Monatshefte für Chemie 124, 881–891 (1993)

*Monatshefte für Chemie*
*Chemical Monthly*

Printed in Austria

# On the Chemistry of Pyrrole Pigments, XC [1]: Pyridinologous Linear Tri- and Tetrapyrroles

**H. Falk*** and **A. Šuste**

Institut für Chemie, Johannes-Kepler-Universität Linz, A-4040 Linz, Austria

**Summary.** One pyridinologous linear tripyrrole and two pyridinologous linear tetrapyrroles were prepared, and their structural aspects derived from spectroscopic measurements and force field calculations. The properties of these novel pyrrole pigments are compared with those of analogous linear tri- and tetrapyrroles.

**Keywords.** Pyridinologous linear tri- and tetrapyrroles; $^1$H-NMR spectra; UV-Vis spectra; Fluorescence; $pK_a$-values; Configuration; Conformation.

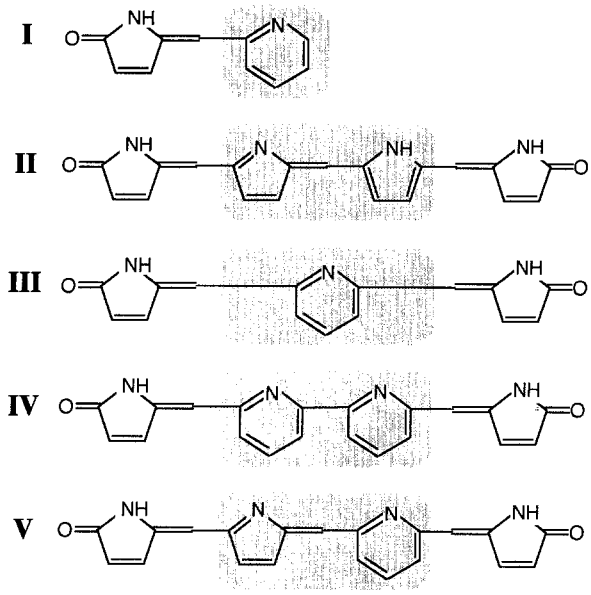
**Zur Chemie von Pyrrolpigmenten, 90. Mitt. [1]: Pyridinologe lineare Tri- und Tetrapyrrole**

**Zusammenfassung.** Ein pyridinologes lineares Tripyrrol und zwei pyridinologe lineare Tetrapyrrole wurden dargestellt und ihre strukturellen Aspekte aus spektroskopischen Messungen und Kraftfeldrechnungen abgeleitet. Die Eigenschaften dieser neuen Pyrrolpigmente werden mit jenen analoger linearer Tri- und Tetrapyrrole verglichen.

## Introduction

Recently we studied a series of artificially modified compounds which were derived from the linear di-, tri-, and the naturally occurring linear tetrapyrroles [1–9]. The analogies introduced used either an elongation of the conjugated system, attaching further pyrrolic units [2, 3, 7], and vinylogous units [1], or they were constructed shortening the $\pi$-electron system by directly linking pyrrole rings [4–6]. Such derivatives are of interest with respect to their unique structural features and their application as potential ligands in the transport of cations through membranes [6, 7, 10]. In addition, these modified linear oligopyrroles also exhibit non-linear optical properties [1, 9].

Although very interesting five-ring heterocyclic analogs of linear tetrapyrroles are known [11], only the pyridine analog of a linear dipyrrinone **I**, which exhibited remarkable photochemical properties has been investigated so far [12, 13]. The way one might think of pyridinologous variation of the bilindione skeleton **II** is shown with **III–V** in Scheme 1. As these systems could exhibit novel structural features or complexation capabilities, we will now report on our investigation of linear tri- and tetrapyrroles modified by means of the pyridinologous substitution of pyrrolic units according to types **III–V**.

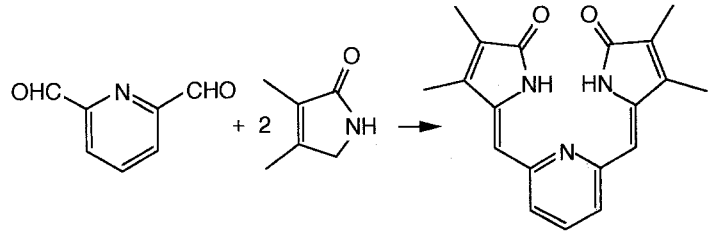



**Scheme 1**

## Results and Discussion

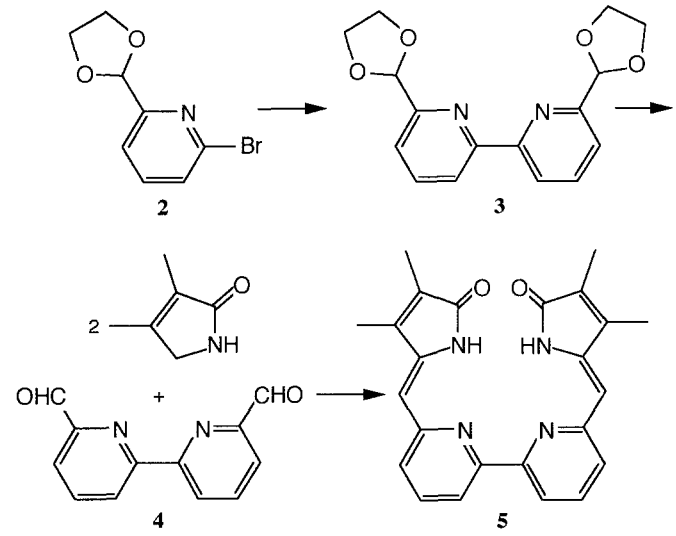
*Synthesis*

The synthesis of **1**, a derivative of type **III**, was achieved following the established route of the preparation of the pyridinologous dipyrrinone **I** [14]. Thus, 2,6-pyridinedicarbaldehyde was condensated under basic conditions with two equivalents of 3,4-dimethyl-3-pyrrolin-2-one providing **1** in 82% yield.

