3,3′- and 4,4′-Dimethoxy-2,2′-bipyrroles: Highly Electron-Rich Model Compounds for Polypyrrole Formation.

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Abstract: 3,3′-Dimethoxy-2,2′-bipyrrole (**1**) and 4,4′-dimethoxy-2,2′-bipyrrole (**2**) were obtained in short sequences and good yields from *N*-benzyl-3-hydroxypyrrole-2,4-dicarboxylic acid. The key intermediate leading to **1** is an *N*-benzyl-3-methoxypyrrole, which is dimerized by lithiation and oxidation with $NiCl_2$. The formation of **2** is achieved by a classical Ullmann coupling of diethyl 1-benzyl-2-bromo-4-methoxypyrrole-3,5-dicarboxylate. The *N*-benzyl protection groups of **1** and **2** are cleaved under reducing conditions with sodium in liquid ammonia. Both isomeric bipyrroles are extremely sensitive toward air. Compound **1** has a very low oxidation potential of 0.09 V against AgCl but film formation hardly occurs. On the other hand, compound **2** with a potential of 0.35 V readily forms stable polypyrrole films with anodic waves at −0.51 and −0.35 V and a cathodic wave at −0.77 V, the lowest potential ever observed for a p-doped polymer.

Keywords: cyclic voltammetry · oxidation · polypyrrole formation · pyrrole dimerization · reductive N-benzyl cleavage · Ullmann coupling

Introduction

Pyrrole is a fairly electron-rich aromatic compound. On exposure to air, pyrrole gradually discolors. Aqueous pyrrole forms a black powder of moderately conducting material on treatment with various oxidants. Electropolymerized polypyrrole[1] is the most-cited organic conducting polymer. To date, about 8500 sources mention polypyrrole, and about 3900 sources can be found for polythiophene.[2] Thiophene can likewise be polymerized by anodic oxidation, but 3-alkylthiophenes give better results.[3] Still more activating are alkoxy substituents in the 3-position or in both the 3- and 4-positions.[4, 5] Ethylendioxythiophene (EDOT) is a commercial chemical with a large range of applications.[6, 7] Dimethoxypyrrole[8] and other 3,4-alkoxypyrroles, including 3,4-ethylendioxypyrrole (EDOP),[9] are quite sensitive to air and must be stored under inert conditions. Remarkably, and contrary to 3-*alkyl*pyrroles, alkoxy substituents facilitate polymerization and enhance the conductivity of the corresponding polypyrrole.[10]

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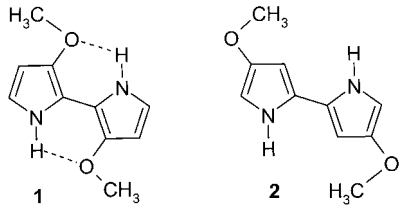
Bipyrrole and thiophene dimers and oligomers have often been used to study the single steps of electrochemical polymerization.[4, 11, 12] The position of substituents in the dimer is of remarkable importance. Thus, 4,4′-dimethoxy-2,2′-bithiophene is a very potent monomer for polymerization whereas 3,3′-dimethoxy-2,2′-bithiophene polymerizes quite slowly.[4, 13] Due to the higher electronegativity of nitrogen as compared with sulfur, the analogous 2,2′-bipyrroles **1** and **2** are expected to have extremely negative oxidation potentials. Though, like in the thiophene case, both isomers should display quite different properties. The syntheses of the title compounds **1** and **2** and their chemical and electrochemical behavior are reported.



Results and Discussion

Diethyl *N*-benzyl-3-hydroxypyrrole-2,4-dicarboxylate[14] **3** is an excellent precursor molecule that is not only readily prepared in large quantities from inexpensive chemicals, but also allows for the preparation of *both* bipyrroles **1** and **2**. The 3-hydroxy group in **3** is the basis of the later methoxy groups

  0947-6539/03/0902-0449 $ 20.00+.50/0

in **1** and **2**. In solution, 3-hydroxypyrroles can exist as the aromatic "phenol" or in equilibrium with the pyrrolone ("keto form") depending on substituents and solvents. For instance, *N-tert*-butylpyrrole exists as 90% keto form in $CDCl_3$, but as 95% hydroxy form in $[D_6]$DMSO, as determined by ^{1}H NMR. 3-Hydroxy-*N*-phenylpyrrole has the pyrrolone structure[15] in the solid state; on the other hand, the solid structure of *N-tert*-butylpyrrole-3-ol is the hydroxy form.[16] Crystalline **3** is a hydroxypyrrole, as shown by the X-ray structure (Figure 1).[17]

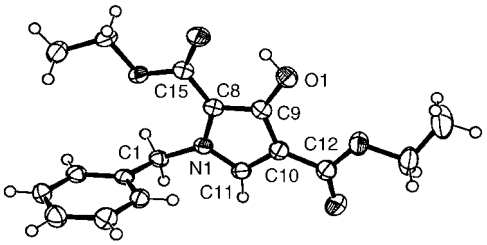
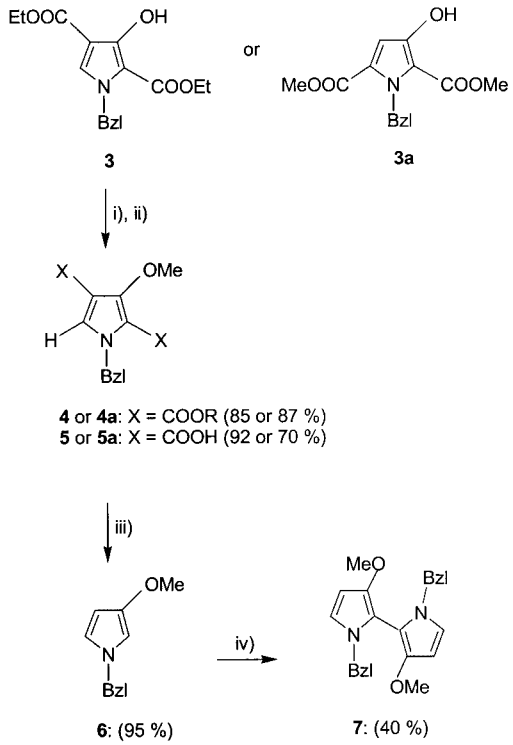


Figure 1. Compound **3**: selected bond lengths: O1–C9 1.3457, N1–C1 1.4597, N1–C8 1.3942, N1–C11 1.3370, C8–C15 1.434, C8–C9 1.388, C9–C10 1.407, C10–C11 1.3910, C10–C12 1.4592; bonds angles: C1-N1-C11 123.82, C8-N1-C11 108.85, C1-N1-C8 127.18, N1-C1-C2 112.76, N1-C8-C9 107.12, O1-C9-C10 126.85, C8-C9-C10 108.01, O1-C9-C8 125.13, C9-C10-C11 106.08, C9-C10-C12 131, C11-C10-C12 122.66, N1-C11-C10 09.93; torsion angles: C1-N1-C8-C9 176.62, C8-N1-C11-C10 – 0.47, N1-C1-C2-C3 – 27.70, N1-C8-C9-C10 – 1.11, C8-C9-C10-C11 0.0, C9-C10-C11-N1 – 0.23.

