On the α,α'-Oxidative Coupling of β-Alkoxy-Substituted 2-Pyrrolecarboxylates

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The electrochemical and chemical oxidative α,α'-coupling of 3-methoxy-4-methyl-2-pyrrolecarboxylic acid (2) and its ethyl ester 4 is compared with that of the corresponding 4-methoxy-2-pyrrolecarboxylates (1 and 3 respectively). The β-alkoxy substituent exerts a strong directing influence on its vicinal α-position, which in the case of compounds 2 and 4 determines the 2,5'-coupling and allows the isolation of the corresponding 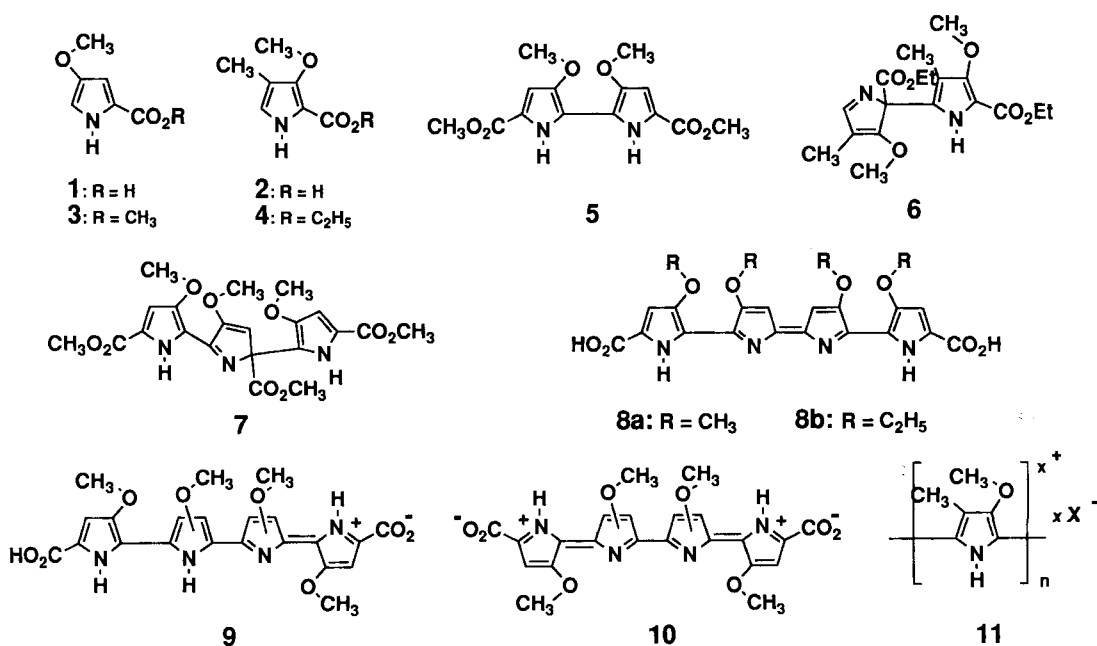1H,2'H-2,2'-bipyrrole 6 in the case of 4. For 2 the polypyrrole can be obtained by exhaustive electrochemical or chemical coupling, whereas in the case of 1 only the corresponding tetramers are formed. The structures of these tetrapyrroles, already described in the literature, here obtained by oxidation of 4-alkoxy-2-pyrrolecarboxylic acid (1), have been reexamined: they are mixtures of tetramers with zwitterionic structure, have at least two substitution patterns and are partially oxidized to the corresponding bipyrrolylidenes.

Symmetrically substituted α,α'-bipyrroles can be obtained by oxidative coupling of 2,3,4-trisubstituted pyrroles[1]. The oxidation of 2,2'-bipyrroles can yield the corresponding 2,2'-bipyrrolylidenes; in some cases, these products can be prepared directly by oxidative coupling of the pyrrole. In these cases the α,α'-bipyrrole must be produced by reduction of the corresponding bipyrrolylidene[1a,1b]. In the case of 2,5-unsubstituted pyrroles oxidative coupling leads to the corresponding polymers, which in the oxidized form are the so-called polypyrrole organic conductors[2]. The neutral polypyrrole, i.e. the linear arrangement of α,α'-bound pyrrole rings, is electrically nonconducting but its oxidation (doping) gives an electrically conducting polypyrrole. From the chemical point of view, this doping process can be considered to result from the oxidation of some of the 2,2'-bipyrrole residues of the polymer to 2,2'-bipyrrolylidenes, the protonation of their basic nitrogens, and the net neutralization of the electric charge by incorporation of an anion into the polymer matrix.

