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Electrochemical Oxidation and EPR Spectroscopy of Radical Cations of *N*-Substituted 2,3,4,5-Tetramethylpyrroles

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Dedicated to Professor Lennart Eberson on the occasion of his 65th birthday

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Electrochemical oxidation of 19 *N*-substituted 2,3,4,5-tetramethylpyrroles has been studied in acetonitrile and dichloromethane by means of slow cyclic voltammetry and coulometry. The first oxidation consumes one electron and occurs within the potential range 0.60–0.94 V in acetonitrile and 0.78–1.17 V in dichloromethane (vs. SCE). Twelve *in situ* generated primary radical cations were sufficiently stable at lowered temperature in dichloromethane for EPR measurement and showed well resolved HFS. The *g*-values ($\approx$2.0026) and the coupling constants of 2,5-methyls ($a_H \approx 1.5$ mT), 3,4-methyls ($a_H \approx 0.35$ mT), and of the pyrrole nitrogen ($a_N \approx 0.42$ mT) are very proximate for all 12 radical cations. It can be concluded, with support from quantum chemical calculations, that the odd electron is localised entirely on the pyrrole ring in the a_2 HOMO of the parent molecule. Despite the odd electron distribution, the stability of the radical cations depends on the particular substituent attached to the pyrrole nitrogen.

The chemistry of pyrroles has recently developed into an extensive field, touching many branches of science and technology. Irreplaceable metabolic redox systems and conducting polymers can be considered as two pre-eminent examples. The development and diversity of pyrrole chemistry are documented in several comprehensive monographs.[1–4] One of the most typical elementary reactions of pyrrole derivatives is a one-electron oxidation step producing a more or less stable intermediate radical cation.

Unless substituted by a strong electron withdrawing group, pyrrole cannot be electrochemically reduced.[5] The electrochemical oxidation of arylpyrroles,[6–16] alkylpyrroles,[14,17,18] other pyrrole derivatives,[19,20] and related isoindoles[21] has been studied in non-aqueous solvents. There are many references to the electrochemical polymerisation of pyrroles, which we do not attempt to list here.

The radical moieties derived from pyrrole have been studied by EPR spectroscopy in solid matrices[22–25] and solutions,[26–28] in which the hyperfine structure (HFS) has not been completely resolved. Davies *et al.*[29–32] measured and interpreted EPR spectra with well resolved HFS for radical cations of various alkylpyrroles with one or two pyrrole rings. Those radicals were generated by photolysis in trifluoroacetic acid. EPR signals and HFS coupling constants have also been obtained for cation radicals of pyrrole derivatives generated in dichloromethane at low temperature by means of electrochemical oxidation.[16,17]

The goal of this study was to explore the electronic structure and stability of primary radical cations and determine the dependence if any on the substituent attached to the nitrogen atom of the pyrrole ring. The methyl groups, in place of hydrogens, on all the pyrrole carbons were used since they greatly increase the stability of radical cations. In addition, the methyls do not seriously disturb the π-electron structure and, at the same time, simplify the determination of the spin distribution through hyperfine splitting.

Results and discussion

Nineteen 2,3,4,5-tetramethylpyrroles with a different substituent on the ring nitrogen were synthesised by Paal–

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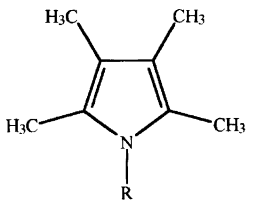
Knorr[33,34] condensation from 3,4-dimethyl-2,5-hexanedione and the appropriate amine.



R	R
1 H	**10** Ph
2 CH_3	**11** p-$C_6H_4CH_3$
3 $CH(CH_3)_2$	**12** p-C_6H_4CN
4 $CH_2CH(CH_3)_2$	**13** p-C_6H_4Br
5 $C(CH_3)_3$	**14** p-$C_6H_4NO_2$
6 CH_2Ad	**15** m-$C_6H_4NO_2$
7 $CH(CH_3)Ad$	**16** o-$C_6H_4NO_2$
8 Cyclohexyl	**17** p-$C_6H_4NH_2$
9 CH_2Ph	**18** p-$C_6H_4NMe_2$
	19 p-$C_6H_4NEt_2$

Electrochemical properties of the pyrrole derivatives were examined by means of slow cyclic voltammetry and controlled potential electrolysis in dichloromethane (DCM) and acetonitrile (AN) with 0.1 M tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$).

All 19 tetramethylpyrroles were subject to internal (*in situ*) electrochemical generation of radicals in the cavity of the EPR spectrometer at controlled potential and temperature. EPR spectra of twelve cation- and three anion-radicals were obtained in dichloromethane. The parameters of hyperfine structure were determined by means of simulation in all cases. The discussion of the electronic structure is based on semiempirical quantum chemical calculations.