Preparation of the 3,3′-dimethoxybipyrrole skeleton: The preparation of **1** starts with the methylation of the 3-hydroxy group of **3** with dimethyl sulfate to give **4**, followed by a classical ester cleavage to give the free diacid **5** (Scheme 1).

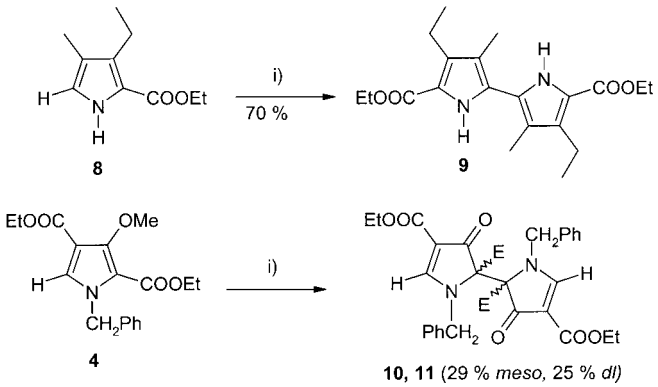


Scheme 1. i) Me_2SO_4, acetone, K_2CO_3, reflux; ii) KOH, EtOH; iii) pyrolysis, 240 °C; iv) THF/Et_2O, *sec*-BuLi, TMEDA, – 60 to 0 °C, then $NiCl_2$.

The thermal decarboxylation of both carboxylates **5** occurs at around 200 °C without a solvent, and the *N*-benzyl-protected 3-methoxypyrrole **6** can be isolated by vacuum distillation. Various substituted 3-methoxypyrroles have been prepared by Wong and Clezy,[18] and the first *N*-alkyl 3-alkoxypyrroles with free 2, 4, and 5-CH positions, were reported by Kochlar and Pinnock.[19] Among these was **6**, which was only marginally characterized. The facile syntheses of 3,4-dialkoxy pyrroles[20, 21] suggested the analogous condensation of a N-benzyliminodiacetic ester with formylacetic ester to give **3a.** Compound **6** was obtained in a similar sequence to the one above; however this approach suffers from a very poor yield (7%) due to the competing Cannizzarro disproportion of the formylacetic ester in the first step. A completely different source of 3-methoxypyrrole **6** is derived from a retro-Diels–Alder product of a diazine.[22] The present procedure, however, is far superior to all others.

The methoxy group and the nitrogen in **6** are in an activated position for lithiation at the 2-position. Compound **6** was lithiated at low temperature with *sec*-BuLi in THF/ether/TMEDA by following a Kaufmann protocol.[23] Subsequently, anhydrous $NiCl_2$ was employed for oxidative dimerization. Bipyrrole **7** was isolated in 35 to 45% yield, but more than 50% starting material **6** can be recovered by distillation. More favorable conditions have not yet been established. Thus, the benzyl-protected bipyrrole **7** with the "inner" methoxy groups is established for deprotection. Compound **7** shows atropic isomerism as shown by the AB splitting of the benzyl-CH_2 group.

Sessler et al. reported the dimerization of known pyrrole **8** to bipyrrole **9** (Scheme 2), which is a building block for sapphyrines.[24] The dimerization of pyrrole **4**, which is similar



Scheme 2. i) NaI/I_2. E = –COOEt.

to **9** with a single hydrogen at the 5-position, appeared to provide easy access to **2**. By using Sessler's protocol, **4** was treated with NaI/I_2 in dichloroethane/aqueous buffered $NaHCO_3$. Dimerization does indeed occur, however at the *2-position*, to give the 2,2′-bipyrrolidone as the crystalline *racemic* ±-**10** and the achiral resinous *meso* form **11.** The assignment of the stereochemistry has been confirmed by an X-ray structure (Figure 2[17]). The ^{1}H NMR spectra of **10** and **11** display manifold diasterotopic -CH_2- groups of the ethyl esters and benzyl groups. Both ethyl -CH_2 groups in **10** show a

0947-6539/03/0902-0450 $ 20.00+.50/0 *Chem. Eur. J.* **2003**, *9*, No. 2

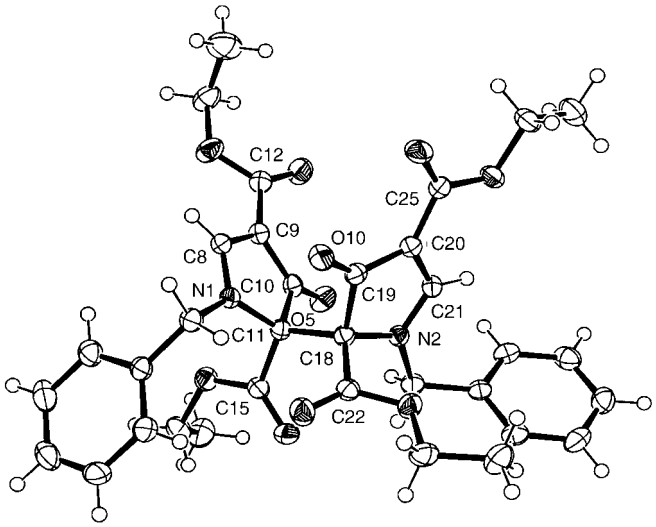
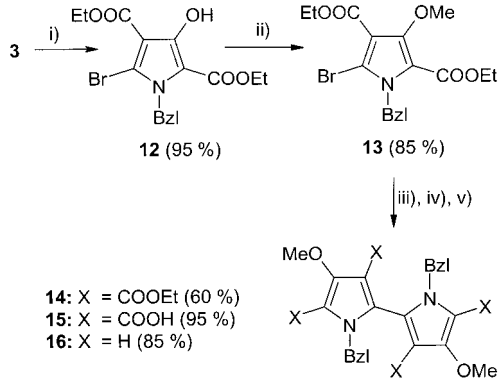


Figure 2. Compound **10**: selected bond lengths: N1–C1 1.48(18), N1–C8 1.3312, N1–C11 1.4717, N2–C18 1.4722, N2–C21 1.3249, N2–C28 1.4878, C8–C9 1.3783, C9–C10 1.433, C10–C11 1.5990, C11–C18 1.580, C18–C19 1.5972(19), C19–20 1.435 (2), C20–C21 1.380(2); bond angles: N1-C11-C18 114.48, C10-C11-C15 107.58, C10-C11-C18 107.22, C15-C11-C18 131.7, N2-C18-C11 113.18, N2-C18-C19 101.86, N2-C18-C22 110.96, C11-C18-C19 81.4, C11-C18-C22 115.24, C19-C18-C22 106.29, O10-C19-C18 122.67, O10-C19-C20 132.20, C18-C19-C20 105.12, C19-C20-C21 108.04, C19-C20-C25 124.64, C21-C20-C25 127.20, N2-C21-C20 114.74(12); torsion angles at C11/C18: C10-C11-C18-N2 37.44, C10-C11-C18-C19 74.62, C10-C11-C18-C22 –166.65, C15-C11-C18-N2 81.03, C15-C11-C18-C19 –166.91, C15-C11-C18-C22 –48.18, N1-C11-C18-N2 49.04, N1-C11-C18-C19 36.98, N1-C11-C18-C22 81.75.

