Monatshefte für Chemie 127, 77–83 (1996)

Monatshefte für Chemie
Chemical Monthly

On the Chemistry of Pyrrole Pigments, XCVII [1]: Synthesis, Stereochemistry, and Solvatochromic Effects of a 1-(Dipyrrinon-9-yl)-3-(dipyrrinon-9-ylidene)-1-propene

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Summary. By condensing a dipyrrinon-9-yl-acrolein with a dipyrrinone unsubstituted in position 9, an unsymmetric *b*-vinylogous verdinoid pigment was prepared. The configuration of this molecule was elucidated by means of 2D ^{1}H NMR experiments to be (4*Z*,10*E*,12*Z*,17*Z*) in solutions of chloroform and dimethylsulfoxide, and its conformation was derived to be 5*syn*,9*syn*,11*anti*,16*syn*. The pronounced solvatochromic effect of this molecule with a cyclic helical geometry could be explained by solvent induced conformational changes.

Keywords. 1-(Dipyrrinon-9-yl)-3-(dipyrrinon-9-ylidene)-propene; *b*-Vinylogous verdin; Synthesis; Spectroscopy; Protonation.

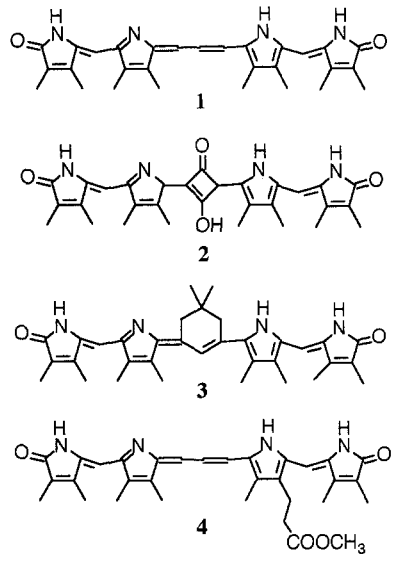
Zur Chemie von Pyrrolpigmenten, 97. Mitt. [1]: Synthese, Stereochemie und Solvatochromer Effekt eines 1-(Dipyrrinon-9-yl)-3-(dipyrrinon-9-yliden)-1-propens

Zusammenfassung. Durch Kondensation eines Dipyrrinon-9-yl-acroleins mit einem in Position 9 unsubstituierten Dipyrrinon wurde ein unsymmetrisches *b*-vinyloges verdinoides Pigment dargestellt. Die Konfiguration dieses Moleküls wurde mit Hilfe von 2D-^{1}H-NMR-Experimenten in Lösungen von und Dimethylsulfoxid als (4*Z*,10*E*,12*Z*,17*Z*) abgeleitet; seine Konformation konnte zu 5*syn*,9*syn*, 11*anti*,16*syn* festgelegt werden. Die ausgeprägte Solvatochromie dieses Moleküls mit cyclisch helikaler Geometrie konnte auf solvensinduzierte konformative Veränderungen zurückgeführt werden.

Introduction

It has been shown recently that *b*-homo-verdinoid linear tetrapyrroles, such as *e.g.* **1**, which are vinylogous to the verdinoid bile pigment chromophore, can be obtained in reasonable yields [2]. This new class of compounds displays an interesting and unusual solvatochromic effect. Whereas in solutions of apolar solvents like chloroform **1** absorbs at 824 nm, its long wavelength band becomes shifted to about 652 nm in polar solvents like dimethylsulfoxide.

However, it has not been possible to establish a correlation of the solvatochromic shifts with solvent polarity parameters. Therefore, the large solvatochromic effect



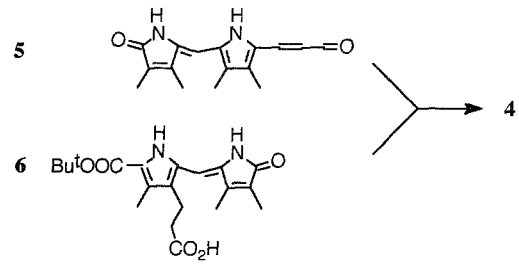
observed for **1** has been tentatively attributed to conformational changes induced by the different solvents. Indeed it has been observed that compounds like **2** and **3**, which are severely restricted in their configurational and conformational freedoms, displayed only negligible solvatochromic shifts. Due to their highly symmetric substitution patterns, compounds **1**–**3** resisted a configurational and conformational analysis. Therefore, the derivative **4**, which is characterized by a significantly unsymmetric substitution pattern, was conceived to allow for such an analysis. Its preparation and stereochemical study is reported in the present paper.

