PROPERTIES OF ELECTROCHEMICALLY GENERATED PRIMARY CATIONRADICALS OF PHENYL- AND 2-(4-TOLYL)-1,3,4,7--TETRAMETHYLISOINDOLES

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The first step of electrochemical oxidation of 2-phenyl- and 2-(4-tolyl)-1,3,4,7-tetramethylisoindoles in anhydrous acetonitrile produces relatively stable cationradicals which have been studied by means of EPR spectroscopy using the method of internal electrochemical generation of radicals under reduced temperature. The same electrochemical behaviour of the both studied derivatives and identical EPR spectra of their cationradicals can be explained within the Hückel MO method The largest contribution to the magnitude of splitting constant of nitrogen nucleus is due to π-σ-spin polarization of C—N bonds caused by high spin abundance of p_z-AO of carbon atoms. Half-life of decomposition of the studied cationradicals is 4 min at −30°C.

Zweig and coworkers[1,2] studied electrochemiluminescence of phenylsubstituted isoindoles and proved (with the use of cyclic voltametry) that electrode oxidation of these compounds produced cationradicals whose decomposition half-life was above 20 s. These radicals were not studied by the EPR method[1,2].

The aim of the present paper is to elucidate the mutual relations between electron structure, electrochemical oxidation, stability of the primary cationradicals and hyperfine structure of their EPR spectra in the case of 2-phenyl- (*I*) and 2-(4-tolyl)-1,3,4,7-tetramethylisoindole (*II*).

EXPERIMENTAL

Reagents

2-Phenyl-1,3,4,7-tetramethylisoindole (*I*) was synthetized according to Bender and Bonnett[3] by reaction of acetonylacetone with 1-phenyl-2,5-dimethylpyrrole (for preparation of the latter see below); m. p. 144—146°C *in vacuo* (ref.[3] m. p. 142—145°C).

2-(4-Tolyl)-1,3,4,7-tetramethylisoindole (*II*) was synthetized in similar way as the compound *I* from acetonylacetone and 1-(4-tolyl)-2,5-dimethylpyrrole; m. p. 149—151°C *in vacuo* (there are no data about this substance in literature).

1-Phenyl-2,5-dimethylpyrrole was synthetized according to Knorr[4] from diethyl diacetylsuccinate (which was synthetized according to Knorr[5]) and aniline.

1-(4-Tolyl)-2,5-dimethylpyrrole was synthetized in the same way as 1-phenyl-2,5-dimethylpyrrole from diethyl diacetylsuccinate and 4-toluidine.

The compounds *I* an *II* are extremely oxidable in air. Therefore, they had to be kept cold in evacuated ampoules, and were vacuum resublimed immediately before measurement.

The compounds *I* and *II* were studied in anhydrous acetonitrile in the presence of 0·1M tetraethylammonium perchlorate (TEAP). The conditions under which the compounds were studied by cyclic voltametry, purification of acetonitrile, and preparation and purification of TEAP are described elsewhere[6].

The EPR spectra were measured with an ER 9 apparatus (Zeiss, Jena; X-band; 100 kH modulation; rectangular resonator H_{102}) using a special vessel[7] for internal electrochemical generation of radicals in the resonator cavity at reduced temperature. A Pt wire gauze (in three-electrode connexion) was used as the anode in generation of cationradicals. The other conditions for the generation of the cationradicals were the same as those for cyclic voltametry.

Procedure of measurement of splitting constants, *g*-factor, simulation of EPR spectra and following of kinetics of decomposition of the radicals was similar to that used in the study[6] of anionradicals of 2,5-dimethyl-1-nitrophenylpyrroles. The magnetic field was calibrated with the use of 2·5 mM solution of 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl in anhydrous dimethylformamide free of oxygen; its splitting constant of nitrogen nucleus $a^N = 1{\cdot}465 \pm 0{\cdot}002$ mT, its *g*-factor $g = 2{\cdot}00607 \pm 0{\cdot}00002$. For determination of the parameters we used the procedures and standards described elsewhere[6].

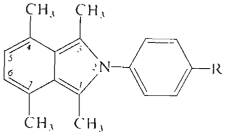
The quantum-chemical calculations inclusive of the calculations of the spin abundances (according to McLachlan) were carried out as in the previous work[6]. For evaluation of the methyl group effect we used both the heteroatom model[8] and the hyperconjugation model[8]. The symbols used for the coulombic and resonance integrals in the case of the hyperconjugation model of methyl group follow from the notation: $\gg C_\mu - C_M \equiv H^3$.

In all calculations we followed the influence of choice of the coulombic (the parameter *h*) and resonance (the parameter *k*) integrals of the heteroatoms on the calculated electronic structure of the molecules. The numerical values of the parameters *h* and *k* are given in Discussion and in footnotes to Table II.