$4 \times 2 \times 2$ line signal, whereas only the inner groups split into a 4×2 signal in **11**).

Surprisingly, the demethylation at the methoxy groups is faster than the direct oxidation. The slightly alkaline aqueous phase together with the organic solvent 1,2-dichloroethane seems to be a mild phase-transfer medium that favors the Finkelstein type S_N2 reaction of the iodide or polyiodide ion to give iodomethane and the mesomeric anion of **3**. Oxidation of $\mathbf{3}^-$ by the I_2/I_n^- system can give rise to the resonance-stabilized neutral radical $\mathbf{3}^{\bullet}$, which then dimerizes to **10** and **11**. A possible route from **10** and/or **11** to bipyrrole **1** by ester hydrolysis, decarboxylation, and re-methylation could not be realized, however.

Preparation of the 4,4′-dimethoxybipyrrole skeleton: The known bromohydroxypyrrole **12**[25] derived from **3** is methylated at the OH group to give **13** in high yield (Scheme 3). Compound **13** is a classical Ullmann precursor[26] with typical electron deficient substituents. The bipyrrole **14** is formed in the melt at ~300 °C with copper powder and a trace of DMF in a quite remarkable yield of 60 %. After removal of the four carboxylic ester groups by hydrolysis (to give **15**) and decarboxylation, the *N*-benzyl-protected **16** is obtained in good yield as a fairly stable compound under N_2. Compounds **14** and **15** show atropic isomerism due to the splitting of the benzyl methylene groups, but **16** does not.

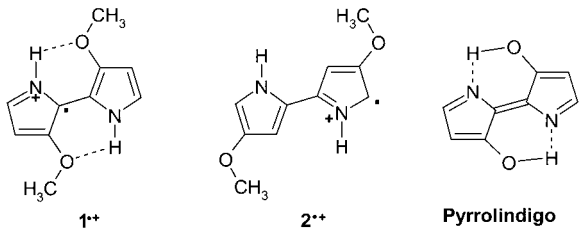


Scheme 3. i) Br_2; ii) Me_2SO_4, acetone, K_2CO_3, reflux; iii) Cu powder, DMF (trace), 300 °C; iv) KOH, EtOH; v) pyrolysis, 240 °C.

Preparation and isolation of 1 and 2: As long as the pyrroles contain electron-deficient substituents, it is possible to cleave the N-benzyl protecting group with CF_3-COOH.[20] Electron-rich bipyrroles such as **6**, **7**, and **16**, however, need reliable procedures in a reducing environment. Solvated electrons in liquid ammonia are excellent for this purpose.[21, 28] In the present case, the reduction products are the bipyrrolyl sodium salt and benzyl sodium. Aqueous-organic workup under argon with adequately adapted conditions guarantees very clean pyrroles.

The twin bipyrroles **1** and **2** are very sensitive to air and to any other oxidation agents. Therefore, each compound is taken up in a toluene solution, from which, at low temperature, the bipyrroles crystallize. Both compounds can be stored under argon at ≤ -20 °C in the dark. The crystals of **2** blacken within minutes on exposure to air, acquiring a soot-like appearance, apparently a sort of polypyrrole. Freshly prepared samples of **1** can be handled in air for some minutes, but the samples begin to turn greenish-blue. The different behavior of the two bipyrroles was expected by analogy with the corresponding thiophenes.[4, 13]

The structure of **1** is related to the well known indigo system, in the sense that **1** is an O-alkyl *leuko*-pyrrolindigo. O-alkyl and O-acyl leukoindigo structures have been described in the literature.[29] In pursuit of the unsubstituted



pyrrolindigo chromophore, Bauer was the first to prepare 3,3′-diethoxy-2,2′-bipyrrole, the homologue of **1**.[30] Furthermore, Bauer obtained several substituted pyrrolindigo structures, for example 4,5,4′,5′-tetramethyl-3,3′-dioxobipyrrole,[31] but the unsubstituted pyrroloindigo has not yet prepared. Compound **1** is certainly a candidate precursor to obtaining this goal.

Electropolymerization behavior of 1 and 2: The electropolymerization experiments that were carried out with compounds **1** and **2** in acetonitrile in the presence of a small amount of water give results in perfect agreement with the expectations. Figure 3 shows a voltammetric multisweep

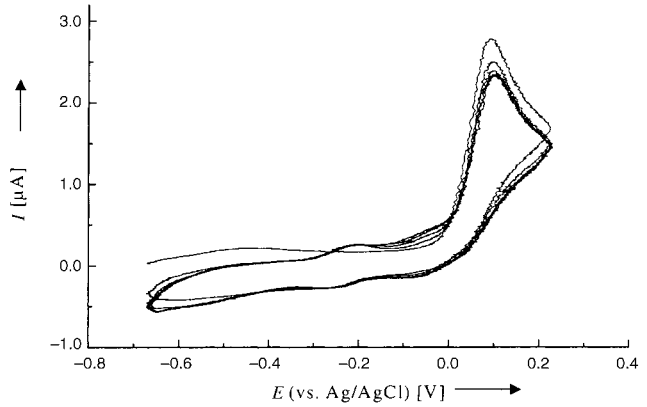


Figure 3. Multisweep voltammogram of **1** ($c = 8 \times 10^{-4}$ M) at a 1 mm platinum disk in Bu_4NPF_6 (0.1 M) in acetonitrile + 1 % water.

experiment with **1**. The oxidation of **1** occurs at the remarkably low reduction potential of +0.09 V vs Ag/AgCl, as an chemically irreversible process. However, no generation or deposition of an extended oligomer or polymer is observed during potentiodynamic cycling, only two small redox waves at potentials of −0.25 and −0.0 V can be seen. Evidently **1**, in accordance with the findings obtained for 3,3′-dimethoxybithiophene,[4, 5, 13] forms a σ-dimer that slowly eliminates protons to give a neutral tetramer. This can be charged up to a dication without further follow-up reactions. The coupling tendency of the tetrameric species is low due to the fact that the spin density at the outer α-positions is low.