Results and Discussion

Synthesis, Constitution, and Absorption Spectra of **4**

The synthesis of **4** could be conducted in a straightforward manner based on the results of recent studies [2, 3]. Thus, the first half of the molecule, the dipyrrinone **5**, was easily accessible from the respective dipyrrinone unsubstituted in position 9 by reaction with 3-dimethylamino-acroleine [3]. The second half, the dipyrrinone **6**, was prepared *via* a conventional path by condensation of an appropriate pyrrole aldehyde with a pyrrolinone [4]. The latter then underwent smooth acid catalyzed condensaion with the first one to yield the desired homoverdinoid derivative **4**. The mechanism of the formation of the pigment **4** is thought to be similar to that of the formation of **1** [2].

The constitutional aspect of **4** was proven by its mass spectrum. Thus, the high resolution molecular ion peak of **4** was observed at $m/e = 540.2736$, which corresponded exactly to the calculated mass of its brutto formula of $C_{32}H_{36}N_4O_4$. Moreover, most of the fragments in its FAB spectrum were in accordance with its constitution. This assignment was corroborated by the number of signals in the ^{13}C NMR spectrum of **4**. In addition, signals at 172.7 and 173.1 ppm were characteristic for the *bis*-lactam tautomer [4]. This information was also in accordance with the IR spectrum of **4**, which displayed the typical lactam vibration at 1687 cm^{-1} [4].



The electronic absorption spectra of **4** in different solvents displayed the unique solvatochromic effects previously described for **1** [2]. Thus, its long wavelength absorption band was observed at 816 nm in chloroform and at 649 nm in dimethylsulfoxide (Fig. 1). The pK_a of **4** was estimated to be 2.1 and was thus similar to the values found for *b*-homo-verdinoid pigments [1, 2, 4]. The pigment **4** was also found to be a suited ligand for metal ions like Zn(II), Cu(II), and Ni(II) in a variety of solvents.

Stereochemical Assignments

The chemical shifts and stereochemical assignments could be obtained by the 2D-N*O*E experiments illustrated in Fig. 2. Thus, the configurations at the terminal fragments could be assigned to be (4*Z*,17*Z*). Both methine fragments displayed *syn* conformations. Moreover, N*O*Es between the methyl groups at positions 89 and 14 together with rather large coupling constants of 13 Hz restrict the configurational and conformational situation to 9*syn*,11*anti*-(10*E*,12*Z*) as shown in Fig. 2. These stereochemical assignments could be made in the case of the two limiting solvents chloroform and dimethylsulfoxide. It should be stressed that in both solvents the apparent symmetry of the tri-methine fragment was found to be C_{2v} at ambient

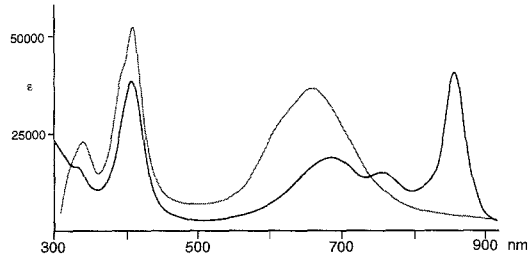


Fig. 1. UV/Vis spectra of **4** in chloroform (black) and dimethylsulfoxide (grey)

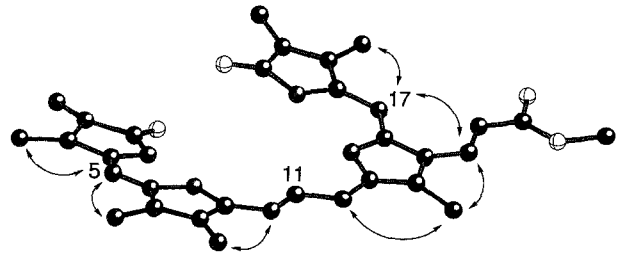


Fig. 2. N*O*E and stereochemistry of **4** dissolved in $CDCl_3$ and *DMSO*-d_6

temperature on the NMR time scale. In addition, the typical signal of the pyrroleninic C=N carbon (position 6 or 16) or "frozen dipyrrin type tautomers" [4] at about 165 ppm in the ^{13}C spectrum of **4** could not be observed. Accordingly, a fast tautomeric exchange between the two dipyrrin type tautomers occurred. This has been derived to be typical of even unsymmetrically substituted verdinoid pigments, like biliverdin itself [4]. Of course, the assignments (10*E*,12*Z*) are arbitrary with respect to the involved positions and could as well read (9*Z*,11*E*).