Electrochemistry. Electrochemical parameters of all 19 compounds in dry DCM and AN are given in Table 1. After tentative experiments with several organic solvents (nitromethane, tetrahydrofuran, *N,N*-dimethylformamide, dimethyl sulfoxide, propylene carbonate) DCM and AN were chosen for the systematic study. Compared with AN, which is a standard non-aqueous solvent in electrochemistry, DCM is much worse with regard to conductivity, which causes a drop in potential, and higher with regard to vapour pressure, which makes steady concentrations difficult to maintain. On the other hand, DCM makes the radical cations more stable. In addition, for the electrochemical generation of radicals, DCM has two more advantages: a relatively low permittivity (9.08 at 293 K) and a much lower melting point (178 K).

The electrochemical behaviour splits the studied compounds roughly into four groups. (1) The 1-H (**1**) derivative and compounds **2**–**9**, which bear a substituent

Table 1. Electrochemical parameters of 1-substituted 2,3,4,5-tetramethylpyrroles in dichloromethane (DCM) and acetonitrile (AN)–0.1 M $TBAPF_6$ at a Pt-electrode.

Compound[a]		E_p/V[b]		n[c]		$i_p c^{-1} \nu^{-1/2}$[d]	
		DCM	AN	DCM	AN	DCM	AN
1	H_2	0.78	0.60	0.92	0.93	1.03	1.36
2	CH_3	0.97	0.62	0.89	0.87	0.91	1.38
3	$CH(CH_3)_2$	0.92	0.68	0.94	0.98	0.85	1.33
4	$CH_2CH(CH_3)_2$	0.85	0.63	0.91	0.91	0.92	1.28
5	$C(CH_3)_3$	0.91	0.66	0.92	0.99	0.89	1.37
6	CH_2Ad	0.80	0.61	0.99	0.95	0.88	1.34
7	$CH(CH_3)Ad$	0.81	0.59	0.90	0.92	0.85	1.30
8	Cyclohexyl	0.93	0.70	0.96	0.96	0.92	1.37
9	CH_2Ph	0.95	0.69	0.98	0.93	0.91	1.20
10	Ph	0.98	0.72	1.02	1.02	0.87	1.19
11	p-$C_6H_4CH_3$	1.03	0.77	0.96	1.02	1.01	1.34
12	p-C_6H_4CN	1.13	0.87	0.95	1.08	0.92	1.17
13	p-C_6H_4Br	1.07	0.83	0.97	0.99	0.87	1.22
14	p-$C_6H_4NO_2$	1.17	0.94	0.96	1.01	0.88	1.31
	Redn.	−1.20		0.98		0.83	
15	m-$C_6H_4NO_2$	1.17	0.93	0.96	1.05	0.90	1.28
	Redn.	−1.2		0.92		0.87	
16	o-$C_6H_4NO_2$	1.17	0.94	1.01	1.03	0.87	1.30
	Redn.	−1.33		0.97		0.82	
17	p-$C_6H_4NH_2$	0.95	0.72	0.98	0.94	0.96	1.16
	2nd oxidn.	1.40	1.38				
18	p-$C_6H_4NMe_2$	1.00	0.72	1.01	0.97	0.85	1.19
	2nd oxidn.	1.50	1.20				
19	p-$C_6H_4NEt_2$	0.92	0.70	1.05	0.92	0.83	1.14
	2nd oxidn.	1.42	1.26				

[a] Data in rows with the compound number refers to the first oxidation step. Data in the extra lines are given either for the first reduction step (**14**, **15**, **16**) or for the second oxidation step (**17**, **18**, **19**). [b] The peak potential in V vs. SCE (cyclic voltammetry; $\nu = 0.2$ V s^{-1}). [c] The number of electrons per molecule in exhaustive electrolysis. [d] i_p/A cm^{-2} = current density at the peak potential; $c = 0.001$ mol dm^{-3} = concentration; $\nu = 0.2$ V s^{-1} speed of polarisation.

connected through a tetravalent carbon to the pyrrole nitrogen, show a simple electrochemical picture. Within the potential windows only one oxidation occurs and there is no reduction step. The oxidation, in either solvent, consumes one electron per molecule. The number of electrons was determined by exhaustive, controlled, potential electrolysis (Table 1). From a comparison of the values of the term $i_p c^{-1} v^{-1/2}$ (Table 1) with that of ferrocene (0.93 in DCM and 1.38 in AN under the conditions and in the units given in Table 1) we can also estimate the number of electrons consumed per molecule to be close to one. Such an estimation is only rough, since the systems studied are neither completely reversible nor irreversible.

The electrochemical reversibility, and also the stability of the radical cation, was estimated from the ratio of the cathodic and anodic currents of a cyclic curve at a sweep rate 0.2 V s^{-1}. This is important for the internal electrochemical generation of radicals; when we see at least a partial counter-peak we have a good chance to observe and record an EPR signal. The lowest reversibility was observed for compounds **1**, **2**, **4** and **9**, where no reverse peak was present at all, even at a sweep rate of 1.0 V s^{-1}. This allowed[35] us to estimate the lifetimes of the radical cations to be shorter than 0.1 s. Compounds **3** and **5–8** show, at ambient temperature and 0.2 V s^{-1}, partial reversibility in either solvent, the cathodic current in AN being only 20–50% of that in DCM. The lifetimes of the radical cations amount[35] roughly to several seconds. The cyclic curve for the compound **5** is shown in Fig. 1.