By contrast, compound **2** polymerizes rapidly in acetonitrile in the presence of 1 % water. It is oxidized at a peak potential of $E_p = +0.35$ V, and shows a following broad cathodic wave in the reverse scan. In a multisweep experiment, fast growth of a conducting polymer film can be observed (Figure 4). The

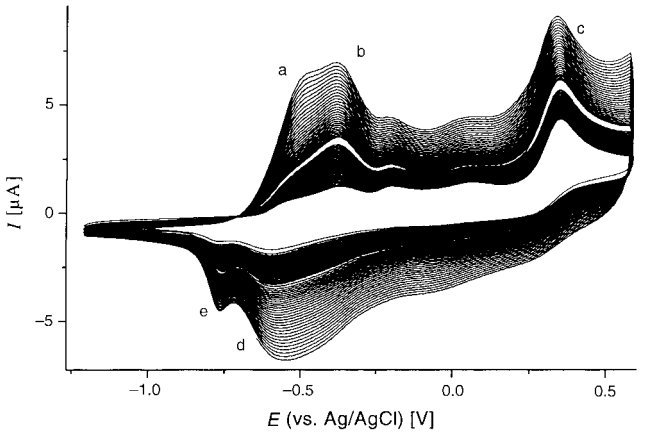


Figure 4. Multisweep voltammogram of **2** ($c = 10 \times 10^{-3}$ M) at a 1 mm platinum disk in Bu_4NPF_6 (0.1 M) in acetonitrile + 1 % water, showing the development of the poly-**3** film: a),b) anodic polymer peaks, c) oxidation of **2**, d),e) cathodic polymer peaks.

current peak in the cyclic voltammogram increases with each scan. The reason for the fast polymerization process lies in the reactivity of the radical cation $\mathbf{2}^{\bullet+}$, which has its highest spin density at the nonblocked α-positions; this favors a fast coupling reaction and evidently also facilitates proton elimination. The further products of the coupling steps again have substituents in the "outer" β-positions of the growing oligomer; these make it very reactive.

The corresponding polymer film of **2** was characterized by using solid state voltammetry (Figure 5). The oxidation potential of the main first wave lies at −0.51 V and a second

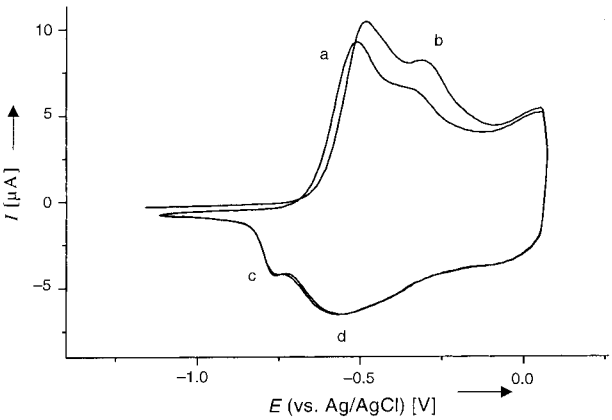


Figure 5. Voltammogram of a PPy-**2** film generated during the potentiodynamic cycling of **2** in acetonitrile in the absence of **2**. The two anodic peaks at −0.51 and −0.35 (a, b) and the cathodic peaks at −0.59 and −0.77 (c, d) indicate the formation of two structurally different polymers.

wave appears at −0.35 V. In contrast to Figure 4, the first oxidation wave is higher than the second one. As in the case of the unsubstituted polypyrrole,[32, 33] we assume that two structurally different polypyrrole systems are generated during the electrochemical oxidation. As usual in conducting polymers, the reduction peak is more negative (peak at −0.56 V). A second reduction wave, at −0.77 V vs. Ag/AgCl, however, is the lowest potential ever observed for the discharging of a p-doped polymer. The strong hysteresis between oxidation and reduction gives evidence that during charging a thermodynamically stabilized network with σ interchain bonds is formed. The σ-bond generation produces a marked stabilization of the charged polymer and, in addition, results in localized charges.

Conclusion

Starting from a readily available pyrrole precursor, bipyrroles **1** and **2** were both synthesized in a few steps. As expected, **1** and **2** are extremely sensitive towards oxygen, but both compounds are stable under argon. Although **1** has the lower oxidation potential, no polymerization was observed due to the location of the electron hole in the inner portion of the molecule. Only **2** is capable of forming a redox polymer.

0947-6539/03/0902-0452 $ 20.00+.50/0 *Chem. Eur. J.* **2003**, *9*, No. 2

Experimental Section

General methods: NMR spectra were recorded on Bruker AC250 or Bruker ARX400 instruments. IR spectra were recorded a Bio-rad Excalibur Series FTIR spectrometer. Mass spectra were obtained with a Finnigan Mat95 or Varian Mat311A. Ethyl *N*-benzylglycine ester was prepared on a 100 g scale in 55% yield according to ref. [34]. Ethyl *N*-benzyl-*N*-[2-bis(ethoxycarbonyl)vinyl]glycinate and diethyl 1-benzyl-3-hydroxypyrrole-2,4-dicarboxylic acid **3** was prepared according to Momose et al.[10]

Electrochemical measurements: The electrochemical measurements were carried out in specially constructed cells containing an internal drying column with highly activated alumina. The working electrode was a Pt disk sealed in soft glass (1.0 mm diameter). This setup was controlled by a Jaissle Potentiostat-Galvanostat IMP88 or IMP88PC. The potential scans were performed with an EG&G PARC Model175 Universal Programmer scan generator and the cyclovoltammetric response was recorded with an IMK PSO8100 transient system. The measured potentials were referenced to the Ag/AgCl electrode and were determined by an internal calibration with the cobaltocinium/cobaltocene redox pair.

Dimethyl 1-benzyl-3-hydroxypyrrole-2,5-dicarboxylate (3a): A solution of Na (7.46 g, 320 mmol) in MeOH (85 mL) and ethyl glyoxylic acid (29 mL, 146 mmol, 50% solution) was heated under reflux for 3 days. The mixture was poured into ice-water, and the product was extracted with diethyl ether. Recrystallization from MeOH gave **3a** 2.98 g (7.05%); m.p. 89 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 3.79$, 3.81 (2s, 3H; CO_2CH_3), 5.95 (s, PhCH_2), 6.53 (s, 1H; CH), 6.97–7,23 (m, C_6H_5), 8.16 (s, 1H; OH); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 49.48$, 51.57, 51.86, 103.90, 111,43, 125.94, 126,11, 128.43, 138,81, 153.30, 160.95, 162.92; IR (KBr) $\tilde{\nu} = 3480$, 3035, 2957, 2950, 1735, 1662 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{17}NO_5$ (289.3): C 62.28, H 5.23, N 4.84; found C 62.16, H 5.28, N 4.83.

