First Synthesis of a Conformationally Restricted 2,2'-Bipyrrole

Martin Bröring,* Stephan Link

Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany
Fax +49(931)8884605; E-mail: Martin.Broering@mail.uni-wuerzburg.de

Received 17 September 2001; revised 23 October 2001

Abstract: A seven-step procedure was developed for the preparation of the cyclooctadiene-annulated 2,2'-bipyrrole **14**, starting from commercially available benzyl bromoacetate **6** and adiponitrile **7**. Although all transformations carried out had to be sufficiently selective to produce the desired functionalities on both sites of the respective dipyrroles, acceptable to good yields were observed throughout the synthesis. The paper reports synthetic and spectroscopic details of the new compounds.

Key words: 2,2'-bipyrroles, pyrroles, conformation, heterocycles, ring closure

2,2'-Bipyrroles are long-known compounds found in nature as structural subunits of the antibiotical, antimalarial, cytotoxic, and immunosuppressive active prodigiosins.[1] Although not suited for the synthesis of porphyrins due to the direct pyrrole–pyrrole linkage, quite a number of porphyrinoid macrocycles[2] and open-chain oligopyrroles[3] were prepared in the past from these simple building blocks. The accessibility of β-alkyl substituted 2,2'-bipyrroles, for a long time the major limiting factor in their chemistry, was greatly improved in 1994 by Sessler et al.,[4] and ever since the number of reports dealing with the use of 2,2'-bipyrroles as precursors – mainly for macrocyclic oligopyrroles – has constantly increased. In the light of conducting polymers, 2,2'-bipyrroles can be regarded as the smallest oligomeric fragment of polypyrrole. Several applications based on the advantageous material properties of oligo- and polypyrroles including supercapacitors, electrochemical sensors, anti-static coating and drug delivery systems have been described,[5] and a recent publication discusses the luminescence properties of 2,2'-bipyrroles in the solid state, based on the molecular conformation.[6]

In the course of studies towards the coordination chemistry of the open-chain tetrapyrrolic ligand 2,2'-bidipyrrin[7] it was recently found, that due to the free rotation around the central bipyrrolic bond mainly two different complex geometries are observed. Besides the porphyrin analogous ML (metal–ligand) complexes of, e.g. Ni(II) and others as depicted in **1**,[8] the binding of two metal centers like Zn(II) through the cooperative action of two ligands yields M_2L_2 compounds of structure **2**,[9] depending on the metal ion involved (Figure). It appears likely, that the latter coordination type is observed in those cases, where the metal–ligand binding strength is too low to balance the tension induced by the helical twist of complexes **1**, with the consequence, that only a limited set of porphyrin-like metallo-2,2'-bidipyrrins is available. To overcome these limitations we sought to prepare a conformationally restricted 2,2'-bidipyrrin, in which the ligand framework ensures a complex geometry of the ML type.

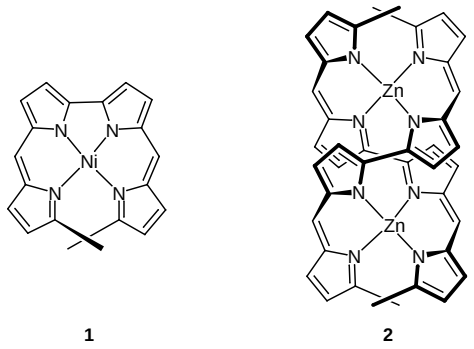
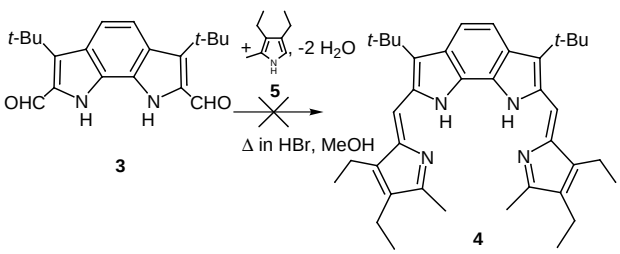