(2) The electrochemical oxidation of the aryl substituted tetramethylpyrroles **10–13** is very similar to the previous group of compounds. The primary radical cations in DCM decay within tenths of a second at ambient temperature.

(3) The three 1-nitrophenyl tetramethylpyrroles, **14–16**, do not differ qualitatively from the previous four compounds with regard to oxidation. The cathodic counter-peak is 50–85% of the anodic current, so the radicals decay within seconds at ambient temperature. Owing to the NO_2 group all three compounds **14–16** can be reduced in a simple one-electron reversible step, as described in Table 1 and depicted in Fig. 1.

(4) In the structure of molecules **17–19** one can identify the pyrrole unit, an aniline unit, and a *p*-phenylenediamine unit, each of which can be easily oxidised as separate moieties. This is the probable cause for the more complex behaviour observed during oxidation. All three cyclic curves are of the same type (Fig. 1) and show two oxidation steps, both irreversible. Small cathodic peaks at about −0.5 and −0.9 V are connected with the oxidation. Electrolysis at the second oxidation potential leads to a sparingly soluble product.

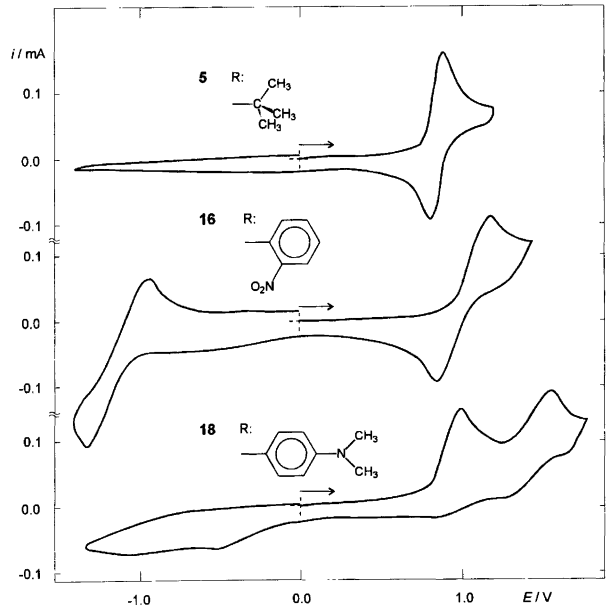


Fig. 1. Cyclic voltammetry of 1 mM solutions of compounds **5**, **16** and **18** in dichloromethane–0.1 M $TBAPF_6$ (0.2 V s^{-1}).

EPR spectroscopy. We attempted to secure EPR signals of all 19 compounds within the temperature range 183–273 K in DCM with 0.1 or 0.2 M $TBAPF_6$. The concentration of the electrolysed compounds was within the range 0.5–10 mM, depending on the stability of the radical cation. The potential of electrolysis usually exceeded the peak potential by ca. 100 mV. Despite the fact that the first oxidation is one-electron step, we did not succeed in recording any EPR signal for seven of the tetramethylpyrroles studied (**1**, **2**, **4**, **9** and **17–19**), even at a concentration of 10 mM and temperature as low as 183 K. The hyperfine couplings, extracted by direct measurement and digital simulation, and other parameters of 12 trapped radical cations, are given in Table 2. In all of the latter cases the EPR data confirm the primary cation radical as the initial product of the electron transfer.

The stability of the radical cations for the *N*-alkylated compounds (**1–9**) is associated with the size of the substituent adjacent to the pyrrole nitrogen. The number of hydrogens on the carbon adjacent to the nitrogen plays a role, too. An adjacent methylene group must bear a bulky substituent (e.g., adamantyl, **6**$^{\cdot+}$) to protect the radical under our conditions. However, Davies *et al.*[30] obtained an EPR spectrum for the radical cation of compound **1** in fluoroacetic acid. The methyl groups in positions 3 and 4 of the pyrrole ring, in addition to the ones in positions 2 and 5, are necessary to increase the stability of the radicals under our conditions. We were not able to see EPR signals for several *N*-substituted 2,5-dimethylpyrroles, but Davies *et al.*[30] described five of them in fluoroacetic acid. 2,5-Di-*tert*-butylpyrroles (i.e., with hydrogen at the 3,4 positions) give reasonably stable primary radical cations (even for 2,5-di-*tert*-butyl-1*H*-pyrrole itself under these conditions[36] and in fluoroacetic acid[30]).

EPR spectra of all five primary radical cations of *N*-alkylated compounds (**3** and **5–8**) were taken around

Table 2. EPR parameters of radical cations of 1-substituted 2,3,4,5-tetramethylpyrroles in DCM–0.1 M $TBAPF_6$.