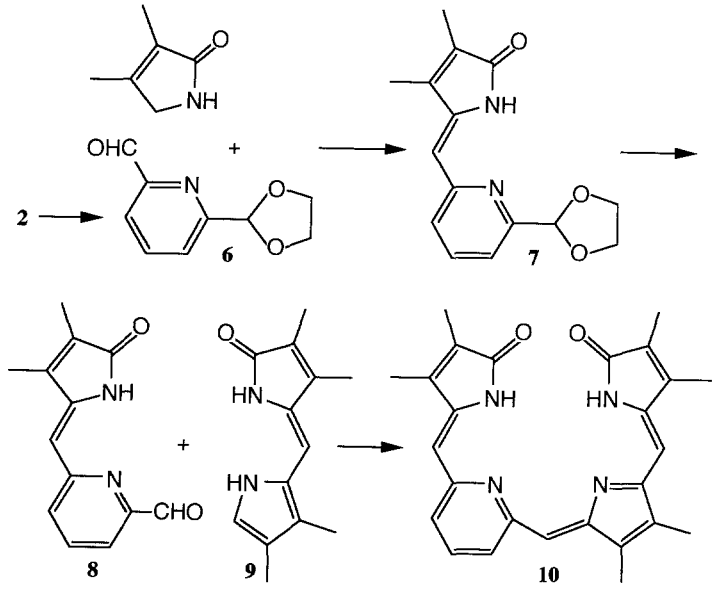



**1**

In order to prepare the derivative **5** of type **III** according to the principle given above for **1**, the 2,2′-bipyridine-6,6′-dicarbaldehyde (**4**) was needed as the key product. As the synthesis available in literature [15] is an extended one providing rather low yields, a short high yield synthesis of **4** was developed. The acetal **2** is readily available in high yield using commercial 2,6-dibromopyridine as its starting material [16]. **2** was dimerized using the nickel catalyst prepared by *in situ* reduction of $NiCl_2(PPh_3)_2$ [17] to yield **3**. Hydrolysis of **3** afforded the dialdehyde **4** (thus available in a 26% overall yield starting from 2,6-dibromopyridine, which should be compared to the 2% overall yield starting from 2-amino-5-methyl-pyridine [15]). On base catalyzed condensation of **4** with two equivalents of 3,4-dimethyl-3-pyrrolin-2-one the desired bipyridinologous compound **5** was formed in 63% yield.



The above mentioned bromoacetal **2** was also used as the starting material in the preparation of the pyridinologous linear tetrapyrrole **10**, which is of type **IV**. By converting the bromine substituent of **2** into the carbaldehyde group by means of *n*-butyl-lithium and dimethylformamide [16], **6** was produced. Under basic conditions [14] it was condensated with 3,4-dimethyl-3-pyrrolin-2-one to produce the pyridinologous dipyrrinone carbaldehyde **8** after hydrolysis of the acetal intermediate **7**. This carbaldehyde **8** was then condensated with the dipyrrinone **9** using acid catalysis as described for the preparation of a variety of bilindione derivatives [18] to yield **10**.



*Structural Aspects and Selected Properties of* **1, 5,** *and* **10**

(*Z*)-**I** has been shown to exhibit an essentially coplanar *synperiplanar* conformation in the crystalline state [12] as well as in solution [14]. This is due to an efficient

intramolecular hydrogen bond between the lactam proton and the pyridine nitrogen [14]. For **1** the (*Z*,*Z*) configuration was deduced from the presence of an NOE between the 4-methyl and the methine protons. Moreover, the latter exhibit the characteristic chemical shift of 5.97 ppm (5.94 ppm for (*Z*)-**I**, which has to be compared with 6.52 ppm for (*E*)-**I** [14]). NOEs between the methine protons and the pyridine-3,5-protons point to a *synperiplanar*, *synperiplanar* conformation of the molecule. A strong intramolecular hydrogen bond was also deduced from the vibrational band at 3227 $cm^{-1}$. Due to its composite nature the mean $pK_{a'}$ value of 6.85 as deduced from fluorescence measurements did not allow to draw conclusions in comparison with the $pK_a$ values [14] for (*Z*)- and (*E*)-**I**.

To obtain a more detailed picture of the conformational situation a force field calculation yielded a system twisted at the two exocyclic single bonds by about 14°. Thus an overall $C_2$ symmetrical chiral conformer is deduced as shown in Fig. 1 by means of a Ball & Stick model.