Figure Chemical structures of ML complex **1** and M_2L_2 complex **2**

A literature survey on the conformationally restricted bipyrroles revealed only derivatives of benzo[2,1-*b*:3,4-*b*']bipyrrole,[10] from which **3** was chosen for a test reaction. Indeed, the HBr induced double condensation of **3** with two equivalents of 3,4-diethyl-2-methylpyrrole (**5**) gave a dark-green powder (Scheme 1). This compound, however, was found to be a tripyrrolic prodigiosin derivative rather than the anticipated 2,2'-bidipyrrin **4**. Most probably, the annulated benzene ring induces a pronounced indole-like character in **3**, which inhibits the double condensation with pyrrole **5**. To enable sufficient reactivity, a $(CH_2)_n$-bridged 2,2'-bipyrrole with n = 3–5 should be more suitable. Here we report on our recent success in synthesizing the required 2,2'-bipyrrol **14** with n = 4.

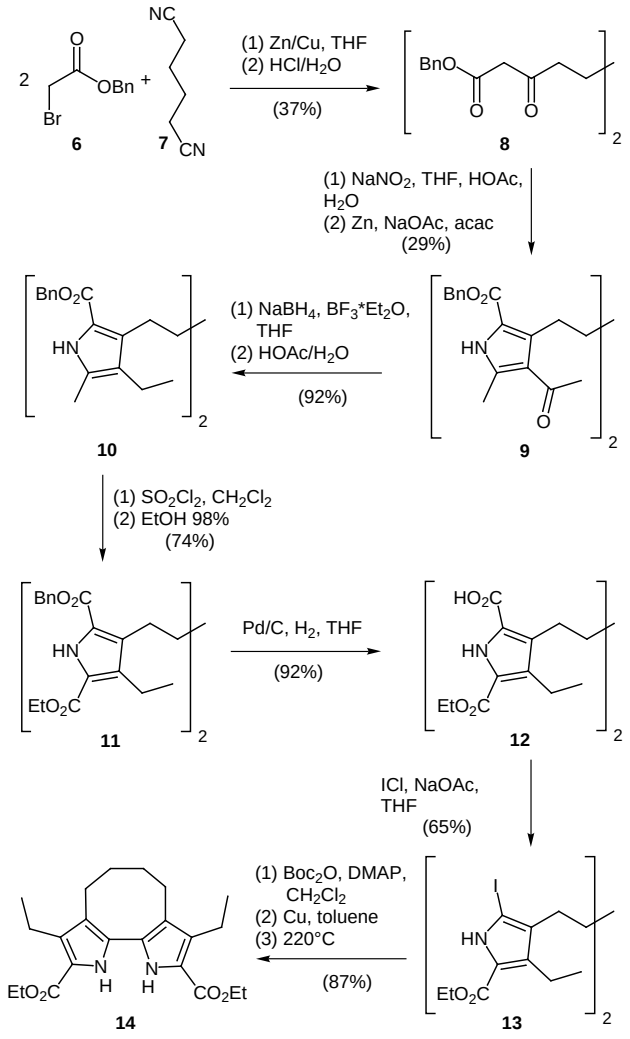


Scheme 1

Synthesis 2002, No. 1, 28 12 2001. Article Identifier:
1437-210X,E;2002,0,01,0067,0070,ftx,en;T09101SS.pdf.

ISSN 0039-7881

The synthesis of **14**, starting from commercially available benzyl bromoacetate **6** and adiponitrile (**7**), makes use of well-known transformations in pyrrole chemistry, which were optimized mainly due to the poor solubility of the new intermediates **8**–**12** (Scheme 2). A double Blaise reaction of **6** and **7** using Zinc/Copper couple in boiling THF results in the di-β-keto ester **8** as a colorless solid in 37% yield. Compound **8** and acetylacetone were then used in a Knorr synthesis to produce the dipyrrolic 1,4-di(4-acetyl-2-benzyloxycarbonyl-5-methyl-3-pyrrolyl)butane (**9**) (29% yield), which was reduced to the diethyl derivative **10** with diborane, produced in situ from boron trifluoride diethyl etherate and sodium borohydride, in 92% yield.