Diethyl 1-benzyl-3-methoxypyrrole-2,4-dicarboxylate (4): K_2CO_3 (33 g, 240 mmol) and dimethyl sulfate (9 mL, 95 mmol) were added to a stirred solution of **3** (30 g, 95 mmol) in dry acetone (300 mL) under N_2, and the reaction mixture was refluxed overnight. The cooled mixture was filtered, and the solvent was removed. Recrystallization from ethanol gave white crystals. Yield: 26.6 g (85%); m.p. 69–71 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.31$ (t, $J = 7.13$ Hz, 3H; CH_2CH_3), 1.34 (t, $J = 7.13$ Hz, 3H; CH_2CH_3), 3.91 (s, 3H; OCH_3), 4.27 (q, $J = 7.13$ Hz, 2H; CH_2CH_3), 4.29 (q, $J = 7.13$ Hz, 2H; CH_2CH_3), 5.46 (s, 2H; CH_2Ph), 7.07–7.38 (m, 6H; Ph, H5-pyrrole); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.24$, 14.39, 53.45, 59.94, 60.18, 62.83, 108.47, 114.30, 127.13, 127.87, 128.78, 130.27, 136.86, 153.36, 160.56, 162.82; IR (KBr): $\tilde{\nu} = 2981$–2870, 1698, 1551, 1449, 1388, 1295, 1247,1202, 1085, 1028, 998, 787, 699 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 331 (37) [M^+], 91 (100) [$C_7H_7^+$]; elemental analysis calcd (%) for $C_{18}H_{21}NO_5$ (331.4): C 65.24, H 6.39, N 4.23; found: C 65.25, H 6.33, N 4.23.

Dimethyl 1-benzyl-3-methoxypyrrole-2,5-dicarboxylate (4a): (Same procedure as given for **4**.) Yield: 2.3 g (87%); m.p. 130 °C; ^{1}H NMR: (250 MHz, $CDCl_3$): $\delta = 3.79$, 3.86 (2s, 3H; CO_2CH_3), 3.80 (s, 1H; -OCH_3,), 6.11 (s, 2H; -CH_2Ph), 6.63–7.21 (m, 6H; -C_6H_5, CH-pyrrol); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 49.16$, 51.47, 51.74, 58.07, 101.66, 126.04, 113.54, 214.68, 126.86, 128.38, 138.90, 152.78, 160.66, 161.16; IR: $\tilde{\nu} = 1718$ cm^{-1}; MS (70 eV, EI): *m*/*z*: 303 [M^+], 272, 91; elemental analysis calcd (%) for $C_{16}H_{17}NO_5$ (303.3) C 63.36, H 5.65, N 4.62; found C 63.27, H 5.69, N 4.60.

1-Benzyl-3-methoxypyrrole-2,4-dicarboxylic acid (5): Compound **3** (19 g, 57 mmol) in ethanol (300 mL) was added to a solution prepared from NaOH (13.8 g, 344 mmol) and H_2O (300 mL), and the mixture was heated under reflux for 12 h. The ethanol was removed in vacuo, and the rest was acidified with H_2SO_4 (10%) to pH 2–3 with cooling. The acid **5** was extracted with diethyl ether. Recrystallization from ethanol gave colorless crystals. Yield: 10.5 g (92%); m.p. 142–143 °C; ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 3.75$ (s, 1H; OCH_3), 5.48 (s, 2H; CH_2Ph), 7.07–7.37 (m, 5H; C_6H_5), 7.65 (s, 1H; H-pyrrole), 12.17 (s, 2H; COOH); ^{13}C NMR (100 MHz, [D$_6$]DMSO): $\delta = 52.05$, 62.09, 107.72, 113.65, 126.79, 127.38, 128.49, 131.07, 138.10, 152.65, 161.09, 163.43; IR (KBr): $\tilde{\nu} = 3434$, 3032–2880, 2615, 1663, 1547, 1461, 1280, 1073, 1001, 924 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{13}NO_5$ (275.2): C 61.09, H 4.76, N 5.09; found C 60.98, H 4.65, N 4.01.

1-Benzyl-3-methoxypyrrole-2,5-dicarboxylic acid (5a): (Same procedure as given for **5**.) Yield: 0.64 g from 1.0 g of **4a** (70%); m.p. 150 °C; ^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 3.76$ (s, 3H; OCH_3), 6.07 (s, 2H; CH_2Ph), 6.69 (s, 1H; Py), 6.88 (m, 2H; *o*-Ph), 7.24 (m, 3H; *m*/*p*-Ph), 12.73 (br s, COOH); ^{13}C NMR (63 MHz): $\delta = 47.90$, 57.60, 101.98, 125.68, 126.64, 128.28, 139.48, 152.13, 161.38, 161.40; IR: $\tilde{\nu} = 3250$–2350, 1702, 1652; MS (70 eV, EI): *m*/*z*: 274 [$M^+ - H$], 230 [$M^+ - CO_2$], 183 [$M^+ - C_7H_7$]; elemental analysis calcd (%) for $C_{14}H_{13}NO_5$ (275.2): C 61.09, H 4.76, 5.09; found C 60.77, H 4.63, N 4.99.

1-Benzyl-3-methoxypyrrole (6): Either compound **5** or **5a** (5 g, 18 mmol) was decarboxylated for 1 h in a round-bottomed flask for 1 h at 150 mbar and 220–230 °C by using a heat gun. The pressure was lowered to 2 mbar, and **5** was distilled (b.p. 160–170 °C) to give a colorless, air-sensitive oil (3.4 g, 95%) to be stored under argon. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta =$ 3.69 (s, 1H; OCH_3), 4.95 (s, 1H; CH_2), 5.86 (d, $J = 2.77$ Hz, 1H; H4-pyrrole), 6.23 (s, 1H; H2-pyrrole), 6.48 (d, $J = 2.77$ Hz, 1H; H5-pyrrole), 7.08–7.37 (m, 5H; C_6H_5); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 53.90$, 57.89, 97.29, 103.11, 119.30, 127.03, 127.65, 128.69, 138.17, 149.34; IR (film): $\tilde{\nu} =$ 2933, 1564, 1339, 1043, 736 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 187 (45) [M^+], 172 (9) [$M^+ - CH_3$], 91 (100) [$C_7H_7^+$]; elemental analysis calcd (%) for $C_{12}H_{13}NO$ (187.2): C 76.98, H 7.00, N 7.48; found: C 76.28, H 6.93, N 7.53.