RESULTS

Electrochemical oxidations. The cyclic polarograms of the compounds *I* and *II* differ but very little. Each of the compounds gives two anodic peaks out of which the first one only has the corresponding cathodic peak. The potentials corresponding to the maximum value of the current of the first (E_p^I) and the second (E_p^{II}) anodic peak are given in Table I along with the voltametric constant $i_p c^{-1} v^{-1/2}$ of the first anodic peak. Comparison of the voltametric constants with the value obtained (under the same conditions) for the one-electron oxidation of 1,4-phenylenediamine[9] (which is 1·06 in the same units as in Table I) indicates that the first step of oxidation of the compounds *I* and *II* is a one-electron step. Hence the cyclic voltametry indicates formation of relatively stable primary cationradical from the both studied derivatives of isoindole.

Ratio of the cathodic to anodic peak height, which characterizes stability of the primary cationradical, increases with increasing polarization rate and decreasing temperature. This fact indicates that the product of the first oxidation step undergoes subsequent chemical reaction of comparable rate with that of polarization of the working electrode. For the case of a reversible charge transfer followed by a first order irreversible chemical reaction, which was theoretically elaborated by Ševčík[10], the experimental data enable the conclusion that decomposition half-life of the primary cationradical is of 10^0 s order of magnitude with the both compounds at room temperature.



I: R = H
II: R = CH_3

EPR *Spectroscopy*. Under the conditions of internal electrochemical generation (IEG) at room temperature the recorded EPR spectra of the two studied compounds could hardly be differentiated from the background noise. EPR spectra of considerably higher quality were recorded by the JEG technique at −30°C. The 5 mM solutions of the compounds *I* and *II* in MeCN/0·1 M-TEAP were electrolyzed at a potential by 200 mV more positive than the E_p^I value given in Table I. The spectra obtained in this way are the same for the both derivatives. Also their *g*-factor values are the same (2·00288). Fig. 1 gives the experimental EPR spectrum of the cationradical of *II* along with the simulated spectrum. The hyperfine structure of the EPR spectrum is formed by two septets with relative intensities 1 : 6 : 15 : 20 : 15 : 6 : 1 with the splitting constant 1·253 mT and 0·322 mT, a triplet (1 : 2 : 1; 0·142 mT) and a triplet (1 : 1 : 1; 0·398 mT). There is no other splitting in the spectrum.

TABLE I

Characteristics of Electrochemical Oxidation of 1,3,4,7-Tetramethylisoindoles

1 mM solutions of the compounds in anhydrous acetonitrile/0·1M-TEAP. The Pt electrode was polarized at a rate 0·2 Vs^{-1}.

Compound	$E_\mathrm{p}^{\mathrm{I}a}$	$i_\mathrm{p}c^{-1}v^{-1/2b}$	$E_\mathrm{p}^{\mathrm{II}a}$
I 2-Phenyl-	0·35	0·91	1·27
II 2-(4-Tolyl)-	0·39	0·93	1·25

[a] The potential corresponding to the maximum current value of the first (E_p^I) and the second (E_p^II) anodic peaks in V (against aqueous calomel electrode with saturated solution of NaCl); [b] for the first oxidation peak; i_p in A cm^{-2}; c in mol l^{-1}; v in Vs^{-1}.

A better agreement between the simulated and the experimental spectra was obtained with presumption of pure Lorentz line shape than with the pure Gauss shape. For the line width in the simulated spectrum (Fig. 1) we used the value $1/2\ \Delta H_{1/2} = 0{\cdot}048$ mT (half width of the non-differentiated line in the half height). Variation of the splitting constants of the given multiplets and that of line width cannot result (with the pure Lorentz line shape) in any better visual agreement between the simulated and the experimental spectra. Smaller discrepancies in relative intensities of the experimental and the simulated spectra can be assigned to the more complex line shape in the experimental spectrum as compared with the pure Lorentz line shape.

We followed the time dependence of intensity decrease of selected lines in the spectra of the cationradicals of *I* and *II* after interruption of the electrolysis to determine kinetics of their decomposition at −30°C. Within the experimental error the cationradicals of *I* and *II* show the same stability. The found decomposition half-life is 4 min at −30°C presuming the first order reaction.