Scheme 2

To set up this dipyrrole for the Ullmann coupling reaction, a proper regiochemical arrangement of the pyrrolic 2- and 5-positions was achieved by selectively oxidizing the 5-situated methyl groups with sulfuryl chloride in dichloromethane and by concomitant hydrolysis/alcoholysis to the tetraester **11** in 74% yield. If standard solvents were employed in this reaction (acetic acid or diethyl ether), only low yields were observed due to a surprisingly non-selective chlorination of α- and β-situated alkyl groups. Hydrogenolytic debenzylation to **12** (92% yield) and decarboxylative iodination using iodine monochloride in THF gave the diiodide **13** in 65% yield, which was finally coupled intramolecularly to the desired 2,2'-bipyrrole **14** by copper powder in 87% yield, using a protocol recently developed for this purpose.[4] No intermolecular Ullmann coupling leading to oligomeric or macrocyclic material was observed.

With respect to a different strategy known for the synthesis of dipyrroles with β-$(CH_2)_n$ joints like **9**–**13**, i.e. a double acylation sequence starting from β-free pyrroles and the respective alkane α,ω-diacid dichlorides,[11] the novel route described here circumvents the problems arising from intramolecular ring closure reactions during the acylation processes, and therefore requires less steps.

NMR spectra were obtained with a Bruker AMX 400 spectrometer. Chemical shifts (δ) are given in ppm relative to TMS. Mass spectra were recorded on a Finnigan 90 MAT instrument. *m*/*z* values are given for the most abundant isotopes only. Melting points were measured by DSC on a Thermoanalyzer DuPont 9000. Elemental analyses (C,H,N) were performed at the microanalytical laboratory of the Institut für Anorganische Chemie, Universität Würzburg. 4,4'-Di-*tert*-butyl-5,5'-diformylbenzo[2,1-*b*:3,4-*b*']bipyrrole (**3**)[10] and 3,4-diethyl-2-methylpyrrole (**5**)[12] were prepared as previously described.

Dibenzyl 3,8-Dioxodecandioate (8)

$Cu(OAc)_2 \cdot H_2O$ (6.4 g, 3.17 mmol) was suspended in glacial AcOH (180 mL) and stirred for 5 min. Zinc powder (60μ; 58.8 g, 1.11 mol) was added with vigorous stirring, and the suspension was stirred until decolorization (about 1 min). The mixture was quickly filtered by suction, the solids were washed successively with MeOH and Et_2O, then transferred into an argon-filled 1 L 3-neck round bottom flask, equipped with a mechanical stirrer, reflux condenser, and dropping funnel. The zinc/copper couple was suspended in anhyd THF (180 mL) and adiponitrile (**7**; 37.8 mL, 332 mmol) and refluxed under N_2. Heating was discontinued, and benzyl bromoacetate **6** (105.6 mL, 664 mmol) was added dropwise in a manner such that constant boiling was maintained (about 30 min). After the addition, the resulting slurry was refluxed for another 2 h, then cooled in an ice bath and poured onto a mixture of crushed ice (90 g) and concd HCl (90 mL). After addition of further ice (90 g), the solids were filtered off, the phases of the filtrate were separated and the aqueous layer was washed with EtOAc (3 × 100 mL). All organic layers were combined and evaporated at reduced pressure to leave a yellowish oil, which crystallized upon addition of MeOH (100 mL). After filtration and excessive washing with MeOH, the title compound was obtained as a colorless powder (50.4 g, 37%); mp 70 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.53 (m, 4 H, H-5,6), 2.47 (m, 4 H, H-4,7), 3.45 (s, 4 H, H-2,9), 5.16 (s, 4 H, CH_2Ph), 7.35 (m, 10 H, C_6H_5).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.5 (C-5,6), 42.6 (C-4,7), 49.2 (C-2,9), 67.1 (CH_2Ph), 128.4, 128.5, 128.6 (CH_{Ph}), 135.2 (C_{ipso}), 167.0 (C-1,10), 202.1 (C-3,8).