Oxidative coupling of pyrroles can be performed by chemical or anodic electrochemical oxidation. In the case of the preparation of symmetrically 5,5'-substituted 2,2'-bipyrroles, the use of chemical oxidants is usually preferred, but in order to obtain a conducting polypyrrole from 2,5-unsubstituted monomers, the formation of anodic deposits of doped polypyrrole is the current preparation method[2].

Improvement of the polymerization processes to give polypyrroles, especially in the case of pyrroles with different substituents in the β positions, requires greater knowledge not only of primary coupling processes but also of the redox interconversion process between the bipyrrole and the bi-

pyrrolydene forms. Such knowledge would contribute to the understanding of the polypyrrole doping process. With this aim in mind, we present results on the dimerization of 3- or 4-methoxy-substituted 2-pyrrolecarboxylic acids and carboxylates 1 − 4.

The oxidation, both chemical ($FeCl_3$) and electrochemical, of 1 results in the formation of an oxidized tetramer. This reaction has already been described by Bauer[3] for the chemical oxidation ($FeCl_3$) of the analogous 4-ethoxy-2-pyrrolecarboxylic acid: structure 8b has been assigned to the obtained tetramer. However, although the data found for this methoxy substituted tetramer are similar to those reported for the ethoxy tetramer, our results point to a structure different from 8a (see below).

The oxidation of acid 2 results in the formation of polymers. Electrochemical oxidation of 2 furnishes a conducting anodic deposit of similar characteristics, but with lower yield than that obtained from the noncarboxylated monomer (3-methoxy-4-methylpyrrole), i. e. doped polymer 11 see ref.[4]). Furthermore, the oxidation of 2 with $FeCl_3$ results in the formation of insoluble polymeric material exhibiting characteristics similar to those obtained under the same experimental conditions from 3-methoxy-4-methylpyrrole, i. e. the doped polypyrrole 11.

This different behavior in oxidative coupling of 1 and 2 is also shown in the case of the corresponding esters 3 and 4:

i) the oxidation of 3 with lead(IV) tetraacetate, as already described[3] for the corresponding β-ethoxy derivative, results in the isolation of the α,α′-bipyrrole 5 besides several unidentified reaction products. Trimer 7 is isolated from the electrolysis of 3 at the potential corresponding to its first anodic oxidation peak (Table 1). The chemical oxidation of 3 with dichromate or $FeCl_3$ affords a mixture of 5 and 7, but lower yields are obtained in the case of the less oxidizing reagent ($FeCl_3$). Therefore, trimer 7 can be assumed to arise from the reaction of 5 with 3;

ii) the anodic electrolysis of 4 at the potentials corresponding to its first voltammetry peak (Table 1) results in the formation of dimer 6 (≈ 40% yield). The oxidation of 4 with

dichromate also affords 6 but in lower yield (≈ 10%) than the electrochemical oxidation. $FeCl_3$ does not oxidize 4.

Voltammetry results (Table 1) agree with the above observations of the oxidative coupling. The 4-methoxy-2-pyrrolecarboxylates 1 and 3 show a lower positive oxidation potential peak (E_{pa}) (≈ 100 mV) than the 3-methoxy-2-pyrrolecarboxylates 2 and 4, although the latter has an additional electron-donor group (the β-methyl group). The partial contribution of a β methyl group to the E_{pa} of pyrroles[5] has been estimated from empirical relationships to be − 125 mV: the E_{pa} expected for 2 or 4 should be about 100 mV lower than that for 1 or 3, i. e. about 200 mV lower than their experimental E_{pa} values. These high E_{pa} values of 2 and 4 may be a consequence of net stabilization by a mutual conjugation effect, already proposed for pyrroles[5], owing to the substitution in the "conjugated" positions 2 and 3 of one electron-acceptor and one electron-donor group. However, they could also be due to a substituent effect on the chemical pathway following the first electron transfer (e. g. deprotonation of the cation radical) or to a different type of coupling mechanism. In the case of $FeCl_3$ oxidation of the acids, 2 can also be oxidized because the real substrate of the reaction is a metal carboxylate complex, which shows a lower E_{p1}[6] than 2.
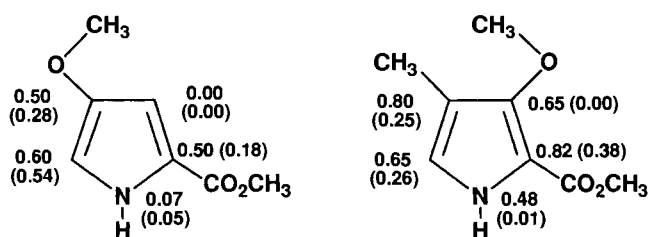