From these experiments, the large solvent effects on the absorption spectra of **4** illustrated in Fig. 1 have to be attributed to conformational distortions of the circular helical arrangement instead of an inversion of configuration. From PCMODEL [5] calculations, the (10*E*,12*Z*) and (10*E*,12*E*) diastereomers were derived to be the most stable ones. They were found to be characterized by dihedral angles at the two adjacent single bonds of about 0°. These calculations indicated also that there were rather shallow conformational minima present in the respective energy hypersurfaces, which would allow for a broad variety of conformational states stabilized by solvation. This conformational situation should result in the fact that dihedral distortions at all the exocyclic single bonds would sum up to a rather large distortion of the overall system. However, preliminary closed shell SCF-CI-PI-MO calculations revealed that upon torsion of the two trimethine single bonds from 0° to 90°, the absorption bands of **4** were shifted in the order of only 30 nm. Instead, their intensity varied dramatically with the long wavelength band vanishing upon distortion of the two bonds by more than 70°. It should be noted that according to distance estimates of the NOE strategic protons by means of Ball & Stick models neither changes of the observed NOE nor varying coupling constants could be expected. Thus it was concluded that the solvatochromic effect observed for compounds like **4** is not based solely on a solvent shift, but consists mainly of a variation of relative band intensities.

The conformational situation of **4** upon protonation might be similar as in the free base. However, it is not clear if the smaller coupling constants observed for the tri-methine fragment were due to configurational changes or to a much less pronounced single bond – double bond alternation within the mesomeric partial structure of the protonated dipyrrinoid fragment.

Experimental

^1H NMR and ^{13}C NMR spectra were recorded on Bruker-AC 200 and WM 360 instruments. The 2D NOE experiments were performed in dilute solutions purged with argon for half an hour and using standard instrument settings. UV/Vis and IR spectra were run on Hitachi-U-3210 and Biorad-FT-IR-45 spectrophotometers. Mass spectra were measured on MAT 95 (Innsbruck) and Hewlett-Packard 5989A (Linz) instruments, and melting points were determined by means of a Kofler hot stage microscope (Reichert, Vienna). Aluminum oxide (active, type 90, neutral) and silica GF_{254} were used for column chromatography. The spectrophotometric pK_a estimate was derived using a trifluoroacetic acid dilution series in dichloromethane as described in Ref. [6]. Metal complex formation was studied by equilibrating 10 mg of the respective metal acetates in 2.10^{-5} molar solutions of **4** in the respective solvents which were used before to record the UV/Vis spectra. Figure 2 was drawn using the Ball & Stick program [7]. This program was also used for estimating proton – proton distances in the methine fragment of **4**.

(4Z,10E,12Z,17Z)-1-(2,3,7,8-Tetramethyl-dipyrrinon-9-yl)-3-(7-methoxycarbonylethyl-2,3,8-trimethyl-dipyrrinon-9-ylidene)-1-propene (**4**; $C_{32}H_{36}N_4O_4$)