MS (DCI, *i*-butane): *m*/*z* = 411 ([M + 1]$^+$).

Anal. Calcd for $C_{24}H_{26}O_6$: C, 70.23; H, 6.38. Found: C, 69.85; H, 6.11.

1,4-Bis(4-acetyl-2-benzyloxycarbonyl-5-methyl-3-pyrrolyl)butane (9)

To a solution of **8** (100 g, 244 mmol) in THF (450 mL) was added AcOH (500 mL). The solution was stirred and kept at r.t. by the aid of a water bath, while a solution of $NaNO_2$ (33.6 g, 487 mmol) in H_2O (100 mL) was added dropwise over a period of 2 h. The resulting mixture was stirred at r.t. for another hour before acetylacetone (57.6 mL, 560 mmol) and AcOH (500 mL) were added. This solution was then heated to 80 °C and treated with a mixture of zinc powder (65.4 g, 1 mol) and NaOAc (99.9 g, 1.22 mol) in small portions to avoid a too vigorous reaction. After the addition was complete, the slurry was heated to 100–110 °C for 2 h, stirred at r.t. for another 12 h, filtered, and the cake washed carefully with MeOH. The precipitate was again suspended in MeOH (500 mL), H_2O (500 mL) was added to this suspension, and the product was again filtered and washed with MeOH. Drying at 60 °C yielded pure product as a colorless powder (40.2 g, 29%); mp 230 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.40 (br s, 4 H, CH_2CH$_2$pyr), 2.31 (s, 6 H, CH_3CO), 2.45 (s, 6 H, CH_3pyr), 2.93 (br s, 4 H, CH_2CH_2pyr), 5.24 (s, 4 H, CH_2Ph), 7.25–7.40 (m, 10 H, C_6H_5), 11.86 (br s, 2 H, NH).

^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 14.7 (CH_3pyr), 25.2 (CH_2CH_2pyr), 31.2 (CH_3CO), 31.4 (CH_2CH_2pyr), 65.2 (CH_2Ph), 117.0 (C-2), 122.1 (C-4), 128.0, 128.1, 128.6 (CH_{Ph}), 135.1 (C-3), 136.6 (C-Ph$_{ipso}$), 139.3 (C-5), 160.7 (CO_2Bn), 194.3 (COCH$_3$).

MS (EI, 70 eV): *m*/*z* = 568 (M^+).

Anal. Calcd for $C_{34}H_{36}N_2O_6$: C, 71.81; H, 6.38; N, 4.93. Found: C, 71.54; H, 6.29; N, 4.80.

1,4-Bis(2-benzyloxycarbonyl-4-ethyl-5-methyl-3-pyrrolyl)butane (10)