Figure 1. Electrophilic reactivity parameters[7,8] and in parantheses unpaired electron distribution in the UHF natural orbital[9]

The differences in the oxidation products derived from 1 and 3 compared to those obtained from 2 and 4 are a consequence of a directing effect of the β-methoxy group on its closer α position. Insight into this difference in the oxidative coupling is obtained from semiempirical quantum-chemical calculations. For model systems (Figure 1), we have estimated the electrophilic reactivity parameters[7,8] and the radical cation unpaired electron distribution from AM1-UHF NO semiempirical SCF MO calculations[9]. In the case of the 2-carboxy-4-alkoxy substitution, both the radical cation-to-radical cation and the radical cation-to-substrate dimerization process would be expected to give 5,5′-coupling, which agrees with the experimental results. In the case of the 2-carboxy-3-alkoxy substitution, the electrophilic reactivity parameters and also the unpaired electron distribution of the radical cation show a higher reactivity and density of the 2-position than the 5-position, which explains the formation of the 2,5′-coupling (6). Futhermore, voltammetry shows that the rate-limiting chemical reaction, following the primary one-electron transfer step[10], is different for 3 and 4; the semilogarithmic plot of E_{pa} vs. the logarithm of the

Table 1. Voltammetry [1 · 10⁻³ mol · l⁻¹ acetonitrile solutions, 0.1 mol · l⁻¹ tetrabutylammonium perchlorate; sweep rate (r) 50 mV · s⁻¹] anodic peak potentials (E_{pa}) and peak intensity (I_d: electrode surface 6.69 mm²) values and slopes of the semilogarithmic plot of the first wave E_{pa} vs. log r

Compound	E_{pa} (V, sce)	I_d (µA)	Slope E_{pa} vs. log r	Formation of anodic deposit
1	1.28	64	[a]	+ [b]
2	1.36	43	[a]	+ [c]
3	1.26	52	22 ± 3	−
4	1.34	43	29 ± 3	−
5	0.82[d] (1.31)	34 (30)	15 ± 3	−
6	1.38 (1.68)	30	31 ± 3	−
7	1.12 (1.65)	52	30 ± 3	−

[a] Nondiffusion controlled. − [b] Deposit of polymeric nature. − [c] Nonadhered to the anode (see text and Experimental Section). − [d] Reversible.

sweep rate (r)[11] varies linearly, with a dependence of 22 mV · $(\log r)^{-1}$ for 3 and 29 mV · $(\log r)^{-1}$ for 4.

The structure proposed in the literature[3] for the tetramer, obtained by $FeCl_3$ oxidation of the ethoxy monomer analogous to 1, is that corresponding to the didehydrotetralkoxytetrapyrrole 8b. According to our results, the tetramer obtained from 1 by chemical and electrochemical oxidation shows a solubility behavior typical of zwitterions (solubility minimum in water at about pH = 4): the changes with pH of the UV spectrum and the IR spectrum are also consistent with the zwitterionic structure. Furthermore, the ^1H NMR (CF_3COOD) spectrum, which has previously not been reported for these tetramers, rules out a symmetric structure of 8, because of the presence of more than two types of aromatic protons and methoxy groups (although several N—H tautomeric and zwitterionic structures are possible we assume their fast interconversion at the NMR time scale). The UV spectra show many similar absorption bands, which can be explained by assuming the presence of several analogous compounds. Bauer[3] has obtained the tetramer 8b in two different ways, i.e. by oxidation of the ethoxy analogue of 1 and oxidation of the symmetrically substituted 3,3'-dimethoxy-2,2'-bi-1H-pyrrole-5,5'-dicarboxylic acid: 8b has been chemically identified[3] on the basis of the product obtained from the oxidation of the dimer. In the case of dimer oxidation the tetramer obtained must have the β-substitution structure of 8a, but by oxidation of the monomer — as reported in this paper — two additional alkoxy substitution patterns for the final tetramer could be expected. The detection of trimer 7 generated by oxidation of ester 3 agrees with a such reaction pathway of acid 1 furnishing the tetramer. The tetramer obtained by electrochemical oxidation shows IR and UV spectra which slightly but clearly differs from those of the product obtained by chemical oxidation ($FeCl_3$). The elemental analysis values (see Experimental) and the differences observed in the UV spectra by acid or base addition (more basic nitrogens in the case of the electrochemical oxidation), suggest the structure of a doubly oxidized tetramer [bis(bipyrrolylidene) 10] as the main product of the electrochemical synthesis and of the monooxidized tetramer (9) for the $FeCl_3$ oxidation[12,13]. In conclusion, the tetramers obtained from the oxidation of 3-alkoxy-2-alkoxycarbonylpyrroles are mixtures of several substitution patterns and of two oxidation levels (9 and 10).