50 mg **6** (0.13 mmol) were introduced to a 250 ml flask filled with argon. Then, 10 ml trifluoroacetic acid were carefully added. The mixture was stirred for 30 min under an argon atmosphere at 45 °C. After cooling to room temperature, a solution of 36 mg **5** (0.13 mol; [2]) in 70 ml methanol, 70 ml dichloromethane, and 2 ml of a solution of HBr (33%) in acetic acid were added. The mixture became green after 5 min. The reaction was monitored by periodically quenching an aliquot of the reaction mixture with saturated aqueous sodium bicarbonate solution and by following the disappearance of **5** and **6** and the appearance of **4** by TLC and UV/Vis spectroscopy. After 4 hours, 100 ml dichloromethane and 50 ml of a 10% solution of aqueous ammonia were added dropwise over 10 min to neutralize the acid. Then the organic layer was separated and the aqueous phase was extracted three times with 50 ml dichloromethane. The combined organic layers were washed 3 times with 50 ml water and 30 ml brine. After drying over anhydrous sodium sulfate and removing the solvent, the residue was purified by means of flash chromatography over alumina (type 90, neutral) using dichloromethane/ethyl acetate (v/v, 6/4) as the eluent. The blue-green band containing **4** was further purified by silica gel column chromatography using dichloromethane/ethyl acetate/tetrachloromethane (v/v/v, 2/2/1). To further purify **4**, the solid product was dissolved in a minimum amount of dichloromethane; then, methanol was added until **4** started to precipitate. The mixture was kept for 4 h, the solid was filtered off and washed with methanol (0 °C). The solid was again dissolved in dichloromethane and passed through a short aluminum oxide (active, type 90, neutral) chromatographic column (3 × 5 cm). Compound **4** was finally crystallized from dichloromethane/methanol, yielding 61 mg (84%); m. p.: 250 °C (dec.). ^{1}H NMR (360 MHz, δ, $CDCl_3$): 1.90 (s, 2 CH_3-2, 20), 2.08 (s, 2 CH_3-3, 7), 2.10 (s, CH_3-19), 2.17 (s, CH_3-8), 2.20 (s, CH_3-14), 2.27 (s, CH_3-14), 2.48 (t, J = 7.5 Hz, CH_2CH_2COO-15), 2.86 (t, J = 7.5 Hz, $\mathbf{CH_2}CH_2COO$-15), 3.66 (s, OCH_3), 5.77 (s, –CH= at 5), 5.81 (s, –CH= at 17), 7.08 (d, J = 13.1 Hz, –**CH**=CH–**CH**=, 10 and at 12), 8.77 (t, J = 13.1 Hz, –CH=**CH**–CH= at 11), 12.5 (br, NH) ppm; 2D-N*O*ESY: CH_3-19↔–CH= at 17↔–$\mathbf{CH_2}CH_2COO$-15↔CH_3-14↔–CH= at 12; –CH= at 10↔CH_3-8; CH_3-7↔–CH= at 5↔CH_3-3; ^{1}H NMR (360 MHz, δ, $CDCl_3$ + 1 drop *TFA*-d): 1.72 (s, 2 CH_3-2, 20), 2.06 (s, CH_3-19), 2.11 (s, CH_3-3), 2.18 (s, CH_3-7), 2.25 (s, CH_3-8), 2.27 (s, CH_3-14), 2.57 (t, J = 7.5 Hz, CH_2CH_2COO-15), 2.88 (t, J = 7.5 Hz, $\mathbf{CH_2}CH_2COO$-15), 3.69 (s, OCH_3), 6.03 (s, –CH= at 5), 6.13 (s, –CH= at 17), 7.36 (d, J = 7.0 Hz, –CH=CH–**CH**=, at 12), 7.40 (d, J = 7.0 Hz, –**CH**=CH–CH= at 10), 8.20 (t, J = 7.0 Hz, –CH=**CH**–CH=, at 11), 10.60 (br s, NH) ppm; N*O*E: –CH= at 5↔$\mathbf{CH_2}$-3, CH_3-7; –**CH**= at 17↔–$\mathbf{CH_2}CH_2COO$–, CH_3-19; –**CH**= at 10↔CH_3-8, –CH= at 12↔CH_3-14; –$\mathbf{CH_2}CH_2COO$–↔–CH= at 17, CH_3-14; CH_3-8↔CH_3-7, –CH= at 10; ^{1}H NMR (360 MHz, δ, *DMSO*-d_6): 1.72, 1.82 (2s, 2CH_3-2, 20), 2.04, 2.09 (2s, 3CH_3-3, 7, 19), 2.13, 2.10 (2s, 2CH_3-8, 14), 2.46 (t, $CH_2\mathbf{CH_2}COO$-15), 2.90 (t, $\mathbf{CH_2}CH_2COO$-15), 3.55 (s, OCH_3), 6.02 (s, –CH=), 6.03 (s, –CH=), 7.17 (d, J = 13.5 Hz, –CH=CH–**CH**=), 7.27 (d, J = 13.5 Hz, –**CH**=CH–CH=), 8.76 (t, J = 13.5 Hz, –CH=**CH**–CH= at 11), 10.40 (br s, NH) ppm; 2D-N*O*ESY: CH_3-19↔–**CH**= at 17↔–CH_2CH_2COO–15↔CH_3-14↔–CH= at 12; –CH= at 10↔CH_3-8; CH_3-7↔–CH= at 5↔CH_3-3; ^{1}H NMR (200 MHz, δ, *DMSO*-d_6): + 1 drop *TFA*-d): 1.83 (s, 2 CH_3-), 1.89 (s, 2CH_3-), 2.10 (s, 3CH_3), 2.30 (br s, CH_2CH_2COO-15), 2.87 (br s, $\mathbf{CH_2}CH_2COO$-15), 3.55 (s, OCH_3), 6.06 (s, –**CH**=), 6.09 (s, –CH=), 7.68 (s, –CH=CH–**CH**=), 7.70 (s, –**CH**=CH–CH=), 10.60 (br s, –CH=**CH**–CH= at 11), 11.70 (br s, NH) ppm; ^{1}H NMR (200 MHz, δ, acetone-d_6): 1.90 (s, CH_3-2), 2.20 (s, CH_3-20), 2.28 (s, CH_3-19), 2.29 (s, CH_3-3), 2.39 (s, CH_3-7), 2.56 (s, CH_3-8), 2.61 (s, CH_3-14), 2.89 (t, J = 7.0 Hz, $\mathbf{CH_2}CH_2COO$-15), 3.15 (t, J = 7.0 Hz, $\mathbf{CH_2}CH_2COO$-15), 3.89 (s, OCH_3), 6.44 (s, –**CH**= at 5), 6.53 (s, –CH= at 17), 7.88 (d, J = 7.0 Hz, –CH=CH–CH= at 12), 7.95 (d, J = 7.0 Hz, –**CH**=CH–CH= at 10), 8.50 (t, J = 7.0 Hz, –**CH**=**CH**–CH= at 11), 11.70 (br s, NH) ppm; ^{1}H NMR (200 MHz, δ, acetone-d_6 + 1 drop *TFA*-d): 1.95 (s, 2CH_3-2, 20), 2.13 (s, CH_3-19), 2.27 (s, CH_3-3), 2.29 (s, CH_3-7), 2.30 (s, CH_3-8), 2.35 (s, CH_3-14), 2.60 (t, J = 7.0 Hz, CH_2CH_2COO-15), 2.90 (t, J = 7.0 Hz, CH_2CH_2COO-15), 3.89 (s, OCH_3), 6.18 (s, –CH= at 5), 6.27 (s, –CH= at 17), 7.64 (d, J = 9.7 Hz, –CH=CH–**CH**= at 12), 7.67 (d, J = 9.7 Hz, –**CH**=CH–CH=, at 10), 8.45 (t, J = 9.7 Hz, –CH=**CH**–CH= at 11) ppm; ^{13}C NMR (50 MHz, δ, $CDCl_2$ + *TFA*-d): 8.12 (CH_3), 9.31