Compound		$a_{\alpha\text{-}CH_3}$[a]	$a_{\beta\text{-}CH_3}$[a]	a_N[b]	a_R[c]	g[d]	ΔH_{pp}[e]	%L[f]
3	$CH(CH_3)_2$	1.540	0.350	0.422	0.055	2.00262	0.030	90
5	$C(CH_3)_3$	1.509	0.335	0.422		2.00265	0.028	50
6	CH_2Ad	1.530	0.340	0.425	0.085	2.00264	0.030	75
7	$CH(CH_3)Ad$	1.535	0.360	0.420	0.063	2.00262	0.030	40
		1.525	0.315					
8	Cyclohexyl	1.524	0.348	0.420	0.065	2.00263	0.045	50
10	Ph	1.554	0.354	0.428		2.00269	0.025	60
11	$p\text{-}C_6H_4CH_3$	1.549	0.355	0.425		2.00268	0.035	65
12	$p\text{-}C_6H_4CN$	1.554	0.360	0.430		2.00264	0.035	65
13	$p\text{-}C_6H_4Br$	1.559	0.353	0.423		2.00263	0.032	70
14	$p\text{-}C_6H_4NO_2$	1.554	0.354	0.429		2.00260	0.030	55
15	$m\text{-}C_6H_4NO_2$	1.554	0.355	0.425		2.00263	0.035	55
16	$o\text{-}C_6H_4NO_2$	1.544	0.349	0.424		2.00263	0.033	50

[a] $a_{\alpha\text{-}CH_3}$ and $a_{\beta\text{-}CH_3}$ are the proton coupling constants (mT) of the methyls in the 2,5 and 3,4 position, respectively (septets 1:6:15:20:15:6:1). [b] a_N is the coupling constant (mT) of the pyrrole nitrogen (triplet 1:1:1). [c] a_R is the proton coupling constant (mT) of the proton(s) of the methine (**3**, **7**, **8**)/methylene (**6**) adjacent to the pyrrole nitrogen (doublet 1:1/triplet 1:2:1). [d] g is the g-factor. [e] ΔH_{pp} is the linewidth (mT) used in the simulation. [f] %L is the % of the Lorentzian shape used in simulation (the rest being the Gaussian shape).

233 K and show well resolved HFS that makes it possible to measure some couplings directly. The data given in Table 2 were confirmed by digital simulation with very good agreement. The basic and common features for the five spectra are two septets 1:6:15:20:15:6:1 and a triplet 1:1:1. The HFS of $\mathbf{5}^{\cdot+}$ displays no additional features. Radicals $\mathbf{3}^{\cdot+}$ and $\mathbf{8}^{\cdot+}$ give rise to an additional doublet 1:1 with a splitting about 0.06 mT. The HFS of $\mathbf{6}^{\cdot+}$ has a triplet 1:2:1 (0.085 mT) instead. The most complex HFS, built up of six different couplings, is contained in the spectrum of $\mathbf{7}^{\cdot+}$ (Fig. 2). Here there is differentiation between the 2,5- and 3,4-methyl groups on the pyrrole ring. Each resulting septet splits into two 1:3:3:1 quartets. This lowering of the local symmetry is distinct and was confirmed by the simulation (Table 2). Nevertheless, the magnitude of either small difference is counterintuitive. For the much bigger coupling of the 2,5-methyls, both of which are closer to the asymmetric $CH(CH_3)Ad$ substituent, the difference is only 0.01 mT, whereas for the more distant 3,4-methyls the difference amounts to 0.045 mT. We still seek an explanation. NMR spectroscopy gives separate signals for all five methyls in compound **7**. The INDO calculation of $\mathbf{7}^{\cdot+}$, on the other hand, produced no significant disturbance of the local C_{2v} symmetry of the pyrrole unit.

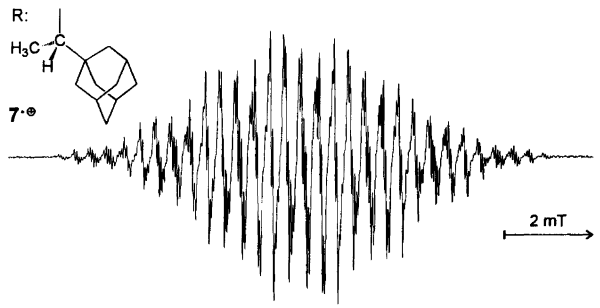


Fig. 2. EPR spectrum of primary radical cation $\mathbf{7}^{\cdot+}$ (1 mM solution of the parent compound in DCM–0.1 M $TBAPF_6$ at 233 K; parameters as given in Table 2).