In a 2 L 3-neck round bottom flask, equipped with an efficient mechanical stirrer, thermometer, and dropping funnel, 1,4-di(4-acetyl-2-benzyloxycarbonyl-5-methyl-3-pyrrolyl)butane (**9**; 93.2 g, 164 mmol) and $NaBH_4$ (22.7 g, 601 mmol) were suspended in anhyd THF (500 mL) under a blanket of argon, and cooled in an ice bath. BF_3·OEt_2 (103 mL, 820 mmol) was added dropwise at such a rate as to maintain the temperature at or below 5 °C (about 1 h). After the addition, the mixture was warmed to r.t. and stirred for an additional hour. The mixture was cooled to 10 °C and hydrolized carefully with AcOH (110 mL), and then with H_2O (620 mL) maintaining the temperature below 15 °C. The resulting slurry was stirred at r.t. overnight, then filtered by suction and the precipitated product carefully washed with H_2O. Drying at 60 °C yielded the title compound as a colorless powder (81.5 g, 92%); mp 188 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.92 (t, *J* = 7.4 Hz, 6 H, CH_3CH$_2$), 1.38 (br s, 4 H, CH_2CH$_2$pyr), 2.10 (s, 6 H, CH_3pyr), 2.23 (q, *J* = 7.4 Hz, 4 H, CH_3CH_2), 2.55 (br s, 4 H, CH_2CH_2pyr), 5.18 (s, 4 H, CH_2Ph), 7.25–7.38 (m, 10 H, C_6H_5), 11.07 (br s, 2 H, NH).

^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 11.0 (CH_3pyr), 16.1 (CH_3CH$_2$), 16.8 (CH_3CH_2), 24.9 (CH_2CH_2pyr), 31.7 (CH_2CH$_2$pyr), 64.4 (CH_2Ph), 115.0 (C-2), 122.4 (C-4), 127.9, 128.0, 128.5 (CH_{Ph}), 130.7 (C-5), 131.5 (C-3), 137.2 (C-Ph$_{ipso}$), 160.6 (CO_2Bn).

MS (EI, 70 eV): *m*/*z* = 540 (M^+).

Anal. Calcd for $C_{34}H_{40}N_2O_4$: C, 75.53; H, 7.46; N, 5.18. Found: C, 74.94; H, 7.54; N, 5.07.

1,4-Bis(2-benzyloxycarbonyl-5-ethoxycarbonyl-4-ethyl-3-pyrrolyl)butane (11)

Under a blanket of argon, compound **10** (48.0 g, 88.8 mmol) was suspended in anhyd CH_2Cl_2 (240 mL), and SO_2Cl_2 (43.3 mL, 533 mmol) was slowly added while keeping the contents of the flask at r.t. by the aid of a water bath. After the addition, the solution was kept at r.t. for another 4 h before all volatiles were evaporated under reduced pressure at r.t. The resulting red solid was treated with 98% EtOH (240 mL), the mixture heated to reflux for 2 h and then allowed to cool slowly to r.t. The product crystallized on cooling, and was collected by suction filtration, washed with EtOH and dried at 60 °C to yield a colorless solid (43.1 g, 74%); mp 106 °C.

^{1}H NMR (400 MHz, C_6D_6): δ = 0.88 (t, *J* = 7.4 Hz, 6 H, CH_3CH$_2$O), 1.24 (t, *J* = 7.4 Hz, 6 H, CH_3CH$_2$pyr), 1.78 (br s, 4 H, CH_2CH$_2$pyr), 2.85 (q, *J* = 7.4 Hz, 4 H, CH_3CH_2pyr), 2.89 (br s, 4 H, CH_2CH_2pyr), 3.97 (q, *J* = 7.4 Hz, 4 H, CH_3CH_2O), 5.08 (s, 4 H, CH_2Ph), 7.00–7.19 (m, 10 H, C_6H_5), 9.49 (br s, 2 H, NH).

^{13}C NMR (100.6 MHz, C_6D_6): δ = 14.2 (CH_3CH$_2$O), 16.0 (CH_3CH$_2$pyr), 18.3 (CH_3CH_2pyr), 24.8 (CH_2CH_2pyr), 32.0 (CH_2CH$_2$pyr), 60.3 (CH_3CH_2O), 66.3 (CH_2Ph), 121.5 (C-2), 122.0 (C-5), 128.4, 128.7, 128.8 (CH_{Ph}), 132.1 (C-3), 133.6 (C-4), 136.4 (C-Ph$_{ipso}$), 160.4 (CO_2Et), 160.5 (CO_2Bn).

MS (EI, 70 eV): *m*/*z* = 656 (M^+).