1,1′-Dibenzyl-3,3′-dimethoxy-2,2′-bipyrrole (7): A solution of **6** (1 g, 5.3 mmol) dissolved in dry THF/diethyl ether (1:1, 15 mL) and TMEDA (0.4 mL, 2.8 mmol) was cooled to –70 °C with stirring and under argon. *sec*-Butyllithium in cyclohexane/hexanes (92:8, 0.34 g, 5.3 mmol) was added. The mixture was allowed to warm to room temperature for 2.5 h. The mixture was cooled again to –40 °C, and dry $NiCl_2$ was added (0.83 g, 6.4 mmol). With vigorous stirring, the mixture was allowed to warm up 0 °C (30 h). MeOH (10 mL) and water (20–30 mL) were added with stirring. Finally all solvents were removed in vacuo, and the dark oily residue was distilled at 80–85 °C (0.013 mbar). The distillate was starting material **6** (ca. 50%), the dark residue was recrystallized from ethyl acetate to give colorless crystals. Yield: 0.38 g (40%); m.p. 69–71 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 3.68$ (s, 6H; 2OCH_3), 4.59 (AB, 4H; 2CH_2Ph), 5.94 (d, $J =$ 3.17 Hz, 2H; 2H-pyrrole), 6.45 (d, $J = 3.17$ Hz, 2H; 2H-pyrrole), 6.86–7.27 (m, 10H; 2C_6H_5); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 50.91$, 58.00, 95.24, 106.82, 118.73, 127.19, 127.83, 128.32, 138.27, 147.39; IR (KBr): $\tilde{\nu} = 3463$, 3062–2831, 1606, 1550, 1479, 1452, 1411, 1330, 1091, 997, 711, 628 cm^{-1}; HRMS (70 eV, PI-EI) calcd. for $C_{24}H_{24}N_2O_2$: 372.1838, found m/z: 372.1836.

***Racemic*- and *meso*-Tetraethyl 1,1′-dibenzyl-3,3′-dioxo-2,2′,3,3′-tetrahydro-2,2′-bipyrrole-2,2′,4,4′-tetracarboxylates (10) and (11)**: A solution of $NaHCO_3$ (2.63 g, 30 mmol) in H_2O (10 mL) was heated to 50 °C, and 1,2-dichloroethane (115 mL) added, followed by **4a** (3 g, 9.1 mmol). A mixture of I_2 (2.6 g, 10 mmol) and NaI (3.2 g, 20 mmol) in water (10 mL) was added within 5 min, and the resulting mixture was heated for one hour. Some undissolved I_2 was washed into the mixture with H_2O during the reaction. The mixture was transferred to a separating funnel, the organic layer was separated, and the aqueous phase was washed with $CHCl_3$ (3 × 30 mL). The combined organic layers were washed with a 5% solution of $Na_2S_2O_3$ (3 × 30 mL), a 5% solution of $NaHCO_3$ (3 × 30 mL), and a saturated brine solution (3 × 30 mL), and then dried over Na_2SO_4. During the stripping off of the solvent, **10** was precipitated.

(±)-10: white crystals, 0.7 g (25%); m.p. 198–199 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.18$ (t, $J = 7.11$ Hz, 6H; 2CH_2CH_3, 3,3′), 1.34 (t, $J = 7.15$ Hz, 6H; 2CH_2CH_3, 4,4′), 4.10 (qdd, $J = 7.32$, $J = 3.52$, 4H; CH_2CH_3), 4.31 (qdd, $J = 7.16$, $J = 3.57$, 2H; 2CH_2CH_3), 4,99, 5.12 (AB, $J = 14.02$ Hz, 4H; 2CH_2Ph), 7.35–7.56 (m, 10H; 2C_6H_5), 8.12 (s, 2H; 2H-pyrrole); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 14.08$, 14.34, 56.22, 59.78, 63.65, 80.06, 101.98, 129.01, 129.31, 130.49, 133.81, 161.75, 164.24, 169.72, 184.78; IR (KBr): $\tilde{\nu} = 3448$, 3039, 2989, 2902, 1745, 1565, 1375, 1340, 1222, 1176, 1083, 1018, 966, 771, 703 cm^{-1}; MS (CI): *m*/*z* (%): 318 (68) [(*M*/2+1)H$^+$], 335 (100) [(*M*/2+1)+NH_4^+], 633 (3) [M^+H], 650 (8) [M^++NH_4]; elemental analysis calcd (%) for $C_{34}H_{36}N_2O_{10}$ (632.67): C 64.55, H 5.74, N 4.43; found: C 64.21, H 5.60, N 4.36.

***rac*-11**: oil, 0.82 g (29%); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.21$ (t, $J =$ 7.11 Hz, 6H; 2CH_2CH_3), 1.26 (t, $J = 7.05$ Hz, 6H; 2CH_2CH_3), 4.15 (qd, $J =$ 7.12 Hz, 2H; 2HC*H*CH_3), 4.16 (q, $J = 7.16$ Hz, 2H; 2*H*$CHCH_3$), 4.22 (q, $J = 7.11$ Hz, 4H; 4CH_2CH_3), 4.93, 4.70 (AB, $J = 14.55$ Hz, 4H; 2CH_2Ph), 7.32–7.46 (m, 10H; 2C_6H_5), 8.33 (s, 2H; 2H-pyrrole); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 13.72$, 14.48, 54.31, 60.04, 63.53, 79.32, 105.37, 128.86, 129.27, 129.38, 134.11, 162.20, 162.74, 171.47, 187.99; IR (KBr): $\tilde{\nu} = 3454$, 2982, 1733,

1689, 1569, 1373, 1238, 1020, 769, 702 cm^{-1}; MS (FI): *m/z* (%): 316 (7) [*M*/2$^+$], 632 (100) [*M*$^+$]; elemental analysis calcd (%) for $C_{34}H_{36}N_2O_{10}$ (632.67): C 64.55, H 5.74, N 4.43; found: C 64.47, H 5.66, N 4.24.