The radical cations of **10**–**16** show EPR spectra that are in all respects very close each other and, in turn, to $\mathbf{5}^{\cdot+}$ (Table 2). No observable HFS splitting arising from the substituent aryl was detected. The coupling, if any, must be below the observed linewidth (ca. 0.03 mT). Therefore, the odd electron is not delocalised onto the phenyl substituent. This is unusual for radicals where an aryl group is adjacent to an atom in conjugation. It is a consequence of the double antisymmetry of SOMO in the (at the least local) C_{2v} point group.

The nitrophenyl pyrrole derivatives, **14**–**16**, which are also subject to one-electron reduction, can be converted electrolytically into the corresponding primary radical anions. The parameters of their EPR spectra are given in Table 3. In contrast with the radical cations of the same compounds, the odd electron in radical anions is localised solely on the nitrophenyl part and the radical anions decay much more slowly. Therefore, the nitrophenyl substituent and the pyrrole ring in **14**–**16** remain largely independent of each other during the process of primary oxidation and reduction. This conclusion, as well as the HFS parameters of radical anions, are in complete agreement with previous results for 2,5-dimethyl-1-nitrophenylpyrroles.[37]

The aminoaryl-substituted tetramethylpyrroles (**17**–**19**) did not give rise to even a weak EPR signal. The compounds were electrolysed *in situ* in the temperature range 183–253 K in concentrations of up to 20 mM. The oxidation potential was set little by little from that of the first peak, going over the second oxidation potential, up to +2.0 V (beyond the limit of the window). This negative result is in accordance with cyclic voltammetry. The behaviour might, in general, be explained by shifting of the HOMO from the pyrrole fragment to the aniline or 1,4-phenylendiamine system.

Table 3. EPR parameters of radical anions of 1-nitrophenyl-2,3,4,5-tetramethylpyrroles in DCM–0.1 M $TBAPF_6$.

Compound		a_o[a]	a_m[a]	a_p[a]	a_N[b]	g[c]
14	*p*-$C_6H_4NO_2$	0.338	0.106		1.002	2.00481
15	*m*-$C_6H_4NO_2$	0.341 0.332	0.109	0.412	0.993	2.00492
16	*o*-$C_6H_4NO_2$	0.324	0.105 0.113	0.409	0.964	2.00487

[a] a_o, a_m, a_p, are the proton coupling constants (mT) in positions *o*, *m*, *p* (referring to the NO_2-group). [b] a_N is the coupling constant (mT) of the nitrogen in the NO_2-group. [c] g is the *g*-factor.

Quantum chemical calculation. Observed hyperfine couplings of the EPR spectra unambiguously characterise the most important MO, the highest occupied molecular orbital (HOMO) in a monomeric pyrrole unit. The HOMO is antisymmetric with respect to either mirror plane (symmetric to the twofold axis, so spans a_2 in C_{2v}), the nitrogen nucleus being in the double node. It is, basically, the HOMO of (*Z*)-butadiene grossly concentrated on terminal carbons. This qualitative picture was confirmed by semiempirical and *ab initio* calculations. The HOMOs of 2,5-dimethylpyrrole and 2,3,4,5-tetramethylpyrrole are very similar to that of pyrrole itself. AM1 and MNDO methods predict that on going from pyrrole, through 2,5-dimethylpyrrole, to 2,3,4,5-tetramethylpyrrole: (1) the ionisation potential decreases and (2) HOMO becomes incrementally more delocalised over the methyl groups. This small delocalisation is much more significant for positions 2 and 5 than for 3 and 4. Both effects can be traced to an interaction between the HOMO of the unsubstituted pyrrole and an appropriate (a_2) filled combination of one or two pairs of methyl fragment orbitals. Interaction of any empty orbitals of the methyl groups is much less important since the orbitals are high-lying and experience poorer overlap with the pyrrole HOMO. That is why, in general, methyl substitution affects the ionisation potential more than the electron affinity and why representative splitting constants in radical cations reach much bigger values than in radical anions.

The splitting constants of $\mathbf{1}^{\cdot+}$, $\mathbf{2}^{\cdot+}$, $\mathbf{3}^{\cdot+}$, $\mathbf{5}^{\cdot+}$, $\mathbf{6}^{\cdot+}$, $\mathbf{7}^{\cdot+}$, $\mathbf{9}^{\cdot+}$ and $\mathbf{10}^{\cdot+}$ were estimated by INDO calculation. To keep the calculation simple, we averaged the three values of proton coupling obtained for each methyl group. For the coupling of Me (2,5) we obtained values between 1.66 and 1.72 mT (average −1.69) and for the coupling of Me (3,4) values between 0.42 and 0.45 mT (average 0.44). The INDO nitrogen splittings were from −0.28 to −0.32 mT (average 0.30). Since the nitrogen nucleus lies in either nodal plane of the SOMO, its non-zero coupling can be rationalised by π–σ[38] and π–π[39] spin polarisation with the former predominating. As in the case of isoindole radical cations[29] the π-spin population of p_z-AOs (−0.04 in HMO model according to McLachlan[39]) accounts for only a minor part of the observed coupling 0.42 mT. The major part originates from π–σ spin polarisation of two C(2,5)–N bonds originating from the large π-spin populations of p_z-AOs of the carbon atoms.