173.14 (C=O at lactam), 175.76 (COO) ppm; IR (KBr):- $\nu = 3046, 3020, 2920, 2900, 1705, 1687, 1573, 1518, 1310, 1277, 1185, 1069, 917, 880, 739\,cm^{-1}$; UV/Vis ($CHCl_3$): $\lambda_{max} = 318$ (10400), 387 (37800), 401 (36300), 665 (18400), 730 (16800), 816 (41100) nm (ε); UV/Vis ($CHCl_3$ + *TFA*): $\lambda_{max} = 318$ (17100), 400 (41500), 818 (60000) nm (ε); UV/Vis ($CHCl_3 + Zn^{2+}$): $\lambda_{max} = 405$ (61300), 722 (32300), 810 (52000) nm (ε); UV/Vis ($CHCl_3 + Ni^{2+}$): $\lambda_{max} = 308$ (70500), 732 (35300), 812 (59300) nm (ε); UV/Vis ($CHCl_3 + Cu^{2+}$): $\lambda_{max} = 388$ (26700), 464 (22600), 704 (14300), 776 (28900) nm (ε); UV/Vis ($CHCl_3 + Cd^{2+}$): $\lambda_{max} = 312$ (29600), 404 (55500), 692 (35000), 824 (5500) nm (ε); UV/Vis (CH_2Cl_2): $\lambda_{max} = 318$ (10400), 387 (37800), 401 (36300), 729 (44700), 821 (32500) nm (ε); UV/Vis (CH_2Cl_2 + *TFA*): $\lambda_{max} = 317$ (19500), 385 (45900), 399 (45900), 727 (38600), 795 (54500) nm (ε); UV/Vis ($CH_2Cl_2 + Zn^{2+}$): $\lambda_{max} = 318$ (28400), 404 (61300), 722 (32300), 810 (52000) nm (ε); UV/Vis ($CH_2Cl_2 + Ni^{2+}$): $\lambda_{max} = 308$ (77200), 388 (81000), 728 (33700), 810 (46300) nm (ε); UV/Vis ($CH_2Cl_2 + Cu^{2+}$): $\lambda_{max} = 344$ (18200), 382 (19100), 442 (22600), 706 (12900), 774 (22400) nm (ε); UV/Vis (acetone): $\lambda_{max} = 378$ (49000), 392 (53900), 640 (30300), 784 (13900) nm (ε); UV/Vis (acetone + *TFA*): $\lambda_{max} = 383$ (45800), 790 (51000) nm (ε); UV/Vis (acetone + Zn^{2+}): $\lambda_{max} = 400$ (48900), 696 (39300), 838 (14300) nm (ε); UV/Vis (acetone + Ni^{2+}): $\lambda_{max} = 386$ (71300), 790 (59200) nm (ε) UV/Vis (acetone + Cu^{2+}): $\lambda_{max} = 436$ (28900), 767 (30600), 846 (15300) nm (ε); UV/Vis (MeOH): $\lambda_{max} = 380$ (31000), 396 (33600), 664 (20500), 772 (16000) nm (ε); UV/Vis (MeOH + *TFA*): $\lambda_{max} = 312$ (19800), 396 (28400), 765 (52700) nm (ε); UV/Vis (MeOH + Zn^{2+}): $\lambda_{max} = 307$ (20400), 388 (23900), 728 (36300) nm (ε); UV/Vis (MeOH + Ni^{2+}): $\lambda_{max} = = 384$ (30400), 765 (33800) nm (ε); UV/Vis (MeOH + Cu^{2+}): $\lambda_{max} = 388$ (13700), 452 (159009, 742 (8200) nm (ε); UV/Vis (*DMF*): $\lambda_{max} = 318$ (12000), 380 (43200), 396 (53600), 648 (41900) nm (ε); UV/Vis (*DMF* + *TFA*): $\lambda_{max} = 321$ (21700), 401 (39400), 778 (108000) nm (ε); UV/Vis (*DMF* + Zn^{2+}): $\lambda_{max} = 322$ (11900), 402 (32200), 686 (29000), 820 (26200) nm (ε); UV/Vis (*DMF* + Ni^{2+}): $\lambda_{max} = = 315$ (16800), 397 (2700), 661 (7000) nm; UV/Vis (*DMF* + Cu^{2+}): $\lambda_{max} = 330$ (13300), 436 (24400), 772 (20600), 856 (28200) nm (ε); UV/Vis (*DMSO*): $\lambda_{max} = 317$ (20400), 386 (41500), 400 (51700), 649 (38200) nm (ε); UV/Vis (*DMSO* + *TFA*): $\lambda_{max} = 320$ (21600), 403 (38000), 791 (95500) nm (ε); UV/Vis (*DMSO* + Zn^{2+}): $\lambda_{max} = 317$ (23400), 397 (31000), 692 (50100) nm (ε); UV/Vis (*DMSO* + Ni^{2+}): $\lambda_{max} = 316$ (19600), 383 (36800), 401 (47700), 653 (32200), 790 (23200) nm (ε); UV/Vis (*DMSO* + Cu^{2+}): $\lambda_{max} = 320$ (8100), 444 (15700), 778 (8200), 865 (25900) nm (ε). The pK_a value was estimated in CH_2Cl_2 from a spectrophotometric titration to amount to 2.1 ± 0.2. The **4** and **4**·H^+ species were characterized by long wavelength absorption bands at 821 (1.0) and 795 (2.5) nm (relative intensity). MS (FAB): *m/e* (%) = 542 (30), 541 (40), 540 (100, M^+), 539 (30), 538 (60), 525 (12), 468 (18), 429 (24), 428 (38), 417 (80), 314 (30), 288 (65), 270 (61), 141 (90), 227 (92), 216 (95), 201 (83), 187 (72), 173 (42), 144 (28), 11 (44), 77 (26), 69 (62), 44 (83); MS (high resoln.): *m/e* = 540.2736; calc.: 540.2736.

