PROPERTIES OF ELECTROCHEMICALLY GENERATED PRIMARY ANION RADICALS OF 2,5-DIMETHYL-1-NITROPHENYLPYRROLES

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The first step of electrochemical reduction of 2,5-dimethyl-1-nitrophenylpyrroles on a platinum electrode in anhydrous acetonitrile consists in an one-electron process producing relatively stable anion radicals. The prediction based on HMO calculations concerning an almost complete localization of the LFMO in the nitrophenyl part of the studied molecules is fully confirmed by means of EPR spectroscopy. Magnitude of the found proton splitting constants is very close to the values found for anion radical of nitrobenzene. The splitting by nucleus of nitrogen atom of pyrrole cycle can be explained exclusively by the mechanism of $\pi - \sigma$ spin polarization of σ C—N bond and by the spin population at the carbon atom. The EPR method has also been used for following the kinetics of decomposition of anion radicals of the molecules studied.

Easy oxidability and difficult reducibility of pyrrole derivatives resembles the corresponding redox properties of aromatic amines more than those of pyridine derivatives. The presence of strong electron-acceptor nitro group in benzene nucleus of 2,5-dimethyl-1-nitrophenylpyrroles, however, results in relatively easy reducibility of these compounds.

The aim of this work is to elucidate mutual relations between electronic structure, electrochemical reduction, stability of the primary anion radicals, and hyperfine structure of their EPR spectra in a set of 2,5-dimethyl-1-nitrophenylpyrroles.
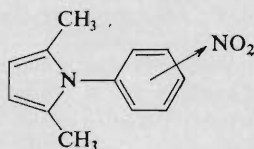
I, 4-nitrophenyl-
II, 3-nitrophenyl-
III, 2-nitrophenyl-

EXPERIMENTAL

Reagents. Acetonitrile (MeCN) was purified by the method described by Coetzee and coworkers[1]. Tetraethylammonium petchlorate (TEAP) was prepared by neutralization of 10% aqueous tetraethylammonium hydroxide (*p.a.*, Lachema) with perchloric acid. The salt was twice crystal-

lized and dried in vacuum at 80°C 24 h. 2,5-Dimethyl-1-(4-nitrophenyl)pyrrole (*I*), 2,5-dimethyl--1-(3-nitrophenyl)pyrrole (*II*), and 2,5-dimethyl-1-(2-nitrophenyl)pyrrole (*III*) were synthezized from 2,5-hexanedione and 4-, 3-, and 2-nitroaniline, respectively, according to the method by Hazelwood and coworkers[2,3]. The products were separated by column chromatography using silica gel and light petroleum, their purity was checked by TLC (Silufol UV 254, Kavalier). The compounds *I*, *II*, and *III* melted at 149°C, 86°C, and 93°C, respectively (the corresponding literature data were not found).

Cyclic voltametry. In this method we used 1 mM solutions of the studied compounds in anhydrous acetonitrile containing 0·1M tetraethylammonium perchlorate. Before measurements the solutions were rid of oxygen by bubbling through dry oxygen-free nitrogen (the latter gas was obtained from commercial nitrogen by a passage through a column ($\varnothing$ 30 mm, length 80 cm) packed with BTS catalyst (Fluka) and through two columns of the same size packed with molecular sieve Calsit 5 (Lachema). Before introduction in the vessel the purified nitrogen was saturated with acetonitrile vapours in a washing bottle. The working electrode was a platinum disc (area $0·30$ cm^2) sealed in a glass tube. The reference electrode was an aqueous calomel electrode with saturated sodium chloride solution separated by fritted glass from fluid coupling with solution of the basic electrolyte and terminated with the Luggin capillary. A platinum wire gauze separated from the area of the working electrode by fritted glass (S 4) served as auxiliary electrode. The measurements were carried out with a potentiostat CPS 1000 (Tacussel) with inner generator of saw tooth voltage TP PRT (Tacussel). The dependence of current on voltage was recorded by means of an X—Y recorder ZSK (Rhode-Schwarz).