In Fig. 2 the UV-Vis spectrum of **1** is compared with the one of (*Z*)-**I**. Both spectra exhibit a double banded system which can be understood on the basis of a electron in a box model [8]. The long wavelength band corresponds to the longitudinally polarized transition of the pyridinologous dipyrrinone unit. It is bathochromically shifted in **1** due to the more extended conjugated system. The short wavelength band corresponds to the transition polarized perpendicular to the first one. Its intensity is enhanced in **1**, but it remains more or less unshifted. A prominent third band in the region down to 250 nm is not observed which points to a rather flat molecule with a, more or less, negligible extension in the third dimension. This is in agreement with the overall geometry deduced above.

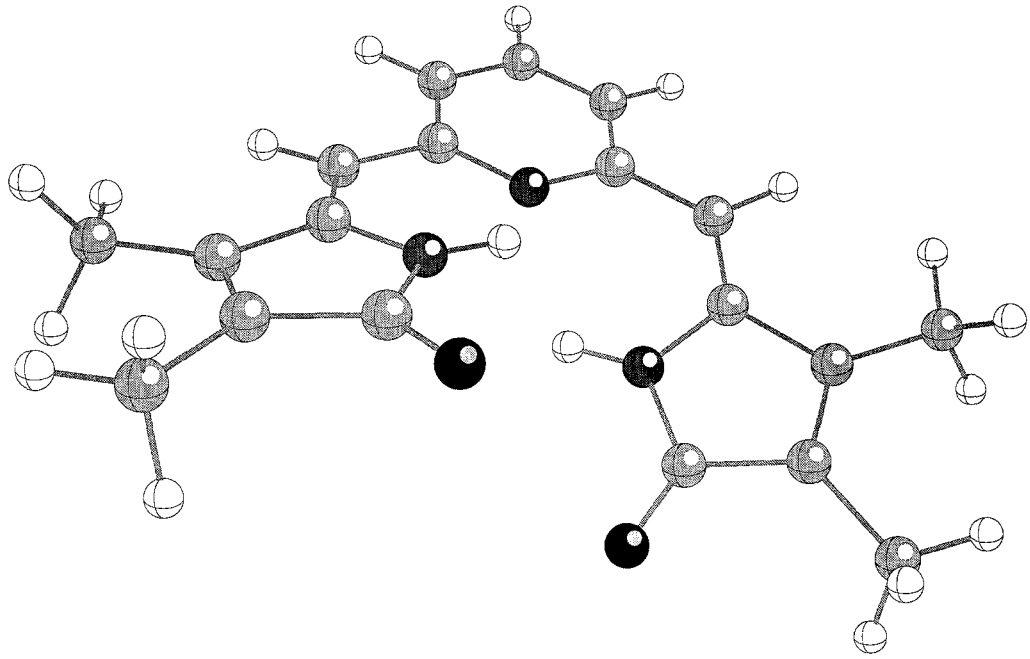


**Fig. 1.** Ball & Stick model of **1** according to force field calculations

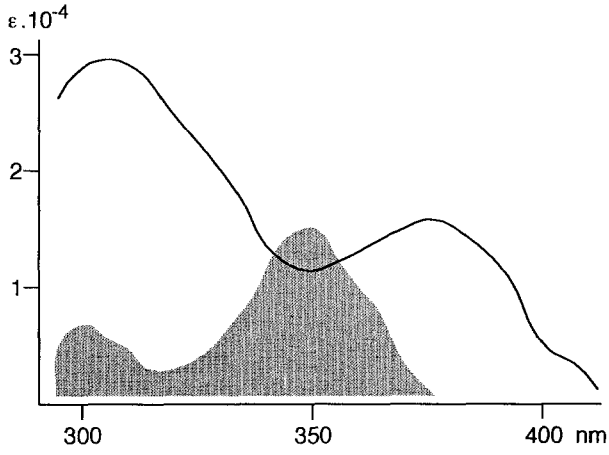



**Fig. 2.** UV-Vis spectra of **1** and (*Z*)-**I** (shaded) in ethanol as the solvent

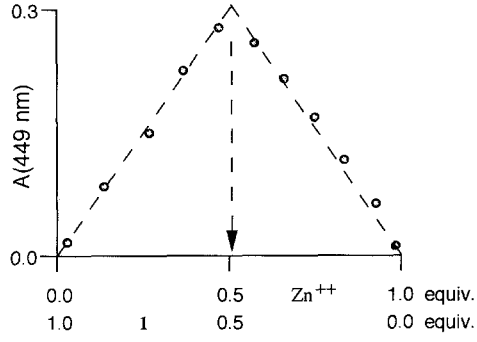



**Fig. 3.** Job plot for the formation of a $Zn^{++}$ chelate of **1** in ethanol as the solvent

The fluorescence of **1** was characterized by a large Stokes shift of 120 nm. It is typical for an emission from the zwitterionic species produced by proton transfer from the pyrrolinone nitrogen to the pyridine nitrogen in the excited state as observed for **I** [13]. The quantum yield ($\Phi_f = 0.05$) was enhanced about tenfold compared to the one of **I** [13].