DISCUSSION

The Hückel MO theory predicts the same energy and shape of the highest occupied molecular orbital (HOMO) of the N-substituted isoindole and 1,3,4,7-tetramethyl-

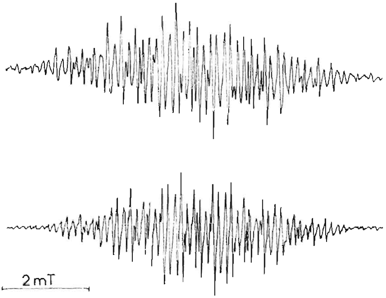


FIG. 1

EPR Spectrum of Cationradical of 2-(4-Tolyl)-1,3,4,7-tetramethylisoindole (*II*)

Top: experimental spectrum (5 mM solution of the parent substance in MeCN/0·1M-TEAP before electrolysis; at −30°C); bottom: the simulated spectrum (the Lorentz line shape; for the parameters see the text).

isoindole derivatives regardless of the substituent at the nitrogen atom. This orbital is antisymmetrical with respect to the σ_v symmetry plane of the isoindole fragment (perpendicular to the plane of the molecule). Approximation of the methyl groups by the heteroatom model ($h_{CH_3} = 2$; $k_{C-CH_3} = 0·7$) and by the hyperconjugation model ($h_{C_\mu} = -0·1$; $k_{C_\mu-C_M} = 1$; $h_{C_M} = 1$; $h_{C_M-H_3} = 3$; $h_{H_3} = -0·5$) gives the values $m_{HOMO} = -0·093$ and $-0·157$, respectively (the MO energy ε is defined as $\varepsilon = \alpha_C - m\beta_{CC}$). Energy and expansion coefficients of the HOMO are independent of the used values h_N and k_{C-N} for the coulombic and resonance integrals of the nitrogen atom and C—N bond. From the viewpoint of the HOMO antisymmetry and independence of its energy and shape with respect to the substituent at the N atom and to the parameters h_N and k_{C-N}, the isoindole system behaves in the same way as that of pyrrole or 2,5-dimethylpyrrole[11], the reverse being true for carbazole and its N-substituted derivatives[12]. Properties of the HOMO in the isoindole system can be generalized in the statement that behaviour of isoindole derivatives with various N-substituents will not be substantially different during electrochemical oxidation (in contrast to N-substituted carbazoles[13]). Similar prediction of the HMO method was confirmed experimentally in a set of N-substituted 2,5-dimethylpyrroles[14].

The localization of the HOMO in the isoindole part of the molecule, predicted for the compounds *I* and *II* by the HMO method, is also confirmed by the experi-

TABLE II

Distribution of Unpaired Electron and Spin Abundances in 1,3,4,7-Tetramethylisoindoles

Position	Heteroatomic model of CH_3[a]		Hyperconjugation model of CH_3[b]	
	c^2_{HOMO}[c]	ϱ^{π}[d]	c^2_{HOMO}[c]	ϱ^{π}[d]
C_1	0·249	0·332	0·258	0·342
C_4	0·095	0·106	0·098	0·112
C_5	0·080	0·064	0·074	0·056
CH_3 on C_1[e]	0·034	0·033	0·029	0·036
CH_3 on C_4[e]	0·013	0·011	0·011	0·012
N	0·000	−0·037	0·000	−0·039

[a] $h_{CH_3} = 2$; $k_{C-CH_3} = 0·7$; [b] $h_{C\mu} = -0·1$; $k_{C\mu-C_M} = 1$; $h_{C_M} = 0$; $k_{C_M-H_3} = 3$; $h_{H_3} = -0·5$; [c] square of the expansion coefficient in HOMO; [d] π-electron spin abundance according to McLachlan; $\lambda = 1·2$; $h_N = 1·5$; $k_{C-N} = 0·8$; [e] in the case *sub a* the quantity relates to the heteroatom CH_3; in the case *sub b* the quantity relates to the group orbital of H_3.

mental EPR spectra of the cationradicals of these compounds: the both spectra show the same HFS, and this HFS can completely be explained without considering the splitting by the protons at phenyl (4-tolyl) group. Table II gives squares of the expansion coefficients of HOMO of the compounds *I* and *II* and the spin abundances in their cationradicals. The values of these quantities depend but little on the model used for the methyl groups. In the case of the hyperconjugation model of methyl the magnitude of the HOMO expansion coefficients and, hence, also that of the spin abundances are most affected by the inductive parameter h_{C_μ} of the carbon atom bearing the methyl group. If we start from the McConnell relation[15,16] $a^{H} = Q^{H}_{C-H} \varrho^{\pi}_{C}$, then the best agreement with the average value $|Q^{H}_{C-H}| = 2{\cdot}54$ mT (ref.[17]) (for the cationradicals of benzenoid hydrocarbons) is obtained with $h_{C_\mu} = -0{\cdot}1$ for the splitting constant of the protons at positions C_5 and C_6.

