = 23 697 cm^{-1}, μ_e = 5.8 D, μ_{eg} = 6.5 D,

$A = -346\,cm^{-1}$, and $B = 117\,cm^{-1}$, β_{xxx} (1907 nm) $= 7 \cdot 10^{-30}\,esu^{-1}\,cm^5$ was deduced for **3**. This value is lower than the one observed for the corresponding dipyrrinone ($23 \cdot 10^{-30}\,esu^{-1}\,cm^5$ [1]). This result may be explained by the different geometry of the two compounds which leads to a substantial canceling of partial dipole moments. In the case of **5** the corresponding normal Ehrlich aldehyde condensate (β_{xxx} (1907 nm) $= 53 \cdot 10^{-30}\,esu^{-1}\,cm^5$ calculated for *DMSO* and acetone as the reference solvents [1]) has a significantly lower non-linear optical property: From ω_{eg} (*DMSO*) $= 18\,615\,cm^{-1}$, ω_{eg} (acetone) $= 19\,380\,cm^{-1}$, $\varepsilon = 30\,000$, $\delta\nu_{1/2} = 1\,736\,cm^{-1}$, $\mu_g = 1.2\,D$, $a = 9.0\,Å$, $\omega_{eg} = 18\,560\,cm^{-1}$, $\varepsilon = 131.3\,D$, $\mu_{eg} = 7.5\,D$, $A = -1\,919\,cm^{-1}$, and $B = 647\,cm^{-1}$, the non-linear optical property β_{xxx} (1907 nm) $= 128 \cdot 10^{-30}\,esu^{-1}\,cm^5$ was deduced for **5**. Thus vinylogous extension of the conjugation path by one double bond led to an increase of β_{xxx} (1907 nm) to about twice its value.

The fluorescence of **3** at room temperature was found to be rather low ($\Phi_f = 5 \cdot 10^{-4}$, ethanol) and was considerably enhanced at 77 K ($\Phi_f = 4 \cdot 10^{-2}$). This behavior is similar to the one observed for corresponding dipyrrinones [8]. Obviously, also in **3** one of the main deexcitation channels is diastereomerization at the exocyclic double bond(s). Indeed, when irradiating a solution of **3** in *DMSO* at room temperature in a NMR tube, a new set of signals developed at 10.43 (broad s, NH), 10.14 (broad s, NH), 6.64 (broad s, =CH), 6.23 (broad s, =CH), 2.03 (s, CH_3-10), 1.92 (s, CH_3-3 + CH_3-9) together with an unchanged signal at 1.75 (s, CH_3-2) ppm. The small coupling which was observed between H-5, H-6, and H-7 would point to the (4*Z*,6*Z*,5*syn*) – or even the (4*E*,6*Z*,5*syn*) – arrangement. Unfortunately, the thermal stability of this photodiastereomer proved to be insufficient for its isolation and further characterization.

Experimental Part

Melting points were taken by means of a Kofler hot stage microscope (Reichert, Vienna). ^{1}H-NMR, IR-, UV-VIS-, fluorescence and M-spectra were recorded using the Bruker AX-200-, Bruker WM-360-, Biorad FTIR-45-, Hitachi U-3210-, Hitachi F-4010-, and Varian MAT-311-A-instruments. Proton signal and stereochemical assignments were achieved using COSY, NOE, and NOESY measurements on degassed solutions; *TMS* was used as the internal reference. Spectrophotometric titrations were recorded using aqueous sulfuric acid of various concentrations or a methanol water mixture (9/1). Ehrlich's aldehyde (**4**) was of commercial origin (Merck). Quinine · HCl (Merck) dissolved in 1 *N* H_2SO_4 was used as a fluorescence standard.

(Z,E)-3,4-Dimethyl-5-[3-(3,4-dimethylpyrrol-2-yl)-prop-2-enylidene]-3-pyrrolin-2-one
[**3**; $C_{15}H_{18}N_2O$]

120 mg (0.8 mmol) **1** [12] and 100 mg (0.9 mmol) **2** [18] were dissolved in 2 ml refluxing methanol. After addition of 1 ml 4 *N* NaOH the mixture was refluxed for additional 20 min. The precipitate was filtered off, washed several times with ether and water, and dried in high vacuum. Yield 169 mg (87%); m. p. > 350°C. ^{1}H-NMR (*DMSO-d*$_6$, δ, 200 MHz): 10.15 (s, broad, NH), 9.78 (s, broad, NH), 6.78 (dd, $J_1 = 15.4$ Hz, $J_2 = 11.1$ Hz, H-6), 6.61 (s, H-11), 6.60 (d, $J = 15.4$ Hz, H-7), 6.01 (d, $J = 11.1$ Hz, H-5), 2.00 (s, CH_3-9), 1.98 (s, CH_3-10), 1.90 (s, CH_3-3), 1.75 (s, CH_3-2) ppm. NOE: CH_3-3 → H-5, CH_3-9 → H-6 and H-7, CH_3-10 → H-11. IR (KBr): $\nu = 1\,670$, 1 619, 1 602 cm^{-1}. UV-Vis ($CHCl_3$): $\lambda = 422$ (23 670) nm (ε). UV-Vis (heptane): $\lambda = 426$ nm. UV-Vis (*DMSO*): $\lambda = 425.8$ (21 080) nm (ε). Fluorescence (degassed ethanol): $\lambda_{excit.} = 365$ nm, $\lambda_{fluor.} = 500$ nm; Φ_f (300 K) $= 5 \cdot 10^{-4}$, Φ_f