Upon addition of zinc ions a new band system developed at 480 and 449 nm which was similar in shape to the spectrum of the free ligand. The Job plot [25] shown in Fig. 3 points to the formation of a 1:1 complex. It is not clear what the geometry of this novel type of complex is, as it could not yet be isolated in a pure form. However, one might speculate that the zinc ion is coordinated to the two lactam nitrogens as well as to the pyridine nitrogen leaving a fourth position for an extra ligand. This was also corroborated by the absence of NH signals in the $^1$H-NMR spectrum. Accordingly, the coordination properties of the novel ligand **1** are dissimilar from the ones known for tripyrrins [8].

The pyridinologous compound **5** may be envisaged either as a dimer of **I** or a 6,6′-disubstituted 2,2′-bipyridine. Following the configurational and conformational analysis of these subsystems [14, 19–24] one could predict **5** to be of configuration (*Z*, *Z*), and to exhibit a *syn,syn* conformation at the methine fragments and an *anti* conformation of the bipyridine moiety. Indeed, NOEs between the lactam-4-methyl

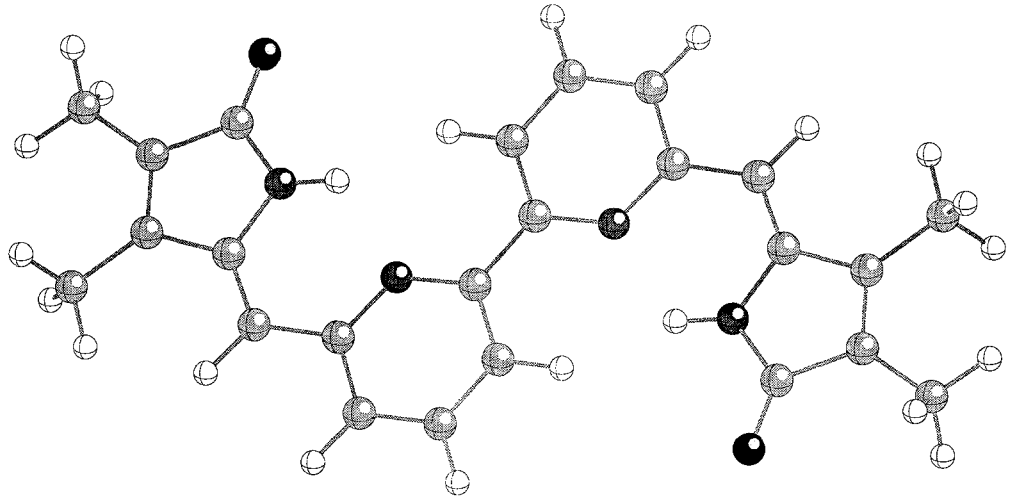


**Fig. 4.** Ball & Stick model of **5** according to force field calculations

protons and the methine protons, as well as the chemical shifts of the methine protons confirmed the (*Z*, *Z*)-configuration. NOEs between the methine protons and the 5-pyridine protons indicated *synperiplanar* or *synclinal* conformations at the methine fragments. The $pK_{a'}$ of 0.33 and the high frequency IR band pointed to planar intramolecularly hydrogen bonded fragments. From the conformational analysis of 2,2′-bipyridine [20, 21] it is known that the *anti* conformation at the single bond joining the two pyridines is characterized by a deshielding of the 3,3′ protons. For **5** these protons were found to be deshielded by 0.8 ppm compared to **1**. Accordingly, **5** was derived to exhibit an *antiperiplanar* conformation at the bipyridine single bond. A force field calculation indicated that the molecule is planar with deviations of the ideal torsion angles of $< 1°$. The geometry of this kind of chromophore is mainly due to the repulsion of the two pyridine nitrogen lone pairs and the dipole–dipole interaction of the two pyridine rings. A Ball & Stick model of **5** in Fig. 4 illustrates its overall stretched arrangement which is quite different from the circular helical geometries observed for common linear tetrapyrroles [8]. For the latter only a few exceptions from the helical arrangement involving *meso* substituted derivatives or bridged systems are known [8].

The UV-Vis spectrum of **5** closely resembles the one of its "half"-compound (*Z*)-**I**. It exhibited a more intense short wavelength band and also a more pronounced structuring of the bands. Its fluorescence was enhanced twofold compared with **1**, which could be expected for a bichromophoric system, and its Stokes shift was even found to be as high as 163 nm. Addition of zinc ions changed this spectrum in a similar way as observed with (*Z*)-**I**. However, this type of ligand could yield a polymeric complex with tetra-coordinating divalent ions as observed with certain bidentate ligands in the dipyrrin series [26].

The *all*-(*Z*) configuration of **10** followed from NOEs between the *endo* lactam methyl groups and the two methines, and the characteristic chemical shifts of these two methine protons on the one hand, and between one of the pyrrolenine methyl groups and the *meso* methine proton on the other hand. The *synperiplanar* con-

formations of the two dipyrrinone halves of **10** were derived from NOEs between the one methine proton and the adjacent pyridine proton in the pyridinologous part and between the second pyrrolenine methyl group and the other methine proton in the dipyrrinone fragment. Judged from the high frequency IR band the two halves adopt more or less planar hydrogen bonded conformations. As no NOE could be observed between the *meso* methine proton and the adjacent pyridine proton an *anticlinal* or *antiperiplanar* conformation at this bond was evident. This *anti* conformation was also corroborated by the strong deshielding of the pyridine proton in position 5 (8.38 ppm) which is due to the adjacent nitrogen lone pair of the pyrrolenine ring. The force field simulation converged also at an *anticlinal* conformation with a dihedral angle of about 30°, indeed, the two halves were found to be almost planar (dihedral angles at the exocyclic single bonds $< 2°$). The latter result was confirmed by the high frequency IR band, which is characteristic of intramolecular hydrogen bonding. Again, in this case the nitrogen lone pair repulsion is the dominating influence on geometry. A Ball & Stick model of the force field structure of **10** is provided in Fig. 5.