The EPR spectra of the cationradicals of *I* and *II* do not settle the assignements of the splitting constants of the septets to the pairs of equivalent methyls. Magnitude of the splitting constants of the methyl protons can be correlated either with the π-electron spin abundance at the carbon atom carrying the methyl group, or direct with the spin abundance of the orbital of π-symmetry with the help of which the methyl group or its hydrogen atoms are described. Ratio of the spin abundances at C_1 and C_3 to those at C_4 and C_7, respectively, is about 3 : 1. The same value is obtained when comparing the respective spin abundances of the heteroatoms CH_3 (in the case of the heteroatomic model of CH_3) or the group orbitals of the centre H_3 (in the case of the hyperconjugation model of CH_3). The experimental ratio of the splitting constants of the septets is 3·9 : 1. Thanks to great difference in magnitude of the both splitting constants and in the calculated spin abundances it is possible to assign univocally the greater splitting constant to the protons of the methyl groups at C_1 and C_3. One of the possible explanations of the incomplete agreement of the splitting constants ratio $a^{H}_{CH_3}$ with the ratio of the calculated values of the spin abundances consists in different geometries of bonds in the benzene and pyrrole rings of isoindole, which is not taken into account by the simple HMO method.

The expansion coefficient of p_z-AO of nitrogen atom in HOMO is zero due to the mentioned antisymmetry of this orbital. Consideration of mechanism of π-π-spin polarization by the McLachlan method leads to negative value of the π-electron spin abundance of p_z-AO of N atom. Magnitude of this spin abundance is given in Table II for the various models of methyl and equals approximately $-0{\cdot}04$. The constant of proportionality Q^{N}_{N} between the splitting constant of the nitrogen nucleus (^{14}N) and the spin abundance of p_z-AO of the N atom has the absolute value 2·0 to 3·0 mT for both the ionradicals of nitrogen heterocycles of pyridine type and aromatic amines[18]. Due to this fact it is impossible to explain the magnitude of the splitting constant $a^{N} = 0{\cdot}398$ mT by the spin abundance $-0{\cdot}04$. If we consider (in accordance with the interpretation of HFS of EPR spectra of anionradicals of 1-nitrophenyl-2,5-dimethylpyrroles[6]) only the mechanism of the π-σ-spin polarization of the

C—N bonds due to relatively high spin abundances at C_1 and C_3 atoms of isoindole, then we obtain the value $|Q^N_{C-N}| = 0{\cdot}6$ mT. This value agrees well with the value 0·55 mT found with the anionradicals of 1-nitrophenyl-2,5-dimethylpyrroles[6]. In analogy with the Karplus–Fraenkel theory[19] of the HFS of EPR spectra of ^{13}C it is justifiable to suppose that negative spin abundance of p_z-AO of N atom induces a positive spin density at the position of N nucleus, the same as the positive spin abundance of p_z-AO of the neighbouring carbon atoms. With this presumption the values $|Q^N_N| = 2{\cdot}5$ mT, $\varrho^\pi_N = -0{\cdot}04$ and $\varrho^\pi_C = 0{\cdot}34$ are obtained along with $|Q^N_{C-N}| = 0{\cdot}44$ mT.

The calculated absolute values of the spin abundances of p_z-AO of carbon atoms of the benzene cycle bound to the atom N in the cationradicals of the compounds *I* and *II* do not exceed the value 0·004.

In the first step of the electrochemical oxidation of N-substituted 2,5-dimethylpyrroles formation of highly reactive primary cationradicals can be presumed which, however, cannot be detected by EPR spectroscopy[14] under the same experimental conditions. The reason of the substantially lower reactivity of the cationradicals of the compounds *I* and *II* can be seen (if their structure is compared with that of the cationradicals of 2,5-dimethylpyrroles) in the extension of the conjugated π-electron system of isoindoles as compared with that of pyrroles and in the fact that benzene ring fusion at the 3,4 positions of 2,5-dimethylpyrroles actually blocks these positions. Reactivity of individual positions of the radical molecule can be expressed by the square of the expansion coefficient of the MO in which the unpaired electron is localized. In the case of N-substituted 2,5-dimethylpyrroles the HMO method gives the following values for HOMO: $c_2^2 = 0{\cdot}294$ (square of the expansion coefficient at the p_z-AO of the C_2 atom), $c_3^2 = 0{\cdot}149$ (heteroatomic model of CH_3) and $c_2^2 = 0{\cdot}312$, $c_3^2 = 0{\cdot}145$ (hyperconjugation model of CH_3). The corresponding values obtained by the HMO method for HOMO of N-substituted 1,3,4,7-tetramethylisoindoles are 0·249 and 0·030 (the heteroatomic model of CH_3), 0·258 and 0·028 (the hyperconjugation model of CH_3). The parameter values of the used coulombic and resonance integrals are given in Table II (footnotes). High probability value of the unpaired electron abundance in p_z-AO of the C atoms neighbouring to the N atom is thus lowered but little when passing from 2,5-dimethylpyrroles to 1,3,4,7-tetramethylisoindoles. However, substantial lowering of the square of the expansion coefficient of HOMO is seen at the second of the discussed centres. This comparison of the unpaired electron distribution in HOMO leads to the conclusion that the high reactivity of the primary cationradicals of 2,5-dimethylpyrroles is rather due to position C_3 than to C_2.

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