EPR *Spectroscopy.* The EPR spectra were measured with an ER 9 apparatus (Zeiss, Jena) (X band, 100 kHz modulation, rectangular resonator H_{102}).

Measurement of splitting constants. The magnetic field scale was calibrated by recording spectrum of standard before and after each spectrum. Each spectrum was recorded several times, and the data obtained were used for calculation of arithmetical mean and probable error. Aqueous 1 mM solution of 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl was used as the standard, its splitting constant of nitrogen nucleus being $1·620 \pm 0·002$ mT. This value was determined with the use of 1,4-benzosemiquinone[4,5] ($a^H = 0·2368 \pm 0·0001$ mT) or aqueous solution of Fremy's salt[5,6] ($a^H = 1·3091 \pm 0·0003$ mT). The measured values were $1·620 \pm 0·002$ mT and $1·619 \pm \pm 0·001$ mT in the two cases, respectively.

Measurement of g-*factor.* For this measurement the spectrum was recorded several times simultaneously with that of the standard, *i.e.* 1 mM aqueous solution of 2,2,6,6-tetramethyl--4-oxopiperidine-1-oxyl sealed in a polyethylene capillary (outside diameter about 0·5 mm) inserted in the cell containing the measured solution. The value $2·00586 \pm 0·00001$ was obtained for the *g* factor of the standard by means of aqueous–ethanolic solution of 1,4-benzosemiquinone ($g = 2·00483$) (ref.[5,7]). Eq. (*I*) was used for calculation of the *g* factor.

$$g_x = g_s(1 + 14·00(g_s/v)\,\Delta H)\,, \tag{1}$$

where g_x and g_s are the *g* factors of the sample and standard, respectively, v means frequency of the micro-wave radiation in MHz, and $\Delta H = H_s - H_x$ means the difference between centres of spectra of the sample and the standard in mT.

Internal electrochemical generation of radicals. For production of the ion radicals to be measured by EPR spectroscopy we used the method of internal electrochemical generation[8]. For the measurements at room temperature we used the electrolytic vessel (Zeiss, Jena; accessory of the ER 9 spectrometer) modified for three-electrodes connection and application of the plati-

num working electrode (wire or gauze). Aqueous calomel electrode with saturated sodium chloride solution served as the reference electrode. The fluid coupling of this electrode was terminated with a capillary reaching to the working electrode. The other conditions of the generation were the same as those used in the cyclic voltametry.

Following of disappearance of radicals. Stability of the electrochemically generated ion radicals was followed quantitatively by means of EPR spectroscopy. The radical was accumulated in the vessel for internal electrochemical generation located in the resonator cavity, then the current was disconnected, and time dependence of decay of the EPR signal (part of spectrum) was followed be repeated recording by means of the recorder of spectrometer. The electrolysis was carried out potentiostatically at a potential of the working electrode by 100 mV more negative than the E_p value obtained by cyclic voltametry. With the ion radicals having long half-lives of decay it was found that, with respect to accuracy of the measurement, the signal intensity changes due to diffusion are negligible. For relative estimation of reactivity of the radicals it is necessary to carry out the measurements at the same experimental conditions and use fresh solvent.

Simulation of EPR *spectra.* The spectra were interpreted by the method of fitting the experimental spectra with the simulated ones. The spectra calculated with a computer Minsk 22 (the respective program was granted by Dr J. Pilař, Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague) and recorded on punched tape were converted with a digital- -to-analog converter constructed in our Department by Dr J. Kunčík.

Quantum-chemical calculations. The calculations were carried out in the Hückel molecular orbital approximation (HMO) using a standard program granted by Dr R. Zahradník (Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Prague). The calculations were carried out with the computer 22. The program was extended for calculation of spin populations by the procedure introduced by McLachlan[9] (with the parameter $\lambda = 1\cdot2$). The Coulombic integral of the atom X and the resonance integral of the bond X—Y are defined by the relations $\alpha_X = \alpha_C + h_X\beta_{CC}$ and $\beta_{XY} = k_{XY}\beta_{CC}$, respectively.