The UV-Vis spectrum, which is shown in Fig. 6, was of the three band type. This spectrum may be interpreted in two ways. On the basis of the electron in a box model (compare [8]) it nicely points to a molecule which extends considerably in all three dimensions, thus corroborating the results of the conformational analysis presented above. From another point of view the long wavelength band position is characteristic of dipyrrin type molecules, whereas the middle band position is characteristic of the pyridinologous dipyrrinone as exemplified by (*Z*)-**I**. This latter picture pointed to a more or less independent system of two sub-chromophores as was also observed before in the case of a *meso-tert*-butyl bilindione [27]. Again, this argument corroborated a system dihedrally distorted at the *meso* position. The $pK_a$

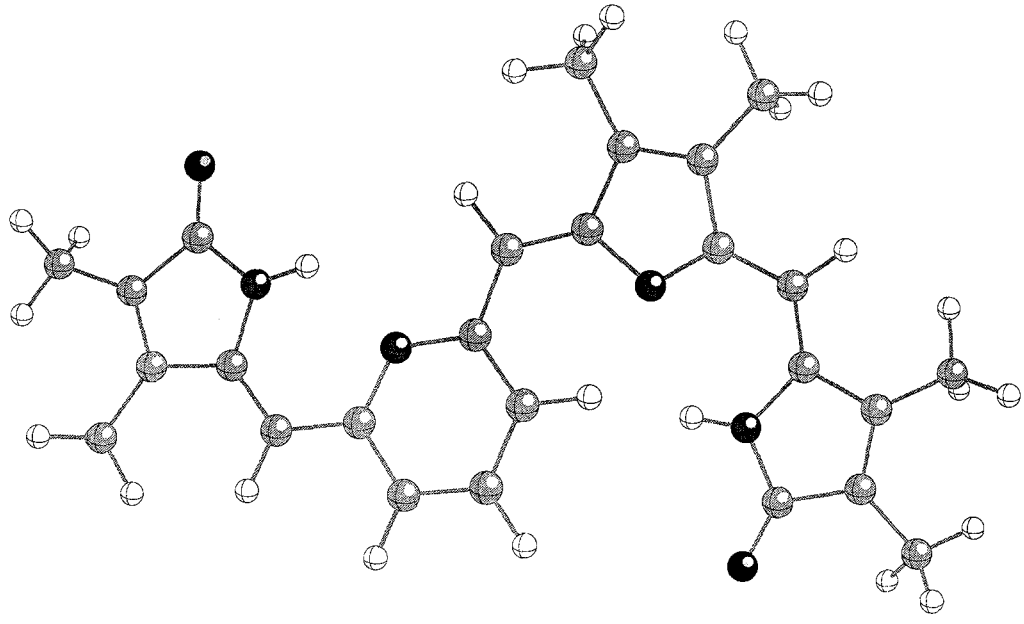


**Fig. 5.** Ball & Stick model of **10** according to force field calculations

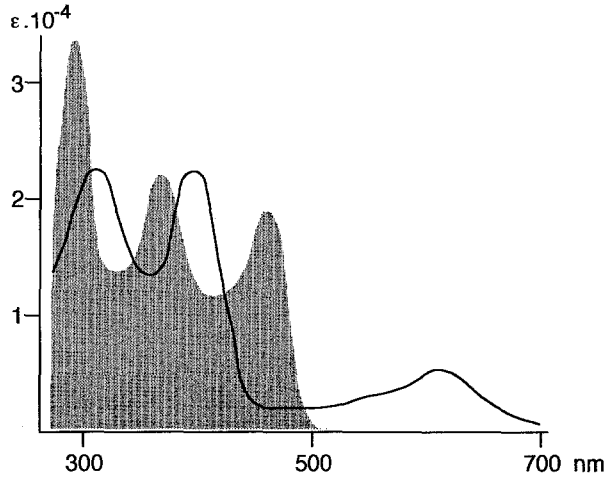



**Fig. 6.** UV-Vis spectra of **10** (shaded) and **10** after addition of $Zn(CH_3COO)_2$ in ethanol as the solvent

values of 6.62 and 0.75 were assigned to the pyridine and pyrrolenine nitrogens according to a small hypsochromic shift for the first protonation step and a large bathochromic shift for the second one. The latter is considerably lowered compared to the bilindiones [8]. As could be expected from the bilindiones [8], **10** exhibited a rather faint fluorescence with $\Phi_f \leqslant 2 \cdot 10^{-4}$, which was Stokes shifted by only 29 nm.

Addition of zinc ions caused a dramatic change of the UV-Vis spectrum as illustrated in Fig. 6. The spectrum now resembled those of circular helical zinc complexes of bilindiones [8]. Obviously, the coordination caused a transformation of the free chromophore which is dihedrally distorted at the *meso* position into the common circular helical arrangement of bilindiones.