Anal. Calcd for $C_{38}H_{44}N_2O_8$: C, 69.49; H, 6.75; N, 4.27. Found: C, 69.26; H, 6.73; N, 4.26.

1,4-Bis(2-carboxy-5-ethoxycarbonyl-4-ethyl-3-pyrrolyl)butane (12)

To a solution of **11** (63.2 g, 96.1 mmol) in anhyd THF (800 mL) was added Pd/C (10%, 7.0 g), and the mixture was hydrogenated at atmospheric pressure and r.t. for 12 h. The mixture was filtered and the dark precipitate was carefully extracted with several small portions of THF at 60 °C (1000 mL in total). After evaporation of the solvent, the title compounds remained as a clean white solid (42.1 g, 92%); mp 253 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.01 (t, *J* = 7.4 Hz, 6 H, CH_3CH$_2$pyr), 1.27 (t, *J* = 7.4 Hz, 6 H, CH_3CH$_2$O), 1.46 (br s, 4 H, CH_2CH$_2$pyr), 2.60 (q, *J* = 7.4 Hz, 4 H, CH_3CH_2pyr), 2.66 (br s, 4 H, CH_2CH_2pyr), 4.21 (q, *J* = 7.4 Hz, 4 H, CH_3CH_2O), 11.31 (br s, 2 H, NH), 12.7 (br s, 2 H, CO_2H).

^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 14.4 (CH_3CH$_2$O), 16.0 (CH_3CH$_2$pyr), 17.6 (CH_3CH_2pyr), 24.0 (CH_2CH_2pyr), 31.4 (CH_2CH$_2$pyr), 60.1 (CH_3CH_2O), 121.1 (C-5), 122.6 (C-2), 130.2 (C-3), 132.5 (C-4), 160.4 (CO_2Et), 162.1 (CO_2H).

MS (EI, 70 eV): *m*/*z* = 476 (M^+).

Anal. Calcd for $C_{24}H_{32}N_2O_8$: C, 60.49; H, 6.77; N, 5.88. Found: C, 60.41; H, 6.81; N, 5.74.

1,4-Bis(5-ethoxycarbonyl-4-ethyl-2-iodo-3-pyrrolyl)butane (13)

Compound **12** (20.0 g, 42.0 mmol) and NaOAc (20.6 g, 252 mmol) were suspended in anhyd THF (400 mL) and heated under a blanket of argon to 70 °C. The resulting suspension was treated dropwise with a solution of ICl (26.6 g, 164 mmol) in anhyd THF (200 mL), whereupon an almost clear, dark brown solution was formed. This solution was stirred at 70 °C for 24 h, then cooled to r.t. and decolorized by the addition of aq $Na_2S_2O_3$. The contents of the flask were extracted with CH_2Cl_2 (3 × 200 mL), the combined organic layers dried (Na_2SO_4) and evaporated to leave a brownish-yellow solid. The solid was dissolved in cold EtOH (100 mL), stirred for 10 min, filtered under suction, and the product was washed with EtOH until colorless (17.5 g, 65%); mp 187 °C (dec.).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10 (t, *J* = 7.4 Hz, 6 H, CH_3CH$_2$pyr), 1.33 (t, *J* = 7.4 Hz, 6 H, CH_3CH$_2$O), 1.49 (br s, 4 H, CH_2CH$_2$pyr), 2.37 (br s, 4 H, CH_2CH_2pyr), 2.72 (q, *J* = 7.4 Hz, 4 H, CH_3CH_2pyr), 4.30 (q, *J* = 7.4 Hz, 4 H, CH_3CH_2O), 8.90 (br s, 2 H, NH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.4 (CH_3CH$_2$O), 15.6 (CH_3CH$_2$pyr), 18.8 (CH_3CH_2pyr), 26.3 (CH_2CH_2pyr), 30.6 (CH_2CH$_2$pyr), 60.1 (CH_3CH_2O), 73.2 (C-2), 123.2 (C-5), 129.8 (C-3), 133.3 (C-4), 160.4 (CO_2Et).