Diethyl 1-benzyl-2-bromo-4-methoxypyrrole-3,5-dicarboxylate (12): This compound was prepared exactly as described for the corresponding *N*-methyl compound.[25] Compound **3** (10 g, 30 mmol) was methylated to give **12**. Yield: 11.8 g (95%); m.p. 87.5–88 °C (MeOH); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.26$ (t, $J = 7.13$ Hz, 3H; CH_3), 1.40 (t, $J = 7.13$ Hz, 3H; CH_3), 4.27 (q, $J = 7.13$ Hz, 2H; CH_2CH$_3$), 4.39 (q, $J = 7.13$ Hz, 2H; CH_2CH$_3$), 5.68 (s, 2H; CH_2Ph), 6.95–7.38 (m, 6H; C_6H_5, H^5-pyrrole), 9.37 (s, 1H; OH); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 14.30$, 50.60, 60.57, 60.84, 103.31, 108.52, 115.15, 126.17, 127.50, 128.66, 130.27, 136.46, 154.63, 160.87, 164.32; IR (KBr): $\tilde{\nu} = 3294$, 2984, 1698, 1493, 1205, 1096 cm^{-1}; MS (70 eV, EI): *m/z* (%): 395 (18) [*M*$^+$], 351 (25) [*M*$^+$ – EtOH], 91 (100) [$C_7H_7^+$]; elemental analysis calcd (%) for $C_{17}H_{18}BrNO_5$ (396.24): C 51.53, H 4.58, N 3.53; found: C 51.48, H 4.48, N 4.47.

Diethyl 1-benzyl-2-bromo-4-methoxypyrrole-3,5-dicarboxylate (13): Compound **12** (4 g, 10 mmol) in dry acetone (60 mL), K_2CO_3 (3.5 g, 25 mmol), and dimethyl sulfate (1.27 g, 10 mmol) were used in the same procedure as for **4**. Compound **13** was recrystallized from MeOH. White crystals, 3.9 g (85%); m.p. 49–51 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.31$ (t, $J =$ 7.13 Hz, 3H; CH_2CH_3), 1.39 (t, $J = 7.13$ Hz, 3H; CH_2CH_3), 3.89 (s, 3H; OCH_3), 4.26 (q, $J = 7.13$ Hz, 2H; CH_2CH$_3$), 4.36 (q, $J = 7.13$ Hz, 2H; CH_2CH$_3$), 5.74 (s, 2H; CH_2Ph), 6.94–7.37 (m, 6H; C_6H_5); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 14.17$, 14.29, 50.54, 60.44, 60.52, 63.20, 109.39, 115.06, 115.89, 126.31, 127.43, 128.63, 136.59, 153.33, 159.81, 162.12; IR (KBr): $\tilde{\nu} =$ 2981, 1706, 1542, 1493, 1416, 1288, 1242, 1095, 1029, 696 cm^{-1}; MS (CI): *m/z* (%): 410 (100) [*M*H$^+$], 330 (54) [*M*H$^+$ – HBr]; elemental analysis calcd (%) for $C_{18}H_{20}BrNO_5$ (410.27): C 52.7, H 4.91, N 3.41; found: C 52.43, H 4.78, N 3.35.

Tetraethyl 1,1′-dibenzyl-4,4′-dimethoxy-2,2′-bipyrrole-3,3′,5,5′-tetracarboxylate (14): A mixture of **13** (4 g, 9.8 mmol) and copper powder (15.6 g, 240 mmol) with a small amount of DMF was heated at 300 °C for 30 min in an open rotating flask with argon flushing. After cooling, the contents were taken up with ethyl acetate, the solvent was evaporated, and the brown-black residue was recrystallized from methanol to gave light-yellow crystals. Yield: 3.80 g (60%); m.p. 90–91 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.03$ (t, $J = 7.12$ Hz, 6H; 2CH_2CH_3), 1.33 (t, $J = 7.12$ Hz, 6H; 2CH_2CH_3), 3.79 (q, $J = 7.12$ Hz, 2H; 2H$_3$CHCHCO), 3.83 (q, $J = 7.12$ Hz, 2H; 2H$_3$CHCHCO), 3.95 (s, 6H; 2OCH_3), 3.98 (q, $J = 7.15$ Hz, 2H; 2H$_3$CHCHCO), 4.02 (q, $J = 7.15$ Hz, 2H; 2H$_3$CHCHCO), 4.30 (q, $J = 7.09$, 4H; 2H$_3$CCH_2CO), 4.88 (d, $J = 2.43$, 4H; 2CH_2Ph), 6.81–7.19 (m, 10H; 2C_6H_5); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 13.91$, 14.21, 49.89, 59.63, 60.53, 63.08, 110.58, 115.30, 127.10, 127.48, 128.31, 129.48,136.52, 153.10, 160.41, 161.69; IR (KBr): $\tilde{\nu} = 2981-2821$, 1714, 1492, 1413, 1286, 1241, 1193, 1083, 1025, 194, 711 cm^{-1}; MS (FD): *m/z* (%): 660 (100) [*M*$^+$]; elemental analysis calcd (%) for $C_{36}H_{40}N_2O_{10}$ (660.73): C 65.44, H 6.10, N 4.24; found: C 65.28, H 6.09, N 4.19.

1,1′-Dibenzyl-4,4′-dimethoxy-2,2′-bipyrrole 3,3′,5,5′-tetracarboxylic acid (15): Compound **14** (19 g, 29 mmol) was dissolved ethanol/water (1:1, 500 mL) containing NaOH (23 g, 580 mmol), and the mixture was heated under reflux overnight. Most of the ethanol was stripped off, and the aqueous solution was brought to pH ≈ 2. The white precipitate was dissolved in diethyl ether. Evaporation of the solvent gave 14.5 g (98%) of the title compound. M.p. 110–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 3.77 (s, 6H; 2OCH_3), 4.84 (d, 4H; 2CH_2Ph), 6.79–7.17 (m, 10H; 2C_6H_5), 12.25 (s, 4H; 4OH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 49.26$, 62.45, 110.13, 114.97, 126.53, 126.97, 128.06, 129.37, 136.98, 152.19, 160.98, 162.78; IR (KBr): $\tilde{\nu} = 3446$, 2940, 2550, 1681, 1494, 1278, 1143, 1079, 993, 898, 750, 698 cm^{-1}; MS (ESI): *m/z* (%): 547 (100) [*M*$^+$ – H]; elemental analysis calcd (%) for $C_{28}H_{24}N_2O_{10}$ (548.51): C 61.31, H 4.41, N 5.11; found: C 61.48, H 4.69, N 5.21.

1,1′-Dibenzyl-4,4′-dimethoxy-2,2′-bipyrrole (16): Tetracarboxylic acid **15** (5 g, 9.1 mmol) was decarboxylated without solvent in a similar manner to **6.** The dark residue was recrystallized from ethyl acetate under argon to give 2.34 g (70%) of **16**. M.p. 135–137 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.37$ (s, 6H; 2OCH_3), 4.58 (s, 4H; 2CH_2Ph), 6.08 (AB, 4H; *H*-pyrrole), 6.77–7.05 (m, 10H; 2C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 50.49$, 57.20, 100.50, 104.14, 122.99, 126.98, 127.29, 128.63, 139.41, 149.33; IR (KBr): $\tilde{\nu} =$ 3440, 3066–2825, 1565, 1405, 1326, 1132, 1035, 771, 698, 630 cm^{-1}; HRMS (70 eV, PI-EI) *m/z*: calcd for $C_{24}H_{24}N_2O_2$: 372.1838, found 372.1835.