*Conclusions*

Pyridinologous substitution of pyrrolic rings of linear tri- and tetrapyrroles resulted in novel types of chromophores. Their structures are mainly determined by dipole–dipole interactions or lone pair repulsion of the pyridine type nitrogen atoms. In addition, intramolecular hydrogen bonding between lactam fragments and the pyridine nitrogen lone pairs provides considerable planarization within the dipyrrinone type fragments of these molecules. The novel ligands resulting from this pyridinologous substitution might be useful in constructing chiral catalysts.

## 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-WM-360-, Biorad-FT-IR-45-, Hitachi-U-3210-, Hitachi F-4010-, and Hewlett-Packard 5989A-instruments. Proton signal and stereochemical assignments were achieved using decoupling and NOE measurements on degassed solutions; *TMS* was used as the internal reference. Spectrophotometric titrations were recorded using a methanol water mixture (9/1) with $H_2SO_4$ as the acid [28]. Ethanol of fluorescence quality (Merck) was used for the fluorescence measurements on degassed solutions; Rose bengal was used as quantum yield standard. Force field calculations were executed using the PCMODEL program of Serena

Software, Bloomington; Figs. 1, 4, and 5 were drawn on Apple Macintosh computers using the Ball & Stick program [29] of Cherwell Scientific, Oxford.

2,6-Pyridine-dicarbaldehyde was obtained from Aldrich, 3,4-dimethyl-3-pyrrolin-2-one was prepared according to [30]. 2-(1,3-Dioxolan-2-yl)-6-bromopyridine (**2**) was prepared from 2,6-dibromopyridine (Fluka AG) as reported earlier [16]. $NiCl_2(PPh_3)_2$ was prepared following [31], and 2,3,7,8-tetramethyldipyrrinone (**9**) was provided by Dr. K. Grubmayr. Elemental analysis (C, H, N) of **1**, **5**, and **10** gave satisfactory results.

*3,4-Dimethyl-5-{2-[6-methyl-(3,4-dimethyl-2-oxo-3-pyrrolin-5-methylidene)-pyridyl]methylidene}-3-pyrrolin-2-one* (**1**; $C_{19}H_{19}N_3O_2$)

**1** was prepared by base catalyzed condensation in analogy to the preparation of the mono-pyridyl condensate [14] from 2,6-pyridine-dicarbaldehyde and 3,4-dimethyl-3-pyrrolin-2-one (twofold molar excess) in 83% yield; m.p. 226–227 °C. $^1$H-NMR(360 MHz, $\delta$, $CDCl_3$): 1.92(s, 6H), 2.10(s, 6H), 5.97(s, 2H), 7.08(d, $J = 8$ Hz, 2H), 7.63(t, $J = 8$ Hz, 1H), 9.06(s, 2H) ppm. NOE: $CH_3$-4↔=CH; =CH↔pyridine-H-2,6. $^1$H-NMR(360 MHz, $\delta$, *DMSO-d*$_6$): 1.83(s, 6H), 2.12(s, 6H), 6.32(s, 2H), 7.37(*d*, $J = 8$ Hz, 2H), 7.77(t, $J = 8$ Hz, 1H), 9.89(s, 2H) ppm. $^{13}$C-NMR(90 MHz, $\delta$, *DMSO-d*$_6$): 8.65, 9.77, 103.95, 122.36, 129.92, 137.31, 140.88, 142.29, 155.26, 172.49. IR(KBr) $\nu = 3227$, 1684, 1645, 1590 cm$^{-1}$. UV-Vis(ethanol): $\lambda_{max.} = 307(29\,630)$, 374(14 560) nm($\varepsilon$). The spectrophotometric titration of this compound was not possible due to only very small shifts and intensity changes upon protonation. Therefore we used the spectrofluorometric titration: $\lambda\phi_B = 495$ nm, $pK_a = 6.85 \pm 0.05$; upon protonation the fluorescence band vanished. Fluorescence: $\lambda_{excit.} = 375$ nm, $\lambda_{fluo.} = 495$ nm, $\Phi_f = 0.05$. MS(70 eV): *m*/e(%) = 321(100; $M^+$), 306(16), 392(15), 198(15).

On complexation with one equivalent of $Zn^{++}$ ion the following spectrum was obtained: $^1$H-NMR (360 MHz, $\delta$, *DMSO-d*$_6$): 1.82(s, 6H), 2.05(s, 6H), 5.91(s, 2H), 7.28(d, $J = 8$ Hz, 2H), 7.81(t, $J = 8$ Hz, 1H) ppm.

*Bis-6,6'-(1,3-dioxolan-2-yl)-2,2'-bipyridine* (**3**; $C_{16}H_{16}N_2O_4$)