The results reported in this paper show that it is difficult to obtain polymers by oxidative coupling in the farthest α position with respect to a β-alkoxy substituent, e.g. in the oxidative decarboxylative polymerization at the tetramer level for 3. In this respect, it should be pointed out that the anodic oxidation of 4,4'-dimethoxybithiophene results in stable polythiophenes in contrast to 3,3'-dimethoxybithiophene, which is only converted into oligomers[14]. This difficulty cannot be attributed to a too high oxidation potential (Table 1); it is probably due to the fact that oxidation to bipyrrolylidene structures is preferred to the intermolecular polymerization.

Experimental

Melting points: Hot-stage apparatus, values are not corrected. — FT-IR: Perkin-Elmer 681. — ^1H- and ^{13}C NMR: $CDCl_3$ (previously filtered through Al_2O_3) solutions, Varian XL-200 instrument (200 MHz for proton); δ values, TMS as internal reference. — Mass spectra: VG Autospec instrument, Cs and a glycerol matrix in the positive FAB mode. — Analytical TLC: Precoated 0.25 mm silica gel 60PF-254 aluminium sheets. — Preparative TLC: 1-mm silica gel 60PF-254 glass plates; the TLC-isolated fractions were purified by chromatography on a small column silica gel 60 (230—400 mesh).

Experiments requiring the exclusion of O_2 were performed in Ar-purged solutions by using a positive pressure of dry Ar. Organic extracts were dried with Na_2SO_4 and concentrated under reduced pressure below 35°C.

Cyclic voltammograms were obtained by using a PAR 174 A analyzer with an interphase AC 174/50. The electrodes used were a Pt bead of 6.69 mm^2 as working electrode, a KCl-saturated calomel electrode as reference electrode and a Pt wire (diameter 0.8 mm) as auxiliary electrode. Voltammograms were recorded between 5 and 200 mV s^{-1} (iR drop compensated). Preparative electrolysis was performed on a Pt mesh. For electrolysis experiments performed to obtain conducting anodic deposits a 7-cm^2 sheet of Pt-coated Ti was employed. Equipment and materials (solvents and supporting electrolytes) used for controlled potential electrolysis and galvanostatic electrolysis are described in ref.[15].

The AM1(UAM1) semiempirical SCF MO method[9a] was applied in a locally modified version[9b] of the MOPAC program[9c].

The preparation and properties of the following compounds are described in the literature: 4-methoxy-2-pyrrolecarboxylic acid[16,17] (1), methyl 4-methoxy-2-pyrrolecarboxylate[19] (2), 3-methoxy-4-methyl-2-pyrrolecarboxylic acid[18] (3) and ethyl 3-methoxy-4-methyl-2-pyrrole carboxylate[20] (4). 3-Methoxy-4-methylpyrrole used for the preparation of the corresponding polymer by chemical and anodic oxidation was obtained as described in ref.[18].