(77 K) = $4 \cdot 10^{-2}$. $pK_a = -0.3$; aqueous sulfuric acid, $\lambda = 420$ nm, $\lambda_H{}^+ = 384$ nm. MS (70 eV, 100°C) *m*/e (%) = 242 (M^+, 100), 227 (11), 199 (8), 185 (11), 147 (10), 121 (18), 95 (15), 32 (11).

(Z,E)-3,4-Dimethyl-5-{3-[5-(4-N,N-dimethylaminophenylmethylene)-3,4-dimethylpyrrol-2-yl]-prop-2-enylidene}-3-pyrrolin-2-one [**5**; $C_{24}H_{28}N_3O$]

62 mg (0.41 mmol) **4** were dissolved in 2 ml trifluoroacetic acid, and at 0°C a solution of 100 mg (0.41 mmol) **3** in 5 ml trifluoroacetic acid was added dropwise during a period of 0.5 h. After refluxing the reaction mixture for 0.5 h, the trifluoroacetic acid was removed by distillation and the resulting salt was triturated with dichloromethane to remove any starting materials. Yield 123 mg (80%). ^{1}H-NMR (CD_3OD, δ, 200 MHz): 7.62 (dd, $J_1 = 15.5$ Hz, $J_2 = 12.0$ Hz, H-6), 7.43 (s, H-10), 7.85, 7.80, 6.92, 6.87 (peaks of the AA'BB' system, 4 H-aromatic) 6.73 (d, $J = 15.5$ Hz, H-5), 6.10 (d, $J = 12.0$ Hz, H-7), 2.23, 2.11, 1.99, 1.78 (s, 6 CH_3) ppm. IR (KBr): ν = 1 683, 1 588, 1 204, 1 133 cm^{-1}. The free base **5** was extremely instable. Therefore, it was set free by dispersing the salt together with an equimolar amount of dimethylaminomethyl-polystyrene (Fluka) in the thoroughly dried solvent used to record the following absorption spectra. UV-Vis (*DMSO*): λ = 537, 359 nm. UV-Vis (pyridine): λ = 537, 361 nm. UV-Vis (acetone): λ = 516, 353 nm. UV-Vis (chloroform): λ = 538, 359 nm. The corresponding extinction coefficients could not be measured due to the instability of these solutions.

(Z,E)-3,4-Dimethyl-5-[3-(5-formyl-3,4-dimethylpyrrol-2-yl)-prop-2-enylidene]-3-pyrrolin-2-one [**6**; $C_{16}H_{18}N_2O_2$]

100 mg (0.41 mmol) **3** were dissolved in 2 ml CF_3COOH, cooled to 0°C, and under vigorous stirring 0.5 ml of triethylorthoformiate were added at once. After stirring for additional 10 min the reaction mixture was poured into 20 ml of ice-water and the mixture was stirred for 10 min. Extraction with dichloromethane, three washings with water, drying over $MgSO_4$, and evaporation resulted in a raw material which was purified by column chromatography on silica (dichloromethane/methanol = 100/3); yield 93 mg (84%), m. p. not below 350°C. ^{1}H-NMR (*DMSO-d_6*, δ, 200 MHz): 11.09 (broad, NH), 9.83 (broad, NH), 9.55 (s, CHO), 7.25 (dd, $J_1 = 15.7$, $J_2 = 11.7$ Hz, H-6), 6.67 (d, $J = 15.7$ Hz, H-7), 6.04 (d, $J = 11.7$ Hz, H-5), 2.18 (s, CH_3-8), 2.05 (s, CH_3-7), 2.00 (s, CH_3-3), 1.77 (s, CH_3-2) ppm. IR (KBr): ν = 1 700, 1 612, 1 453 cm^{-1}. UV-Vis ($CHCl_3$): λ = 421 (32 480), 296 (22 830) nm (ε).