To the nickel catalyst prepared from 1.00 g (1.7 mmol) $NiCl_2(PPh_3)_2$, 0.55 g (8.5 mmol) of zinc powder, and 0.87 g (3.4 mmol) $(C_2H_5)_4NI$ in 10 ml tetrahydrofurane (*THF*) [17], a solution of 0.80 g (3.4 mmol) of **2** in 5 ml *THF* was added, and the mixture was stirred at 50 °C for 24 h under an argon atmosphere. The reaction mixture was poured into 25 ml 2*M* aqueous ammonia, and 25 ml ether and 25 ml benzene were added. The precipitate was filtered off and the organic layer was separated. The aqueous layer was extracted with ether/benzene (1:1) (2 × 25 ml). The combined organic layers were washed successively with water and saturated aqueous NaCl solution, dried with anhydrous $Na_2SO_4$, and evaporated in *vacuo*. The residue was chromatographed on silica gel using chloroform/ether (3:1) as eluent to yield 0.33 g **3** (65%); m.p. 106–108 °C. $^1$H-NMR(360 MHz, $\delta$, $CDCl_3$): 4.10–4.26(m, 8H), 5.93(s, 2H), 7.54(d, $J = 7.0$ Hz, 2H), 7.8(t, $J = 7.5$ Hz, 2H), 8.49(d, $J = 8.4$ Hz, 2H) ppm. IR(KBr) $\nu = 2861$, 1579, 1118 cm$^{-1}$.

*2,2'-Bipyridine-6,6'-dicarbaldehyde* (**4**)

A solution of 200 mg (0.6 mmol) of the acetal **3** in 20 ml wet acetone containing 50 mg 4-toluenesulfonic acid was refluxed for 4 h (procedure according to [32]). Excess solvent was then removed in *vacuo*, 15 ml ether and an aqueous solution of $K_2CO_3$ were added. The organic layer was separated, and the aqueous layer was extracted with ether (2 × 20 ml). The combined organic layers were washed with water, dried with anhydrous $Na_2SO_4$, and evaporated in *vacuo* to yield 80 mg (63%) **4**; m.p. 232–234 °C (m.p. [17] 234 °C). $^1$H-NMR(360 MHz, $\delta$, *DMSO-d*$_6$): 8.05(d, $J = 7.8$ Hz, 2H), 8.29(t, $J = 7.8$ Hz, 2H), 8.77(d, $J = 7.0$ Hz, 2H), 10.11(s, 2H) ppm. IR(KBr): $\nu = 3075$, 2862, 1703 cm$^{-1}$.

*6,6'-Bis-(3,4-dimethyl-2-oxo-3-pyrrolin-5-methylidene)-methyl-2,2'-bipyrdidyl* (**5**; $C_{24}H_{22}N_4O_2$)

Preparation from **4** and 3,4-dimethyl-3-pyrrolin-2-one in analogy to **1**. The product was obtained in 63% yield; m.p. > 300 °C. $^1$H-NMR(360 MHz, $\delta$, $CDCl_3$): 1.95(s, 2 $CH_3$-3), 2.13(s, 2 $CH_3$-4), 6.00(s,

2 =CH), 7.32(d, $J$ = 7.5 Hz, 2H-5), 7.88(t, $J$ = 9.8 Hz, 2H-4), 7.98(d, $J$ = 8.8 Hz, 2H-3), 10.17(s, 2H) ppm. NOE: $CH_3$-4,4′↔=CH; =CH↔pyridine-H-5. The $^{13}$C-NMR could not be recorded due to solubility problems IR(KBr): $\nu$ = 3343, 3060, 1704, 1615, 1570 cm$^{-1}$. UV-Vis(ethanol): $\lambda_{max.}$ = 302 (8950), 359 (10 840), 378 (9010) nm ($\varepsilon$). The spectrophotometric titration was not possible due to only very small shifts and intensity differences upon protonation. Therefore we used the spectrofluorimetric titration: $\lambda\phi_B$ = 540 nm, the fluorescence vanished upon protonation, $pK_a = 0.33 \pm 0.10$. Fluorescence: $\lambda_{excit.}$ = 378 nm, $\lambda_{fluo.}$ = 540 nm, $\Phi_f$ = 0.1. MS(70 eV): $m$/e(%) = 398(100; $M^+$), 383(25), 369(12), 276(12), 199(12, $M^+$/2), 11(10).

*2-(1,3-Dioxolan-2-yl)-pyridine-6-carbaldehyde* (**6**; $C_9H_9NO_3$)

**6** was prepared in analogy to 6-bromopyridine-2-carbaldehyde from **2** by the method of [33]. The product was obtained as an oil in 20% yield. $^1$H-NMR(360 MHz, $\delta$, $CDCl_3$): 4.08–4.26(m, 4H), 5.94(s, 1H), 7.77–7.81(m, 1H), 7.94–7.99(m, 2H), 10.11(s, 1H) ppm. IR(film): $\nu$ = 3077, 2967, 2891, 1713, 1109 cm$^{-1}$.

*3,4-Dimethyl-5-[6-(1,3-dioxolanyl)-2-pyridinylmethylidene]-3-pyrrolin-2-one* (**7**; $C_{15}H_{16}N_2O_3$)

Preparation from **6** and 3,4-dimethyl-3-pyrrolin-2-one in analogy to **1** in 82% yield; m.p. 117–119 °C. $^1$H-NMR(360 MHz, $\delta$, $CDCl_3$): 1.93(s, 3H), 2.07(s, 3H), 4.06–4.19((m, 4H), 5.84(s, 1H), 5.91(s, 1H), 7.22(d, $J$ = 9.4 Hz, 1H), 7.34(d, $J$ = 9.2 Hz, 1H), 7.69(t, $J$ = 10.3 Hz, 1H), 10.24(s, 1H) ppm. IR(KBr): $\nu$ = 3359, 1696, 1650, 1114 cm$^{-1}$. UV-Vis(ethanol): $\lambda_{max.}$ = 285 (12 120), 342 (21 630) nm($\varepsilon$).