The splitting of methine or methylene adjacent to N depends[40] strongly on the torsion angle and INDO is able to match the observed couplings (around 0.07 mT) reasonably well. The methine or methylene splittings are due to the direct overlap of the hydrogen s-orbitals with the SOMO of the pyrrole radical cation. First, the hydrogens can and do reach the space out of the nodal planes. Second, the observed values, 0.055–0.085 mT, cannot be caused by π–σ spin polarisation simply because the hydrogen/s in question is/are separated by two σ-bonds from the nitrogen, which has only a very small π-spin population.

For the hypothetical $\mathbf{17}^{\cdot+}$, $\mathbf{18}^{\cdot+}$ and $\mathbf{19}^{\cdot+}$, INDO places the SOMO on the aniline part of the molecule, a fact which, in this study was only indirectly experimentally proven. For a similar tetraphenylpyrrole there is a EPR evidence[11] for this type of SOMO displacement.

Experimental

Electrochemistry. For cyclic voltammetry (with a built in generator Tacussel TP PRT), coulometry (with an integrator Tacussel IG 6-N), and the internal electrochemical generation of radicals, a Tacussel CPS 1000 potenciostat was used. The voltammetry and coulometry were performed for 0.1 mM solutions of the compound in question in dichloromethane (DCM) – or acetonitrile (AN) – 0.1 M $TBAPF_6$. The useful windows were −1.6 to +1.8 V in DCM and −2.0 to +2.1 V in AN. Oxygen was removed from the solutions by bubbling through nitrogen or argon dried with molecular sieves (Calsit 5, Lachema) and freed from residual O_2 by BTS catalyst (Fluka). The gas was saturated with vapour of the solvent used. Cyclic curves were recorded on a Pt disc (0.32 cm^2) sealed in a glass tube. For coulometry and the *in situ* generation a Pt gauze was used as the working and auxiliary electrodes, the latter separated by fritted glass (S4). All potentials are given vs. a saturated (NaCl instead of KCl) aqueous calomel electrode (SCE) that was separated from the measured solution by a salt bridge (non-aqueous) ending with a Luggin capillary. The potentials in DCM are somewhat inaccurate because of the *iR* drop that we did not succeed in compensating.

EPR spectroscopy. The spectra were measured on a Radiopan SE/X-2547 spectrometer (X band, 100 kHz modulation, resonator TM110 Radiopan RCX-661, microwave frequency meter Radiopan MCM 101, Radiopan NMR-magnetometer, and temperature unit Radiopan RPG-221). For calibration and the measurement of *g*-factor[21] an internal standard, 2,2,6,6-tetramethyl-4-oxopiperidin-1-oxyl (solution without O_2 in a thin capillary) was used. The values of the nitrogen HFS coupling constant and the *g*-factor for the standard were measured for water,[37] *N,N*-dimethylformamide,[21] and ethyl acetate ($a_N = 1.459$ mT; $g = 2.00626$) at ambient temperature. For the internal (*in situ*) electrochemical generation of radicals quartz cells,[41] modified for the resonator and the solvents, were used. The internal thickness of the flat end of the cell reaching into the EPR cavity was optimised for DCM 1.0 mm and for AN 0.5 mm (6 mm internal width).

NMR spectroscopy. ^{1}H NMR spectra were recorded on a Tesla BS 567 100 MHz instrument in the solvent indicated ($CDCl_3$ or CCl_4), chemical shifts (δ) being given in ppm downfield with respect to Me_4Si.

Chemicals. Acetonitrile (BDH) was purified using N_2O_4 and CaH_2 according to combined procedures described by Coetzee[42] and Sherman.[43] The water content (Fischer) was 1.5–3.0 mM.

Dichloromethane (Lachema) was initially dried over P_4O_{10}. Further drying, first with fresh P_4O_{10} (10 g l^{-1}) and then verification with CaH_2 (5 g l^{-1}) was carried out. The water content (Fischer) was 1.0–1.5 mM.

$TBAPF_6$ was prepared from concentrated water solutions of TBABr (from *n*-butylamine and tri-*n*-butylamine, m.p. 100–102 °C) and HPF_6 (Fluka), dried at 80 °C *in vacuo*, and twice crystallised from ethyl acetate, and dried *in vacuo*, m.p. 251–253 °C, lit.[44] 239–241 °C.

3,4-Dimethyl-2,5-hexanedione (dione) was prepared according to a modified[45] procedure of Kharash,[46] *meso*:*racemic* ca. 1:1 by ^{1}H NMR spectroscopy.