MS (EI, 70 eV): *m*/*z* = 640 (M^+).

Anal. Calcd for $C_{22}H_{32}I_2N_2O_4$: C, 41.27; H, 4.72; N, 4.38. Found: C, 41.65; H, 4.72; N, 4.31.

3,3'-(1,4-Butandiyl)-5,5'-diethoxycarbonyl-4,4'-diethyl-2,2'-bipyrrole (14)

Compound **13** (18.5 g, 28.9 mmol) and di-*tert*-butyl dicarbonate (13.8 g, 63.1 mmol) were suspended in anhyd CH_2Cl_2 (190 mL) and treated with 4-dimethylaminopyridine (185 mg) at r.t. for 2 h. Silica gel (20 g) was added to destroy excess anhydride, and after stirring for 1 h, the mixture was filtered, the cake carefully washed with CH_2Cl_2, and the combined organic washings were evaporated to leave a yellowish semi-solid. This solid was dissolved in anhyd toluene (270 mL), copper powder (22.4 g, 353 mmol) was added and the slurry was refluxed for 3 d. Copper was filtered off over Celite and the solids washed carefully with additional toluene. The combined toluene solutions were washed with H_2O (2 × 200 mL), dried (Na_2SO_4), and evaporated to a brown, heavy oil. This was pyrolyzed at 200 °C/20 mbar for 1 h, cooled to r.t., and treated with hexane in a sonic bath for 15 min, whereupon the title compound solidified. The fine, greenish powder was filtered with suction, washed with hexane, and dried in vacuo to yield 9.71 g (87%) of **14**; mp 177 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (t, *J* = 7.4 Hz, 6 H, CH_3CH_2pyr), 1.32 (t, *J* = 7.4 Hz, 6 H, CH_3CH_2O), 1.72 (br s, 4 H, CH_2CH_2pyr), 2.59 (br s, 4 H, CH_2CH_2pyr), 2.72 (q, *J* = 7.4 Hz, 4 H, CH_3CH_2pyr), 4.28 (q, *J* = 7.4 Hz, 4 H, CH_3CH_2O), 9.11 (br s, 2 H, NH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.4 (CH_3CH_2O), 15.4 (CH_3CH_2pyr), 18.2 (CH_3CH_2pyr), 22.5 (CH_2CH_2pyr), 26.6 (CH_2CH_2pyr), 60.1 (CH_3CH_2O), 118.7 (C-5), 123.2 (C-3), 125.5 (C-2), 133.9 (C-4), 161.7 (CO_2Et).

MS (EI, 70 eV): *m*/*z* = 386 (M^+).

Anal. Calcd for $C_{22}H_{32}N_2O_4$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.36; H, 7.74; N, 7.13.

Acknowledgement

This work was funded by the Deutsche Forschungsgemeinschaft (Emmy-Noether-Programm) and the Fonds der Chemischen Industrie. The authors thank Professor H. Werner for his continuing support. Help with the NMR spectroscopic characterization by R. Bertermann is gratefully acknowledged.

References

(1) For a recent overview, see: Fürstner, A.; Fürstner, A.; Grabowski, J.; Lehmann, C. W.; Kataoka, T.; Nagai, K. *ChemBioChem.* **2001**, *2*, 60 and Ref. [4,9a,10]cited therein.

(2) (a) For an overview, see: Sessler, J. L.; Weghorn, S. J. *Expanded, Contracted & Isomeric Porphyrins*; Elsevier: Oxford, **1997**. (b) Setsune, J.-i.; Maeda, S. *J. Am. Chem. Soc.* **2000**, *122*, 12405. (c) Wytko, J. A.; Michels, M.; Zander, L.; Lex, J.; Schmickler, H.; Vogel, E. *J. Org. Chem.* **2000**, *65*, 8709.