Dimethyl 3,3'Dimethoxy[2,2'-bi-1H-pyrrole]-5,5'-dicarboxylate (5) was prepared in 9—10% yield by oxidation of 3 with Pb(IV) tetraacetate according to the procedure described in ref.[3] for the corresponding 3-ethoxy derivative: m. p. 220—222°C. — R_f = 0.68 (CH_2Cl_2/MeOH, 20:1). — IR (KBr): $\tilde{v}$ = 3445 cm^{-1}, 1698, 1222, 1198. — Uv ($CHCl_3$): λ_{max} (ε) = 386 nm (32000), 368 (31250). — ^1H NMR ($CDCl_3$): δ = 9.45 (br. s, 1H, NH), 6.60 (d, 2H, —CH=, J_{NH-CH} = 2.9 Hz), 3.91 (s, 6H, CO_2CH_3), 3.86 (s, 6H, OCH_3). — MS (70 eV), m/z (%): 308 (62)[M⁺], 293 (40), 154 (10). — $C_{14}H_{16}N_2O_6$: calcd. 308.1008, found 308.1006.

Ethyl 5-(2-Ethoxycarbonyl-3-methoxy-4-methyl-2H-pyrrol-2-yl)-3-methoxy-4-methyl-1H-pyrrole-2-carboxylate (6). — *Electrochemical Synthesis:* 54 mg (0.30 mmol) of 4 in 25 ml of a 0.1 mol l^{-1} tetrabutylammonium perchlorate/acetonitrile solution was electrolyzed under potentiostatic conditions (+1.3 V SCE). After consumption of 0.28 mF the solution was concentrated in a rotary evaporator and the residue was dissolved in ether. The solution was filtered, dried and concentrated in vacuo. Preparative TLC (ethyl acetate/toluene, 2:1; R_f = 0.33) afforded 20 mg (38%) of 6 (oil): R_f = 0.66 ($CHCl_3$/MeOH, 25:1). — IR (KBr): $\tilde{v}$ = 3430 cm^{-1}, 1735, 1700, 1675, 1650 cm^{-1}. — UV/VIS ($CHCl_3$): λ_{max} (ε) = 272 nm (2100). — ^1H NMR ($CDCl_3$): δ = 9.0 (br. s, 1H, NH), 8.05 (s, 1H, —CH=N), 4.29 (q, 2H, CO_2—CH_2—CH_3, J = 7 Hz), 4.22 (q, 2H, CO_2—CH_2—CH_3, J = 7 Hz), 4.04 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 2.06 (s, 3H, =C—CH_3), 1.97 (s, 3H, =C—CH_3), 1.35 (t, 3H, CO_2—CH_2—CH_3, J = 7 Hz), 1.26 (t, 3H, CO_2—CH_2—CH_3, J = 7 Hz). — ^{13}C NMR (DEPT analysis, $CDCl_3$): δ = 176.0 (C=N).

173.4, 168.5 (2 C=O), 159.9, 151.0 (2 CH$_3$O—C), 167.0, 123.5, 112.3, 109.7, 83.0 (5 C quat.), 62.5, 59.8 (2 CO$_2$—CH$_2$—CH$_3$), 62.2, 59.4 (2 OCH$_3$), 14.5, 13.9 (2 CO$_2$—CH$_2$—CH$_3$), 9.6, 7.8 (2 =C—CH$_3$). — MS (70 eV), m/z (%): 364 (87) [M$^+$], 349 (23), 292 (40). — C$_{18}$H$_{24}$N$_2$O$_6$ (364.4): calcd. C 59.33, H 6.63, N 7.68; found C 59.16, H 6.67, N 7.53.

Chemical Synthesis: A solution of 55 mg (0.18 mmol) of sodium dichromate in 2.8 ml of water was added dropwise under Ar atmosphere to a solution of 103 mg (0.56 mmol) of **4** in 2.8 ml of trifluoroacetic acid. The mixture was stirred for 12 h and extracted with CHCl$_3$ (27 ml)/H$_2$O (5 × 10 ml). Preparative TLC as before yielded 12 mg (12%) of **6**.