(4Z,9Z,15E,17Z)-2,3,7,8,12,13-Hexamethyl-14-[3-(3,4-dimethyl-2-oxo-3-pyrrolin-5-ylidene)-propenyl]-(24H)-tripyrrinone [**8**; $C_{29}H_{32}N_4O_2$]

20 mg (0.082 mmol) **3** were dissolved in 1 ml trifluoroacetic acid, and 20 mg (0.082 mmol) **7** [19] were added at once. The mixture was stirred for 10 min at room temperature, and 6 ml methanol of 0°C were added. The resulting dark-blue solution was stirred at room temperature for additional 10 min, poured into 20 ml dichloromethane, washed twice with 2% $NaHCO_3$ solution and water, dried over $MgSO_4$, and evaporated. Column chromatography (silica, chloroform/methanol = 100/3) afforded 12 mg (31%) **8**; m. p. >350°C. Alternatively, **8** was also formed on analogous condensation of **6** with 2,3,7,8-tetramethyldipyrrinone [20]. ^{1}H-NMR ($CDCl_3$, δ, 360 MHz): 9.17 (s, broad, NH), 6.76 (s, H-10), 6.64 (s, broad, H-15 + H-16), 6.06 (s, H5), 5.96 (d, $J = 10.0$ Hz, H-17), 2.21 (s, CH_3-12), 2.18 (s, CH_3-2 + CH_3-8), 2.14 (s, CH_3-3), 2.10 (s, CH_3-13), 2.09 (s, CH_3-7), 2.04 (s, CH_3-19), 1.90 (s, CH_3-20) ppm. COSY and NOESY experiments see Fig. 3. ^{1}H-NMR (*HMPT-d_{18}*, δ, 360 MHz): 10.03 (s, broad, NH), 7.26 (dd, $J_1 = 15.3$ Hz, $J_2 = 11.9$ Hz, H-16), 7.04 (s, H-10), 6.96 (d, $J = 15.3$ Hz, H-15), 6.32 (s, H-5), 6.18 (d, $J = 11.4$ Hz, H-17), 2.26 (s, CH_3-12), 2.20 (s, CH_3-3), 2.19 (s, CH_3-8), 2.18 (s, CH_3-13), 2.10 (s, CH_3-7), 2.07 (s, CH_3-19), 1.96 (s, CH_3-2), 1.81 (s, CH_3-20) ppm. COSY and NOESY experiments see Fig. 5. Due to the insufficient solubility of **8**, its ^{13}C-NMR spectrum could not be obtained. IR (KBr): ν = 1 696, 1 600, 1 507, 1 152, 940 cm^{-1}. UV-Vis ($CHCl_3$): λ = 699 (13 620), 650 (sh), 391 (58 300) nm (ε). UV-Vis (*HMPT*): λ = 649 (13 860), 397 (43 350) nm (ε). UV-Vis (*DMSO*): λ = 663 (10 340), 397 (39 050) nm (ε). UV-Vis (pyridine): λ = 699 (8 330), 652 (sh), 396 (44 190) nm (ε).

UV-Vis (acetone): $\lambda = 685$ (11 160), 649 (sh), 388 (49 720) nm (ε). UV-Vis (CH_2Cl_2): $\lambda = 696$ (9 680), 649 (sh), 391 (40 760) nm (ε). UV-Vis (toluene): $\lambda = 700$ (11 310), 650 (sh), 397 (47 760) nm (ε). UV-Vis (heptane): $\lambda = 698$, 650 (sh), 392 nm. $pK_a = 5.0$; aqueous methanol (1/9) $\lambda = 650$ nm, $\lambda_H{}^+ = 690$ nm. MS (70 eV; 100°C): *m/e* (%) = 468 (M^+, 100), 453 (20), 234 (13), 209 (4), 32 (4).

Condensation of **3** *and* **6**: **10** · CF_3COOH

10 mg (0.041 mmol) **3** were dissolved in 1 ml CF_3COOH and 11 mg (0.041 mmol) **6** were added at once. The solution was stirred at room temperature for 10 min, cooled to 0°C and 6 ml methanol was added. The resulting mixture was evaporated and triturated with dichloromethane to remove the educts. The residue (yield 90%) was only soluble in trifluoroacetic acid and pyridine. In the latter solvent decomposition prevented recording of an NMR spectrum. ^{1}H-NMR (CF_3COOD, δ, 200 MHz): 7.55 (dd, $J_1 = 15.4$ Hz, $J_2 = 12.2$ Hz, H-6 + H-18), 7.26 (s, H-12), 6.90 (d, $J_1 = 15.4$ Hz, H-17 + H-17), 6.52 (d, $J_2 = 12.2$ Hz, H-5 + H-19), 2.26 (s, CH_3-10 + CH_3-14), 2.21 (s, CH_3-9 + CH_3-15), 2.11 (s, CH_3-3 + CH_3-21), 1.90 (s, CH_3-2 + CH_3-23) ppm. UV-Vis (CF_3COOH): $\lambda = 706$ (1), 396 (3) nm (rel. intensity). UV-Vis (pyridine): $\lambda = 658$ (1), 409 (5) nm (rel. intensity).

Acknowledgements

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