(3) (a) Drews, A.; Schönemeier, T.; Seggeweis, S.; Breitmaier, E. *Synthesis* **1998**, 749. (b) Vogel, E.; Bröring, M.; Weghorn, S. J.; Scholz, P.; Deponte, R.; Lex, J.; Schmickler, H.; Schaffner, K.; Braslavsky, S. E.; Müller, M.; Pörting, S.; Fowler, C. J.; Sessler, J. L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1651; *Angew. Chem.* **1997**, *109*, 1725. (c) Morosini, P.; Scherer, M.; Meyer, S.; Lynch, V.; Sessler, J. L. *J. Org. Chem.* **1997**, *62*, 8848. (d) Vogel, E.; Binsack, B.; Hellwig, Y.; Erben, C.; Heger, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2612; *Angew. Chem.* **1997**, *109*, 2725. (e) Sessler, J. L.; Weghorn, S. J.; Lynch, V.; Fransson, K. *J. Chem. Soc., Chem. Commun.* **1994**, 1289. (f) Sepulveda-Boza, S.; Breitmaier, E. *Liebigs Ann. Chem.* **1983**, 894. (g) Kazlauskas, K.; Marwood, F. F.; Murphy, P. T.; Wells, R. J. *Aust. J. Chem.* **1982**, *35*, 215. (h) Dolphin, D.; Grigg, R.; Johnson, A. W.; Leng, J. *J. Chem. Soc.* **1965**, 1460. (i) Grigg, R.; Johnson, A. W. *J. Chem. Soc.* **1964**, 3315. (j) Bullock, E.; Grigg, R.; Johnson, A. W.; Wasley, J. W. F. *J. Chem. Soc.* **1963**, 2326. (k) Johnson, A. W.; Kay, I. T.; Rodrigo, R. *J. Chem. Soc.* **1963**, 2336.

(4) Sessler, J. L.; Hoehner, M. C. *Synlett* **1994**, 211.

(5) (a) Scrosati, B. *Applications of Electroactive Polymers*; Chapman & Hall: London, **1993**. (b) Rodriguez, J.; Grande, H. J.; Otero, T. F. *In Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; Wiley: New York, **1997**, 415.

(6) Che, C.-M.; Wan, C.-W.; Lin, W.-Z.; Zhou, Z.-Y.; Lai, W.-Y.; Lee, S.-T. *Chem. Commun.* **2001**, 721.

(7) (a) Johnson, A. W.; Price, R. *J. Chem. Soc.* **1960**, 1649. (b) Bröring, M. *Synthesis* **2000**, 1291. (c) Bröring, M.; Griebel, D.; Hell, C.; Pfister, A. *J. Porphyrins Phthalocyanines* **2001**, *5*, 708.

(8) (a) Dolphin, D.; Harris, R. L. N.; Huppatz, J. L.; Johnson, A. W.; Kay, I. T.; Leng, J. *J. Chem. Soc. (C)* **1966**, 98. (b) Bröring, M.; Brandt, C. D.; Lex, J.; Humpf, H.-U.; Bley-Escrich, J.; Gisselbrecht, J.-P. *Eur. J. Inorg. Chem.* **2001**, 2549.

(9) Zhang, Y.; Thompson, A.; Rettig, S. J.; Dolphin, D. *J. Am. Chem. Soc.* **1998**, *120*, 13537.

(10) (a) Vogel, E. *Pure Appl. Chem.* **1993**, *65*, 143. (b) Berlin, A.; Bradamante, S.; Ferraccioli, R.; Pagani, G. A.; Sannicolò, F. *J. Chem. Soc., Chem. Commun.* **1987**, 1176.

(11) Paine, J. B. III.; Dolphin, D. *Can. J. Chem* **1978**, *56*, 1710.

(12) Tang, J.; Verkade, J. G. *J. Org. Chem.* **1994**, *59*, 7793.