Energy of the j-th MO is defined by the relation $\varepsilon_j = \alpha_C - m_j\beta_{CC}$. The following parameters were used for nitro group[10]: $h_N = 2\cdot2$, $h_O = 1\cdot4$, $k_{CN} = 1\cdot2$, $k_{NO} = 1\cdot67$. For nitrogen atom in pyrrole cycle it was used[11]: $h_N = 1\cdot5$, $k_{CN} = 0\cdot8$. Effect of methyl group was involved by application of heteroatomic or hyperconjugation models[11] (influence of all the parameters which characterize the atoms of the pyrrole section of the molecule is negligible with respect to distribution of spin populations in anion radicals of the studied compounds).

RESULTS

Electrochemical reduction. The electrochemical reduction of the compounds *I, II,* and *III* was followed by cyclic voltametry. The potentials corresponding to the maximum value of current of the first cathodic peak and the corresponding values of the voltametric constants $i_p c^{-1/2} v^{-1/2}$ are given in Table I.

The cyclic polarograms of the compounds *I, II, III,* and nitrobenzene have the same character: at about $-1\cdot1$ V they exhibit a cathodic peak and the thereto corresponding anodic peak of the same height. Comparison of the voltametric constants of the compounds *I, II, III* (Table I) with that of nitrobenzene (which accepts one electron during the first step of reduction in anhydrous medium) reveals that the

TABLE I

Characteristics of electrochemical reduction of 2,5-dimethyl-1-nitrophenylpyrroles (1 mM solutions of the compounds in anhydrous $MeCN/0\cdot1M$-TEAP; the Pt electrode polarized at a speed $0\cdot2\ Vs^{-1}$)

Compound	Pyrroles	$E_p{}^a$	$i_p c^{-1} v^{-1/2}$ [b]
I	4-nitrophenyl-	$-1\cdot13$	$1\cdot31$
II	3-nitrophenyl-	$-1\cdot06$	$1\cdot30$
III	2-nitrophenyl-	$-1\cdot20$	$1\cdot37$
	nitrobenzene	$-1\cdot15$	$1\cdot28$

[a] The potential corresponding to the maximum value of current of the first cathodic peak in V againsts aqueous calomel electrode (with saturated NaCl solution); [b] the voltametric constants; i_p means the value of current corresponding to the potential E_p (A cm^{-2}); c means concentration (mol l^{-1}); v means velocity of polarization of the working electrode (C s^{-1}).
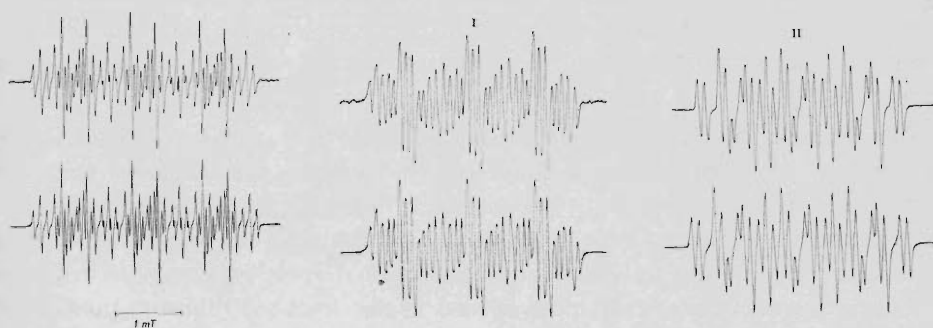

FIG. 1

EPR spectra of anion radicals of 2,5-dimethyl-1-(4-nitrophenyl)pyrrole (I, top middle), 2,5-dimethyl-1-(3-nitrophenyl)pyrrole (II, top right), 2,5-dimethyl-1-(2-nitrophenyl)pyrrole (III, bottom) and nitrobenzene (top left). The upper spectrum was obtained experimentally (1 mM solution of the parent substance in MeCN/0·1M-TEAP before electrolysis; room temperature); always below are given the simulated spectra (the Lorentz line shape; parameters of spectra are given in Table II)
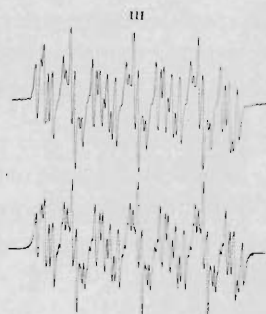
2,5-dimethyl-1-nitrophenylpyrroles undergo one-electron reduction, too. In analogy to electrochemical behaviour of nitrobenzene the cyclic voltametry of the compounds *I, II, III* indicates formation of a relatively stable redox system composed of a neutral depolarizer molecule and the corresponding primary anion radiacl.