*3,4-Dimethyl-5-(6-formyl-2-pyridinylmethylidene)-3-pyrrolin-2-one* (**8**; $C_{13}H_{12}N_2O_2$)

Prepared by acidic hydrolysis of **7** in wet acetone analogous to **4**. After crystallization from benzene/petrolether the product was obtained in 85% yield; m.p. 207–209 °C. $^1$H-NMR (360 MHz, $\delta$, $CDCl_3$): 1.95(s, 3H), 2.11(s, 3H), 5.97(s, 1H), 7.43–7.47(m, 1H), 7.75–7.88(m, 2H), 10.12(s, 2H) ppm. IR(KBr): $\nu$ = 3350, 2846, 1710, 1684, 1638, 1583 cm$^{-1}$. UV-Vis(ethanol): $\lambda_{max.}$ = 235(10 650), 340(18 760) nm($\varepsilon$).

*3,4-Dimethyl-5-[2-{6-[2-(3,4-dimethyl-5-oxo-3-pyrrolin-2-ylidene)-methyl-3,4-dimethyl-2H-pyrrolylidene]-methylpyridyl}-methylidene]-3-pyrrolin-2-one* (**10**; $C_{26}H_{26}N_4O_2$)

Prepared from **4** by condensation with **9** in trifluoroacetic acid as described in Ref. [18]. After crystallization from chloroform/methanol the product was obtained in 80% yield; m.p. 250–255 °C (dec.). $^1$H-NMR(360 MHz, $\delta$, $CDCl_3$): 1.93(s, $CH_3$-3 + $CH_3$-3′), 2.067(s, pyrrolenine-$CH_3$-4), 2.102(s, $CH_3$-4′), 2.105(s, $CH_3$-4), 2.204(s, pyrrolenine-$CH_3$-3), 5.86(s, =CH′), 5.96(s, =CH), 6.99(s, =CH-*meso*), 7.18(d, $J$ = 10.0 Hz, pyridine-H-3), 7.81 (t, $J$ = 10.0 Hz, pyridine-H-4), 8.38(d, $J$ = 10.0 Hz, pyridine-H-5), 10.29(s, 2NH) ppm. NOE: $CH_3$-4↔=CH; =CH↔pyridine-H-2; =CH-*meso*↔pyrrolidine-$CH_3$-3; pyrrolidine-$CH_3$-3↔pyrrolidine-$CH_3$-4; pyrrolidine-$CH_3$-4↔=CH′; =CH′↔$CH_3$-4′. $^1$H-NMR(360 MHz, $\delta$, *DMSO-d*$_6$): 1.74, 1.78(2s, $CH_3$-3 + $CH_3$-3′), 1.98(s, $CH_3$), 2.03(s, 3$CH_3$), 5.87, 5.92, 6.18(3s, 3 =CH), 7.31(d, $J$ = 10 Hz, pyridine-H), 7.52(d, $J$ = 10 Hz, pyridine-H), 7.81(t, $J$ = 10 Hz, pyridine-H-4), 9.93(s, NH), 10.06(s, NH) ppm. $^{13}$C-NMR(90 MHz, $\delta$, *DMSO-d*$_6$): 7.9, 8.7, 9.3, 9.4, 10.0, 11.1 (6 $CH_3$), 68.7, 97.8, 103.7, 115.8, 118.1, 122.8, 122.9, 123.1, 124.0, 128.3, 129.5, 134.4, 137.5, 140.8, 141.45, 141.47, 154.0, 162.5 (pyrrolidine C=N), 171.1 (C=O), 172.1 (C=O) ppm. IR (KBr) $\nu$ = 3314, 1699 cm$^{-1}$. UV-Vis(ethanol): $\lambda_{max.}$ = 277(33 350), 345(22 590), 431(18 250) nm($\varepsilon$). Spectrophotometric titration: $\lambda_B$ = 430 nm, $\lambda_{BH^+}$ = 403, 353 nm, $\lambda_{isosb.}$ = 428, $\varepsilon_B/\varepsilon_{BH^+}$ = 1.77, $pK_a = 6.62 \pm 0.1$; $\lambda_{B2H^+}$ = 294, 338, 472 nm, $\lambda_{isosb.}$ = 436, $\varepsilon_B/\varepsilon_{B2H^+}$ = 1.83, $pK_a = 0.75 \pm 0.15$. Fluorescence: $\lambda_{excit.}$ = 431 nm, $\lambda_{fluo.}$ = 460 nm, $\Phi_f \leqslant 0.0002$. MS(70 eV): $m$/e(%) = 426(65; $M^+$), 411(100), 227(11), 213(43), 199(16), 185(7), 131(15), 115(8), 89(10).

## Acknowledgment

This work was supported by the Oberösterreichische Landesregierung providing a grant of an Alpen–Adria Stipendium to A. Š. We are grateful to Doz. Dr. N. Müller and Dr. W. Schmitzberger for executing the advanced NMR experiments, Mag. G. Grienberger for recording the M spectra, Dipl.-Ing. J. Meyer for measuring the fluorescence data, and Doz. Dr. K. Grubmayr for providing us with **9**.

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*Received October 12, 1992. Accepted October 29, 1992*