(Z)-9-Butoxycarbonyl-7-carboxyethyl-2,3,8-trimethyl-dipyrrinone (**6**; $C_{20}H_{26}N_2O_5$)

A round bottom flask was charged with 500 mg 2-butoxycarbonyl-5-formyl-3-methyl-4- methoxycarbonyl-pyrrole (1.69 mmol; [8]), 188 mg 2,3-dimethyl-3-pyrrolin-2-one (1.69 mmol; [9]), 50 ml 40% aqueous potassium hydroxide, and 60 ml 95% methanol. The mixture was refluxed for 4 hours and then kept overnight at −20 °C. The mixture was carefully neutralized with cold 10% HCl(−10 °C) under stirring. The solid was collected and crystallized from 90% aqueous methanol yielding 442 mg (70%); m.p.: 256 °C (dec.). ^{1}H NMR (200 MHz, δ, *DMSO*-d_6): 1.52 (s, $C(CH_3)_3$), 1.77 (s, CH_3-2), 2.05 (s, CH_3-8), 2.16 (s, CH_3-3), 2.30 (t, $J = 7.0$ Hz, CH_2CH_2COO), 2.77 (t, $J = 7.0$ Hz, CH_2CH_2COO), 5.99 (s, –CH=), 10.47 (s, NH), 10.92 (s, NH) ppm; ^{1}H NMR (200 MHz, δ, $CDCl_3$): 1.57 (s, $C(CH_3)_3$), 1.83 (s, CH_3-2), 2.04 (s, CH_3-8), 2.09 (s, CH_3-3), 2.17 (t, $J = 7.0$ Hz, $CH_2\mathbf{CH_2}COO$), 2.24 (t, $J = 7.0$ Hz, $\mathbf{CH_2}CH_2COO$), 5.32 (s, –CH=), 9.57 (s, NH), 10.22 (s, NH) ppm; NOE: –CH=↔–CH_3-3, –$\mathbf{CH_2}CH_2CO_2$–; CH_3-2↔–CH_3-3; ^{13}C NMR (50 MHz, δ, *DMSO*-d_6): 8.24 (CH_3), 9.60 (CH_3), 9.60 (CH_3), 10.45 (CH_3), 19.26 ($\mathbf{CH_2}CH_2COO$), 28.16 ($OC(\mathbf{CH_3})_3$), 35.18 ($\mathbf{CH_2}CH_2COO$), 80.07 ($\mathbf{O}C(CH_3)_3$), 96.07 (–CH=), 122.49, 124.87, 126.24, 126.38, 127.53, 134.37, 142.14, 160.56 (COOBu^t), 172.24 (C=O, lactam), 173.95 (CH_2CH_2COO) ppm; IR (KBr): $\nu = 3430, 3380, 2920, 2910, 1700, 1683, 1640, 1550, 1440, 1230, 1180, 1120, 1148\,cm^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max} = 380$ (19300), 401 (15500) nm (ε); UV/Vis (*DMSO*): $\lambda_{max} = 384$ (36000), 405 (32000) nm (ε); UV/Vis (MeOH): $\lambda_{max} = 381$ (48300), 402 (41500) nm (ε).

Acknowledgements

A *Lise-Meitner* postdoctral stipendium of the *Fonds zur Förderung der wissenschaftlichen Forschung* to *Q.-Q.C.* is gratefully acknowledged. The MS were kindly measured by Doz. Dr. *K. Ongania* (Univ. Innsbruck) and DI. *K. Haider* (Univ. Linz). We are also grateful to Dr. *C. Etzlstorfer* (Univ. Linz) for calculating the closed shell SCF-CI-PI-MO absorption spectra of **4** by means of the PEP PI electron program of *U. Mueller-Westerhoff.*

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Received July 6, 1995. Accepted August 8, 1995