3,3′-Dimethoxy-2,2′-bipyrrole (1): By using syringe techniques and strict argon protection, sodium (50 mg, 2.2 mmol) was dissolved in liquid ammonia (5–10 mL) at −60 to −70 °C. Compound **7** (0.1 g, 0.27 mmol) was dissolved in THF (2 mL) and added dropwise to the blue solution. After 2 h, the mixture was allowed to warm to ambient temperature, and a solution of $NaHCO_3$ (0.18 g, 2.2 mmol) in argon-saturated water (3 mL) was added carefully. When the excess sodium was completely dissolved, toluene (2 mL) was added, and the contents were stirred for 10 min. The toluene phase was removed by syringe under argon, and the extraction was repeated with toluene (2 mL). The total toluene solution was placed in a freezer at ≥ −20 °C, and **1** was obtained as colorless crystals. The crystal suspension is recommended for storage. Yield: 36 mg (70%); m.p. 173–175 °C; ^{1}H NMR (250 MHz, C_6D_6): $\delta = 3.44$ (s, 6H; 2OCH_3), 5.93 (t, $J =$ 3.07 Hz, 2H; 2H4-pyrrole), 6.16 (t, $J = 3.07$ Hz, 2H; 2H5-pyrrole), 8.49 (s, 2H; 2N*H*);^{13}C NMR (63 MHz, C_6D_6): $\delta = 58.19$, 96.30, 113.35, 142.23; IR (KBr): $\tilde{\nu} = 3354$, 2964, 1540, 1262, 1103, 1069, 1036, 803, 695 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (ε) = 286 (17210); HRMS (70 eV, PI-EI) *m/z*: calcd for $C_{10}H_{12}N_2O_2$: 192.0899, found 192.0896.

4,4′-dimethoxy-2,2′-bipyrrole (2): Compound **2** was prepared from **16** in exactly the same manner as **1**. Again, the product **2** crystallized from the toluene solution at low temperature, and the suspension was put in the freezer under argon. The crystal suspension is recommended for storage. Colorless crystals, yield: 32 mg (70%); m.p. (under argon in a sealed capillary) black melt ca. 130–140 °C; ^{1}H NMR (250 MHz, C_6D_6): $\delta = 3.51$ (s, 6H; 2OCH_3), 5.87 (s, 4H; 4H-pyrrole), 6.48 (br s, 2H; 2N*H*); ^{13}C NMR (63 MHz, C_6D_6): $\delta = 99.24$, 93.59, 58,07; ^{1}H (250 MHz, CD_2Cl_2): 3.70 (s, 6H; 2OCH_3), 5.90 (d, $J = 1$ Hz, 2H; 2-H, H2,2′), 6,25 (d, $J = 1$ Hz, 2H; 2H; H6,6′), 6.69 (br s, 2H; 2N*H*); ^{13}C NMR (63 MHz, CD_2Cl_2): $\delta = 99.11$, 93.68, 57.50. In both solvents, the fourth quaternary-carbon (C2,2′) signal was too weak to be observed in NMR. IR (KBr): $\tilde{\nu} = 3354$, 2964, 1540, 1262, 1103, 1069, 1036, 803, 695 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (ε) = 286 (11937); MS-CI: *m/z* (%): 193 (100) [*M*$^+$H], 373 (100) [*M*$^+$H]; HRMS (70 eV, PI-EI) *m/z*: calcd for $C_{10}H_{12}N_2O_2$: 192.0899, found 192.0896.

3-Methoxypyrrole (17): Compound **6** (0.25 g 11 mmol) was treated with Na/liquid NH_3 as described for **1** and **2**. Vacuum distillation of the crude material gave a colorless oil at *RT* under argon, which crystallizes in the freezer. Yield: 84 mg (87%); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 3.78$ (s, 3H; OCH_3),5.99 (d, 1H; H4-pyrrole), 6.37 (s, 1H; H2-pyrrole), 6.59 (d, 1H; H5-pyrrole), 7.86 (s, 1H; NH); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 58$, 97, 99, 117, 149; IR (film): $\tilde{\nu} = 3402$, 3000–2900, 2829, 1571 cm^{-1}; MS (70 eV, EI): *m/z* (%): 97 (75) [*M*$^+$], 82 (100) [*M*$^+$ – CH_3]; elemental analysis calcd (%) for C_5H_7NO (97.12): C 61.84, H 7.26, N 14.42; found: C 61.51, H 7.28, N 14.57.

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft (Me 409/27-1).

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[17] Crystal structure analysis of **3**: $C_{17}H_{19}NO_5$, M_W 317.33, crystal size: $0.40 \times 0.20 \times 0.15$ mm, prism, translucent, colorless, monoclinic, space group $P21/n$; unit cell dimensions [Å]: $a = 7.7114(5)$, $b = 11.2152(6)$, $c = 18.6717(14)$, $\alpha = 90°$. $\beta = 99.5549°$, $\gamma = 90°$; volume: 1592.42(18) Å^3, $Z = 4$, calculated density 1.324 Mg m^{-3}, absorption coefficient: 0.098 mm^{-1}, $F(000)$: 672, $\mu(Mo_{K\alpha})$, θ range: 2.86° to 25.90°, data collected: 19810, independent data 2556 ($R_{int} = 0.0303$); observed data [$I > 2\sigma(I)$] 2915, goodness-of-fit on $F^2 = 1.052$.
Crystal structure analysis of **10**: $C_{34}H_{36}N_2O_{10}$, M_W 632.65, crystal size: $0.36 \times 0.20 \times 0.10$ mm, prism, translucent, colorless, monoclinic, space group: $P21/n$; unit cell dimensions [Å]: $a = 10.1451(5)$, $b = 16.2191(9)$, $c = 19.0030(11)$, $\alpha = 90°$, $\beta = 94.141(5)°$, $\gamma = 90°$; volume: 3118.7(3) Å^3, $Z = 4$, calculated density 1.347 Mg m^{-3}, absorption coefficient: 0.098 mm^{-1}, $F(000)$: 1336, $\mu(Mo_{K\alpha})$, θ range: 2.21° to 25.81°, data collected: 31053, independent data 5861 ($R_{int} = 0.0303$); observed data [$I > 2\sigma(I)$] 4182, goodness-of-fit on $F^2 = 0.052$.
Data collection was on a STOE-IPDS diffractometer, method: rotation, $T = 173$ K, $\lambda = 0.71073$, graphite monochromator.
CCDC-187623 (**3**) and CCDC-187624 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).
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Received: June 24, 2002 [F4204]

  0947-6539/03/0902-0455 $ 20.00+.50/0