The other reduction steps of the given compounds were not investigated.

EPR *Spectroscopy*. Using the method of internal electrochemical generation of radicals at room temperature, we measured the EPR spectra of the primary anion radicals of the compounds *I, II, III*, and nitrobenzene. The measured spectra are given in Fig. 1. The simulated spectra are given along with the experimental ones. Values of the splitting constants and the line width for which the simulated and experimental spectra showed the best agreement are given in Table II along with the measured values of g factors.

All the given spectra agree better with the Lorentz line shape than with the Gaussian shape. The well-resolved spectrum of nitrobenzene anion radical allowed to evaluate the splitting constants direct from the experimental spectrum. These splitting constants agree quite well with the literature[10,12] data given for nitrobenzene anion radical in acetonitrile.

With the anion radicals of the compounds *I, II*, and *III* it is impossible to obtain a better visual agreement than that given in Fig. 1 between the simulated and experimental spectra by a change of parameters given in Table II in the case of pure Lorentz line shape.

No splitting by nucleus of nitrogen atom of the pyrrole cycle can be seen in the measured spectrum of the anion radical of *II*. However, the simulated spectrum depends strongly on magnitude of the splitting constant $s_{pyrrole}^N$. When using a greater value of the line width and neglecting the nitrogen triplet, it was impossible to reach agreement between the simulated and experimental spectra (strong discrepances in lines intensities or greater number of lines in the simulated spectrum than in the experimental one).

Whereas with the anion radical of *III* the shape of the simulated spectrum greatly depends on the relatively small difference of splitting constants of the protons at m-positions (with respect to nitro group), and determination of their non-equivalence is thus reliable, with the anion radical of *II* the non-equivalence of a_0^H is only suggested on the basis of not very large changes in the lines intensities.

Kinetics of disappearance of radicals of the compounds I, II, and III. This kinetics was followed by the time dependence of decrease of height of several chosen spectral lines. The measurement was carried out at room temperature. All the three kinetics agree far better with presumption of the first order with respect to concentration of the anion radical than with presumption of the second order reaction. Using the former presumption, the following half-lives of decomposition of the anion radicals of *I, II*, and *III* were found, respectively: 2·9 min, $2·2 . 10^2$ min, and 35 min.

DISCUSSION

Identical course of the first step of electrochemical reduction of the compounds I, II, III, and nitrobenzene agrees very well with the HMO theory. The lowest free molecular orbital (LFMO) of these compounds has the energy $m_{LFMO} = 0.416$ (I), 0.399 (II), 0.413 (III), 0.398 (nitrobenzene). Small differences between these HMO-approximated values m_{LFMO} agree well with the close values E_p (Table I). Furthermore, the LFMO of the compounds I, II, and III is considerably localized in the nitrophenyl

TABLE II

Parameters of EPR spectra and distribution of spin populations in anion radicals of 2,5-dimethyl-
-1-nitrophenylpyrroles. Concentration of the parent substance before electrolysis; 1 mM in MeCN/
/0.1M-TEAP; for assignement of the splitting constants see the text; in brackets are given the
calculated values of π electron spin populations ϱ^{π} (for the proton splitting constants a^H the
values ϱ^{π} are given at the C atom to which the proton is bound)