2,3,4,5-Tetramethylpyrrole (**1**). The compound was prepared according to Whippl and Hinmann[47,48] from the dione and gaseous ammonia in benzene in the presence of a catalytic amount (a few drops) of 37% HCl. It was twice recrystallised from ethanol and sublimed *in vacuo*, m.p. 112 °C, lit.[48] 109 °C. ^{1}H NMR (CCl_4): d 1.74 (s, 6 H, α-CH_3), 1.98 (s, 6 H, β-CH_3), 6.82 (s, ^{1}H, NH).

1,2,3,4,5-Pentamethylpyrrole (**2**). The compound was prepared[48] from the dione and 30% aqueous methylamine without solvent in the presence of a catalytic amount of 37% HCl. It was twice recrystallised from ethanol and sublimed, m.p. 71 °C, lit. [48] 70 °C. ^{1}H NMR (CCl_4): δ 1.75 (s, 6 H, α-CH_3), 1.97 (s, 6 H, β-CH_3), 3.22 (s, 3 H, CH_3).

1-Isopropyl-2,3,4,5-tetramethylpyrrole (**3**). The compound was prepared[49] from the dione and isopropylamine in toluene under catalysis by acetic acid, the product water being removed by azeotropic distillation. After solvent removal, the liquid compound was distilled through a Vigreux column at ambient pressure, b.p. 85–89 °C (ambient pressure). ^{1}H NMR ($CDCl_3$): δ 0.95 [s, 6 H, $(CH_3)_2CH$], 1.10 (s, 1 H, CH), 1.81 (s, 6 H, α-CH_3), 1.98 (s, 6 H, CH_3). Anal: C, H, N, O.

1-Isobutyl-2,3,4,5-tetramethylpyrrole (**4**). The compound was prepared as described for **3** using isobutylamine, b.p. 76–78 °C (1.5 kPa). ^{1}H NMR ($CDCl_3$): δ 0.82 [d, 6 H, $(CH_3)_2CH$, $J = 6.5$ Hz], 1.15 (m, 1 H, CH,), 1.86 (s, 6 H, CH_3), 2.03 (s, 6 H, CH_3), 3.42 (d, 2 H, CH_2, $J =$ 7.3 Hz). Anal: C, H, N, O.

1-tert-butyl-2,3,4,5-tetramethylpyrrole (**5**). The compound was prepared in toluene from the dione and *tert*-butylamine with $TiCl_4$.[49] After removal of the TiO_2 and the solvent, the liquid compound was distilled through a Vigreux column, b.p. 101–104 °C (1.5 kPa). ^{1}H NMR ($CDCl_3$): δ 1.66 (s, 9 H, *t*-Bu), 1.92 (s, 6 H, CH_3), 2.33 (s, 6 H, CH_3). Anal: C, H, N, O.

1-Adamantylmethyl-2,3,4,5-tetramethylpyrrole (**6**). From the dione and adamantylmethylamine in ethanol with acetic acid as a catalyst. On cooling, the crude product crystallised from the solution. The dried product was sublimed *in vacuo*, m.p. 105–106 °C. ^{1}H NMR ($CDCl_3$): δ 1.57 and 1.67 (m, 15 H, adamantyl), 1.94 (s, 6 H, CH_3), 2.12 (s, 6 H, CH_3), 3.42 (s, 2 H, CH_2). Anal: C, H, N, O.

1-Adamantylethyl-2,3,4,5-tetramethylpyrrole (**7**). From the dione and 1-adamantylethylamine in toluene with acetic acid as a catalyst, the product water being removed by azeotropic distillation. The product was crystallised from methanol, m.p. 77–78 °C. ^{1}H NMR ($CDCl_3$): δ 1.45 (d, 3 H, CH_3, $J = 7.5$ Hz), 1.63 and 2.01 (m, adamantyl), 1.91 (s, 3 H, CH_3), 1.93 (s, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 2.24 (s, 3 H, CH_3), 3.86 (q, 1 H, CH, $J = 7.5$ Hz). Anal: C, H, N, O.

1-Cyclohexyl-2,3,4,5-tetramethylpyrrole (**8**). From the dione and cyclohexylamine without solvent under catalysis by HCl. The product was crystallised from methanol and sublimed *in vacuo*, m.p. 37–39 °C. ^{1}H NMR ($CDCl_3$), d 1.61 (m, 11 H, cyclohexyl), 1.92 (s, 6 H, α-CH_3), 2.19 (s, 6 H, β-CH_3). Anal: C, H, N, O.

1-Benzyl-2,3,4,5-tetramethylpyrrole (**9**). From the dione and benzylamine without solvent under catalysis by HCl. The product was twice crystallised from methanol and sublimed *in vacuo*, m.p. 28–29 °C, lit.[50] 21–21.5 °C. ^{1}H NMR ($CDCl_3$): δ 1.97 (s, 6 H, CH_3), 2.04 (s, 6 H, CH_3), 4.96 (s, 2 H, CH_2), 7.12 (m, 5 H, phenyl).