Methyl 4-Methoxy-2,5-bis(3-methoxy-5-methoxycarbonyl-1H-pyrrol-2-yl)-2H-pyrrole-2-carboxylate (**7**). — *Electrochemical Oxidation:* 40 mg (0.26 mmol) of **3** in 25 ml of a 0.1 mol l^{-1} tetrabutylammonium perchlorate/CH$_2$Cl$_2$ solution was electrolyzed under potentiostatic conditions (+1.1 V, SCE). After consumption of 0.27 mF, the solution was washed with H$_2$O (3 × 30 ml) and concentrated in vacuo. The residue was dissolved in ether and the solution filtered. Preparative TLC (ether/toluene, 2:1; R_f = 0.12) afforded 19.4 mg (48%) of **7**: mp.p. 150—152 °C. — IR (KBr): $\tilde{v}$ = 3402 cm^{-1}, 1740, 1720, 1710, 1630, 1570. — UV (CHCl$_3$): λ_{max} (ε) = 405 nm (4050), 331 (20600), 294 (17100), 256 (16800). — ^{1}H NMR (CDCl$_3$): δ = 10.1 (s, 1 H, NH, coupled with d at 6.58), 9.6 (s, 1 H, NH, coupled with d at 6.57), 6.73 (s, 1 H, —C=CH), 6.58 (d, 1 H, —CH=, $J_{NH-C=C-CH}$ = 2.1 Hz), 6.57 (d, 1 H, —CH=, $J_{NH-C=C-CH}$ = 2.9 Hz), 3.94 (s, 3 H, CO$_2$—CH$_3$), 3.93 (s, 3 H, CO$_2$—CH$_3$), 3.89 (s, 3 H, CO$_2$—CH$_3$), 3.8 (s, 3 H, OCH$_3$), 3.78 (s, 3 H, OCH$_3$), 3.67 (s, 3 H, OCH$_3$). — ^{13}C NMR (DEPT analysis, CDCl$_3$): δ = 161.1, 160.8, 160.7 (3 C=O), 157.3, 152.0, 145.7, 128.2, 121.8, 114.1, 79.5 (7 C quat.), 117.2 (2 C quat.), 115.6, 101.4, 99.9 (3 CH), 58.8, 58.6, 58.3 (3 OCH$_3$), 53.2, 51.9, 51.3 (3 CO$_2$—CH$_3$). — MS (70 eV), m/z (%): 461 (100) [M$^+$], 446 (29), 402 (48). — C$_{24}$H$_{20}$N$_3$O$_9$: calcd. 461.1434, found 461.1434.

Chemical Oxidation with Dichromate: Compounds **5** and **7** were obtained in 7% and 34% yield, respectively, by using the same procedure for **3** as applied to the oxidation of **4** to **6** with dichromate.

Chemical Oxidation with FeCl$_3$: A mixture of 26.4 mg (0.17 mmol) of **3**, 96 mg (0.35 mmol) of FeCl$_3$ and 0.9 g of potassium carbonate in 25 ml of CH$_2$Cl$_2$ was stirred under argon for 12 h. The residue obtained after filtration of the reaction mixture and concentration of the filtrate was subjected to PTLC (ethyl acetate/toluene, 2:1) to yield 3.5 mg (13%) of trimer **7** ans as main compound unreacted **3**, which was contaminated with dimer **5** (TLC and ^{1}H-NMR detection).

Oxidation of 2 and of 3-Methoxy-4-methylpyrrole to Polymers 11: Electrochemical oxidation. Electrically conducting polymeric anodic deposits were obtained as films (poor mechanical properties) from **2** at working electrode potentials of +1.4 V SCE and under the same experimental conditions as those reported for 3-methoxy-4-methylpyrrole[15b]. The film showed reversible cycling at E_{pa} = +0.02 V SCE and E_{pc} = −0.26 V SCE. Chemical oxidation with FeCl$_3$. 1 mmol of monomer in 20 ml of ethanol was added dropwise with stirring and under argon to 15 ml of an aqueous solution of 3.1 mmol of FeCl$_3$. After 18 h the residue was centrifuged and washed several times in water and in ethanol. After drying about 110 mg of a black polymer was obtained.

The electrical conductivities of pressed pellets (10 TN cm^{-2}) were in the order of 1 · 10^{-3} Ω^{-1} · cm^{-1} (four-point method[21]). The combustion analytical data were in agreement with the following relation: C$_{6.0-6.1}$, H$_{7.0-7.2}$, N$_{1.0}$, Cl$_{0.1-0.2}$.