a	I 4-nitro-phenyl-	II 3-nitro-phenyl-	III 2-nitro-phenyl-	nitro-benzene
a_0^H	0.343 (0.141)	0.336 (0.137) 0.346 (0.149)[b]	0.328 (0.151)	0.345 (0.141)
a_m^H	0.108 (−0.049)	0.107 (−0.047)	0.108 (−0.039)[b] 0.118 (−0.051)	0.111 (−0.048)
a_p^H	—	0.408 (0.167)	0.406 (0.168)	0.389 (0.170)
$a_{NO_2}^N$	0.994	0.990	0.952	1.108
$a_{pyrrole}^N$ c	0.081 (0.000) (0.155)	0.017 (−0.002) (−0.045)	0.070 (−0.001) (0.122)	—
$1/2\,\Delta H_{1/2}$ g-factor	0.031 2.00494	0.023 2.00500	0.032 2.00512	0.018 2.00500

^{a} a_{μ}^X is the absolute value of the splitting constant of nucleus of the atom X in mT; μ denotes position of the atom X (positions of the protons at the nitrophenyl part of the molecule are denoted with the prefixes o-, m-, p-, with respect to nitro group); $1/2\,\Delta H_{1/2}$ is half-width of non--derived line at its half-height in mT; ^{b} the value ϱ^{π} belongs to the atom C located nearer to 2,5-dimethylpyrrol-1-yl; ^{c} the above-given ϱ^{π} value belongs to the N atom of pyrrole cycle, the below-given ϱ^{π} value belongs to the C atom to which 2,5-dimethylpyrrol-1-yl is bound.

ection of the molecules, and the expansion coefficients of p_z AO have very similar magnitudes to those of LFMO of nitrobenzene. The electron in the LFMO of the compound *I* has the highest probability of occurrence in the pyrrole section of the molecule. However, even in this case more than 96% of the electron is localized (according to the HMO model) in the nitrophenyl group.

Correctness of the prediction of HMO theory concerning localization of the un-paired electron in the nitrophenyl section of the molecule is obviously supported by the found values of the splitting constants of HFS EPR spectra of the anion radicals of *I*, *II*, and *III* (Table II) which are very close to those found for the nitro-benzene anion radical. The calculated values of π electron spin populations ϱ^π of p_z AO of the carbon atoms to which the protons in nitrophenyl are bound are given in Table II. On the basis of the McConnell theory[14,13] and the given ϱ^π values the splitting constants could also be assigned to the individual protons (Table II). This assignment follows (presuming the unpaired electron to be localized in nitro-phenyl group) already from analogy with the anion radical of nitrobenzene, where it was unambiguously carried out by the method of specific deuteration[15]. Of course, the assignement of the little differing splitting constants of the individual protons in *ortho* position (with respect to nitro group) of the compound *II* and the protons in *meta* position (with respect to nitro group) in the compound *III* is little reliable on the basis of ϱ^π values.

From the HMO calculations it follows that in the anion radicals of *I* and *III* the unpaired electron is located more probably in the pyrrole section of the molecule. In connection therewith it is possible to explain broadening of EPR spectral line of these anion radicals (as compared with that of *II* or nitrobenzene) by interactions with the protons of 2,5-dimethylpyrrol-1-yl. The spin populations in this part of the molecules of anion radicals of *I* and *III* reach the values about $1 \cdot 10^{-3}$.

Comparison of experimental values of the splitting constants a^H (Table II) with the calculated values ϱ^π (according to McLachlan[16]) and with values of squares of the expansion coefficients in the LFMO shows that (especially with respect to magnitude of the splitting constant of the proton in *meta* position to nitro group) the values ϱ^π correspond substantially better to real spin distribution in the anion radicals of *I*, *II*, and *III*.

Differences between the splitting constants of nitrogen nucleus in nitro group $a^N_{NO_2}$ are so small that their discussion using the spin populations at N and O atoms of nitro group is not justifiable with respect to accuracy of the Karplus–Fraenkel theory[15] and McLachlan approximation of the ϱ^π values. The comparable experi-mental values $a^N_{NO_2}$ only confirm the theoretical presumption concerning close distri-bution of ϱ^π in nitrophenyl sections of molecules of anion radicals of *I*, *II*, and *III*.