1-Phenyl-2,3,4,5-tetramethylpyrrole (**10**). From the dione and aniline in methanol under catalysis by few drops of 37% HCl. After solvent removal, the liquid compound was distilled through a Vigreux column, b.p. 77–80 °C (1.5 kPa). ^{1}H NMR ($CDCl_3$): δ 1.96 (s, 6 H, CH_3), 2.00 (s, 6 H, CH_3), 7.30 (m, 5 H, Ph). Anal: C, H, N, O.

1-(4-Tolyl)-2,3,4,5-tetramethylpyrrole (**11**). From the dione and 4-toluidine without solvent under catalysis by HCl. The product was twice crystallised from ethanol and sublimed *in vacuo*, m.p. 115 °C. ^{1}H NMR (CCl_4): δ 1.82 (s, 12 H, CH_3), 2.32 (s, 3 H, CH_3), 6.98 (m, 4 H, C_6H_4). Anal: C, H, N, O.

1-(4-Cyanophenyl)-2,3,4,5-tetramethylpyrrole (**12**). From the dione and 4-aminobenzonitrile in methanol with HCl as the catalyst. With partial solvent evaporation the crude product crystallised. The dried product was sublimed *in vacuo*, m.p. 114–115 °C. ^{1}H NMR ($CDCl_3$): δ 1.95 (s, 12 H, CH_3), 7.55 (m, 4 H, C_6H_4). Anal: C, H, N, O.

1-(4-Bromophenyl)-2,3,4,5-tetramethylpyrrole (**13**). The compound was prepared using 4-bromoaniline as described for **12**. The crude product was twice crystallised from methanol, m.p. 134–135 °C. ^{1}H NMR ($CDCl_3$): δ 1.94 (s, 6 H, CH_3), 2.01 (s, 6 H, CH_3), 7.52 (m, 4 H, C_6H_4). Anal: C, H, Br, N, O.

1-(4-Nitrophenyl)-2,3,4,5-tetramethylpyrrole (**14**). From the dione and 4-nitroaniline without solvent under catalysis by HCl. The crude product was twice crystallised from Et_2O–pentane (7:3), m.p. 122 °C. ^{1}H NMR (CCl_4): δ 1.85 (s, 6 H, α-CH_3), 1,90 (s, 6 H, β-CH_3), 7.73 (m, 4 H, C_6H_4). Anal: C, H, N, O.

1-(3-Nitrophenyl)-2,3,4,5-tetramethylpyrrole (**15**). From the dione and 3-nitroaniline without solvent under catalysis by HCl. The crude product was twice crystallised from dichloromethane, m.p. 80 °C. ^{1}H NMR (CCl_4): δ 1.85 (s, 6 H, α-CH_3), 1.90 (s, 6 H, β-CH_3), 7.81 (m, 4 H, C_6H_4). Anal: C, H, N, O.

1-(2-Nitrophenyl)-2,3,4,5-tetramethylpyrrole (**16**). From the dione and 2-nitroaniline without solvent under catalysis by HCl. Since the conversion did not exceed 60% the reaction mixture was column chromatographed [dichloromethane–SiO_2 (100–250 μm)]. The crude product was twice crystallised from dichloromethane, m.p. 120 °C. ^{1}H NMR (CCl_4): δ 1.77 (s, 6 H, α-CH_3), 1.84 (s, 6 H, β-CH_3), 7.52 (m, 4 H, C_6H_4). Anal: C, H, N, O.

1-(4-Aminophenyl)-2,3,4,5-tetramethylpyrrole (**17**). 1-(4-Acetamidophenyl)-2,3,4,5-tetramethylpyrrole (prepared from the dione and 4-aminoacetanilide without solvent under catalysis by HCl) was deacetylatedwith KOH in ethanol. The crude product was twice crystallised from methanol, m.p. 166 °C. ^{1}H NMR ($CDCl_3$): δ 1.87 (s, 6 H, α-CH_3), 1.92 (s, 6 H, β-CH_3), 3.67 (s, 2 H, NH_2), 6.90 (m, 4 H, C_6H_4). Anal: C, H, N, O.

1-(4-Dimethylaminophenyl)-2,3,4,5-tetramethylpyrrole (**18**). From the dione and 4-amino-*N,N*-dimethylaniline without solvent under catalysis by HCl. The crude product was twice crystallised from methanol, m.p. 136 °C. ^{1}H NMR (CCl_4): δ 1.82 (s, 12 H, CH_3), 2.90 (s, 6 H, CH_3), 6.71 (m, 4 H, C_6H_4). Anal: C, H, N, O.

1-(4-Diethylaminophenyl)-2,3,4,5-tetramethylpyrrole (**19**). From the dione and 4-amino-*N,N*-diethylaniline without solvent under catalysis by HCl. The crude product was twice crystallised from methanol, m.p. 99 °C. ^{1}H NMR (CCl_4): δ 1.15 (t, 4 H, CH_2), 1.80 (s, 12 H, CH_3), 3.31 (q, 6 H, CH_3), 6.67 (m, 4 H, C_6H_4). Anal: C, H, N, O.

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