Didehydro-3,β',β'',3'''-tetramethoxy-2,2':5',2'':5'',2'''-quaterpyrrole-5,5'''-dicarboxylic acid (**9**) was obtained in 45% yield by FeCl$_3$ oxidation of **1** according to the procedure described in the literature[3] for the corresponding ethoxy derivative. Some of the spectral data were very similar to those of the tetramer obtained by electrochemical oxidation but some differences in the IR, UV/VIS and NMR spectra indicated that they do not arise from the same type of compound or that they belong to a mixture with different isomer ratio; m. p. > 300 °C. — IR (KBr): $\tilde{v}$ = 3394 cm^{-1} (br. down to 2000), 1559 (s), 1320 (s), 1160 (vs), 1042 (m), 966 (w), 933 (m), 903 (w) cm^{-1}. — UV (pyridine): λ_{max} = 587 nm (br.); (DMSO) λ_{max} (ε) = 621 nm (br., 10900), 575 sh, 720 sh; (MeOH, 1 N HCl) λ_{max} (ε) = 638 nm (12000), 675 sh, 790 sh; (H$_2$O, 0.5 N NaOH) λ_{max} (ε) = 645 nm (22000), 685 sh, 775 sh. — ^{1}H NMR (CF$_3$COOD): δ = 7.1, 6.9, 6.85, 6.6 and 5.8 (br. s, ≈ 1:2:1:0.3:0.1 ratio), 4.4—4.1 (several s, CH$_3$O, ratio of aromatic plus olefinic signals, 3:1) (low resolution spectrum). — MS (FAB), m/z: 471 [M$^+$ + 1] (reduced compound, see ref.[13]). — C$_{22}$H$_{20}$O$_8$N$_4$ · 2 H$_2$O (504.5): calcd. C 52.38, H 4.80, N 11.11; found C 51.50, H 4.58, N 11.40.

Tetradehydro-3,β',β'',3'''-tetramethoxy-2,2':5',2'':5'',2'''-quaterpyrrole-5,5'''-dicarboxylic acid (**10**): 40 mg (0.28 mmol) of **1** in 25 ml of a 0.1 mol l^{-1} tetraethylammonium perchlorate/acetonitrile solution was electrolyzed at potentiostatic conditions (+1.2 V SCE) after consumption of 0.4 mF. The reaction mixture was centrifugated and the residue was washed several times (H$_2$O and THF). The blue solid residue was centrifugated and the residue was washed several times (H$_2$O and THF). The blue solid residue was purified by dissolution in 0.5 mol l^{-1} NaOH and precipitation after acidification to pH = 3.5 with 1 mol l^{-1} of HCl. Recrystallization in (DMSO/H$_2$O, 1:1) afforded 13 mg (39% yield) of **10**; m. p. > 300 °C. — IR (KBr): $\tilde{v}$ = 3394 cm^{-1} (br. down to 2000), 1559 (vs), 1316 (s), 1166 (s), 1050 (m), 966 (m), 899 (w): — UV (pyridine) λ_{max} = 579 nm, 525 sh, 620 sh, 675 sh, 750 sh; (DMSO) λ_{max} (ε) = 597 nm (11900), 720 sh, 800 sh; (MeOH, 1 N HCl) λ_{max} (ε) = 585 nm (10300), 615 sh, 750 sh; (H$_2$O, 0.5 N NaOH) λ_{max} (ε) = 631 nm (18900). — ^{1}H NMR (CF$_3$COOD): δ = 7.14, 6.94, 6.88, 6.7, 5.8 (br. s, ≈ 1:2:1:0.3:0.1 ratio), 4.46—4.18 (several singlets, CH$_3$O, ratio to the aromatic plus olefinic signals 3:1) (low resolution spectrum). — MS (FAB), m/z: 471 [M$^+$ + 1] (reduced compound, see ref.[13]). — C$_{22}$H$_{18}$O$_8$N$_4$ · 3 H$_2$O (520.5): calcd. C 50.77, H 4.65, N 10.76; found C 50.37, H 4.18, N 10.57.

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[12] Formula **8** does not imply the structural assignment of the exocyclic double bond configuration or of the NH tautomerism.

[13] The MS analysis (EI, CI, and FAB modes) does not reveal the molecular mass of the tetramer: only the MS recorded in the FAB mode does show *m/z* peaks close to the molecular mass, but they correspond to the [M$^+$] and [M$^+$ + 1] peaks of the reduced tetramer (*m/z* 470 and 471), which does not agree with the strong low-energy absorption of the UV/VIS spectra of the isolated compounds: the reduction of compounds by the FAB MS mode is a common fact for some type of organic compounds. D. H. Williams, A. F. Findeis, S. Naylor, B. W. Gigson, *J. Am. Chem. Soc.* **1987**, *109*, 1980−1986.

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