With respect to the above-discussed localization of the LFMO of the molecules *I*, *II* and *III* it is noteworthy that splitting by nitrogen nucleus of pyrrole cycle was found experimentally (Table II). The calculated ϱ^π values pertaining to N atom of the pyrrole

cycle are given in the same Table (the calculated values of squares of the expansion coefficients in the LFMO are also negligibly small for this atom). Obviously these values cannot explain quantitatively the magnitude of the splitting constants a_{pyrr}^N. As the ϱ^π values are practically zero also at $C_{(2)}$ and $C_{(5)}$ atoms of pyrrole cycle, the magnitude of a_{pyrr}^N can be quantitatively explained within the framework of the Karplus–Fraenkel theory[15] only by the $\pi - \sigma$ spin polarization of the C—N bond due to non-zero value of π electron spin population at C atom of nitrophenyl. The found values a_{pyrr}^N for the individual anion radicals of I, II, and III, really, are proportional to values of spin populations at the carbon atom to which 2,5-dimethyl-pyrrol-1-yl is bound (Table II). Due to the above-discussed similarity of the LFMO of the studied compounds with that of nitrobenzene the a_{pyrr}^N constant of the individual anion radicals is proportional to splitting constant of the corresponding proton in the anion radical of nitrobenzene.

Planarity of the compound III cannot be pressumed due to sterical reasons. As the splitting constant $a_{NO_2}^N$ of anion radical of this compound is close to the values of anion radicals of I and II, it is justifiable to presume that the planes of benzene ring and 2,5-dimethylpyrrole section are mutually deviated. If nitro group were deviated, an increase in $a_{NO_2}^N$ value could be expected[10]. Deviation of the pyrrole ring, however, cannot affect the effectiveness of $\pi - \sigma$ spin polarization of σ bond $C_{benzene} - N_{pyrrole}$ due to its axial symmetry.

The Karplus–Fraenkel equation[15] assumes a simple form (2) for the splitting constant of the N nucleus of pyrrole cycle in anion radicals of 2,5-dimethyl-1-nitro-phenylpyrroles.

$$a_{pyrr}^N = Q_{C-N}^N \varrho_C^\pi, \qquad (2)$$

where Q_{C-N}^N is a constant expressing the magnitude of $\pi - \sigma$ spin polarization of σ bond C—N by the spin population ϱ_C^π at the C atom. As theoretical prediction of small values of spin populations is frequently loaded with a greater relative error, it is more justifiable to consider only the data for anion radicals of I and III when calculating the average absolute value of the parameter Q_{C-N}^N. The absolute value Q_{C-N}^N obtained in this way is 0.55 mT which agrees well with the value found for cation radicals of tetramethylisoindoles[17].

It is interesting that the rate constant value of decomposition of the anion radicals decreases in the same order (*i.e.* I, III, II) as the absolute value of splitting constant of nitrogen nucleus of pyrrole cycle a_{pyrr}^N and the abovementioned quantities parallel thereto. This fact is obviously connected with the magnitude of mutual influence of pyrrole and nitrophenyl sections of the molecule decreasing in the given order. If the presumption is justifiable that the first phase of decomposition of the anion radicals takes place at nitro group, then it is noteworthy that position of 2,5-dimethyl-pyrrol-1-yl (which is *de facto* unsubstantial for the shape of the LFMO and distribution of electron densities at nitro group in the anion radical) plays an important

part in the reactivity of the respective anion radical. This conclusion represents, besides others, evidence of the fact that predictions and explanations concerning dynamic properties of molecules are more exacting than those concerning static properties.

From electrochemical study of oxidation[18] and HMO approximation of the HOMO of *I*, *II*, and *III* it follows that the electron which is withdrawn from the molecule in the first step of the oxidation is localized in the pyrrole section of the molecule. If the 2,5-dimethyl-1-nitrophenylpyrrole molecules are viewed as a combination of an easily oxidable pyrrole cycle and an easily reducible nitrobenzene, then it is obvious that these molecular sections retain high extent of their autonomies during the process of primary electrochemical oxidation and reduction.

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