

POLAROGRAPHIC REDUCTION OF 1-BENZYL-N-(*p*-X-PHENYL)-3-AMINOCARBONYLPYRIDINIUM SALTS

Jiří KRECHL^a, Šárka BERANOVÁ^a, Věra VOLKEOVÁ^b, Jiří VOLKE^b
and Josef KUTHAN^a

^a Department of Organic Chemistry,

Prague Institute of Chemical Technology, 166 28 Prague 6 and

^b The J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 182 23 Prague 8

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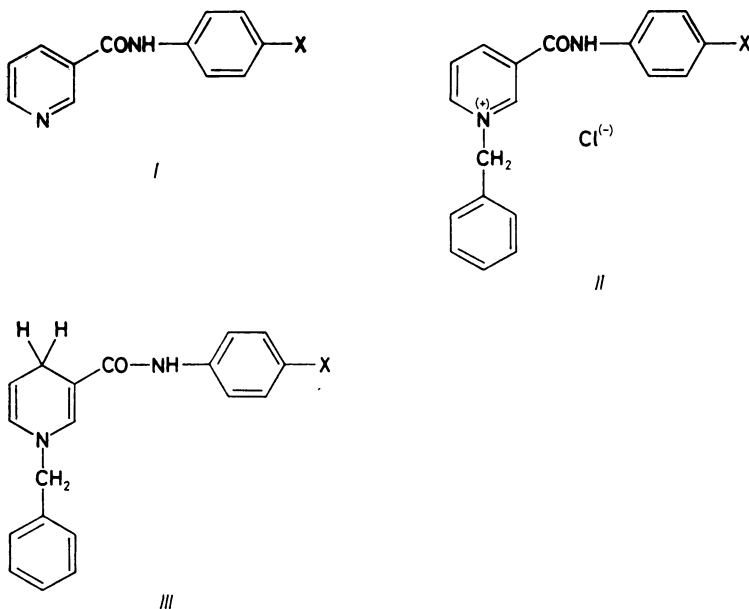
The substitution effect of different groups X (N(CH₂CH₃)₂, OH, OCH₃, CH₃, NHCOCH₃, H, Cl, COOCH₂CH₃ and NO₂) on the polarographic behaviour of 3-(N-*p*-X-phenylaminocarbonyl)pyridines (*I*), 1-benzyl-N-(*p*-X-phenyl)-3-aminocarbonylpyridinium cations (*II*) and their respective 1,4-dihydroderivatives (*III*) has been investigated in anhydrous solutions of dimethylformamide with 0.1 mol l⁻¹ (n-C₄H₉)₄N⁺PF₆⁻ as supporting electrolyte. The half-wave potentials of the reduction wave of *I* and *II*, which correspond to the uptake of a single electron (wave B) and to the formation of a primary radical, obey a Hammett correlation in a similar way as it is in the case of 1-benzyl- and 1-phenyl-3-amino-carbonylpyridinium cations substituted at carbon 4 on the benzene nucleus. The slope $\rho_{\pi, R}$ in the Hammett plot equals 0.192 V (*I*) and 0.104 V (*II*) for anhydrous DMF and compares thus with this slope obtained with the 1-benzyl- and 1-phenyl derivatives in our previous communications.

1,3-Disubstituted quaternary pyridinium salts are interesting as simple bioorganic models of NAD(P) coenzymes. The electrochemical reduction of the corresponding cations can yield valuable information about the ability of these models to take up electrons from the immobilized substrate which in the first approximation can be represented by a mercury electrode. A useful approach to the investigation of such an electron transfer mechanism proved to be a research of the substitution effect¹⁻⁴. An application of the Hammett correlation⁵ (*I*)

$$\Delta E_{1/2}(\text{solvent}) = \rho_{\pi R} \cdot \sigma_X \quad (I)$$

to the half-wave potentials in the case of *p*-substituted 1-benzyl-3-aminocarbonylpyridinium² and *p*-substituted 1-phenyl-3-aminocarbonylpyridinium⁴ salts pointed to the sensitivity of the potentials followed toward a change in the substituent. Our present aim was to prepare compounds *I*, *II* and *III* with different substituents at position 4' of the benzene ring in the N-(4'-X-phenyl)-3-aminocarbonyl moiety,

to investigate their electrode reactions and to establish if they oblige the above mentioned Hammett plot.



In formulae I-III: *a*, X = N(C₂H₅)₂; *b*, X = OH; *c*, X = OCH₃; *d*, X = CH₃; *e*, X = NHCOCH₃; *f*, X = H; *g*, X = Cl; *h*, X = CO₂C₂H₅; *i*, X = NO₂

EXPERIMENTAL

The temperature data are not corrected. The spectral characteristics were measured with following instruments: Bruker AM 400 (NMR), solutions in (CD₃)₂SO at 25°C with tetramethylsilane as internal standard; Specord UV/VIS (UV), solutions in ethanol, concentration $5 \cdot 10^{-5}$ mol l⁻¹ (compounds I) and saturated solutions (compounds II and III).

N-(4'-X-Phenyl)-3-aminocarbonylpyridines (Ia-Ii)

p-Substituted nicotinilides were prepared according to methods⁶⁻⁸: Nicotinic acid chloride (0.145 mol) in the hydrochloride form, prepared according to⁹ was dissolved in 200 ml of pyridine. A solution of 0.140 mol of *p*-X-aminobenzene dissolved in the lowest possible pyridine volume was added dropwise within 45 minutes. (In the case of diethylaminoderivative Ia the freshly distilled aniline was added without solvent). The mixture was then stirred for 1 h on a steam bath. The reaction mixture was then neutralized with Na₂CO₃ and extracted into dichloromethane. Crude product was repeatedly recrystallized from ethanol (lower solubility complicates the purification of compounds Ib, Ie, Ii). Compound Ia was obtained from its salt by Na₂CO₃ neutralization. Melting points and elemental analyses of compounds Ia-Ii are summarized in Table I, their absorption and NMR spectra in Table II.

TABLE I
Melting points and elemental analyses for compounds *I*, *II*, and *III*

Compound	Formula (M.w.)	M.p., °C	Calculated/Found			
			% C	% H	% N	% Cl
<i>Ia</i>	C ₁₆ H ₁₉ N ₃ O (269·4)	125—127	71·35	7·11	15·60	
		—	70·98	7·11	15·61	
<i>Ib</i>	C ₁₂ H ₁₀ N ₂ O ₂ (214·2)	259—260	67·28	4·71	13·08	
		252—253 ^a	67·27	4·84	13·12	
<i>Ic</i>	C ₁₃ H ₁₂ N ₂ O ₂ (228·3)	151—154	68·41	5·30	12·27	
		146—148 ^b	68·52	5·30	12·44	
<i>Id</i>	C ₁₃ H ₁₂ N ₂ O (212·3)	148—151	73·56	5·70	13·20	
		139—142 ^b	73·39	5·67	13·25	
<i>Ie</i>	C ₁₄ H ₁₃ N ₃ O ₂ (255·3)	270—273	65·87	5·13	16·46	
		275—278 ^c	65·43	5·00	16·45	
<i>If</i>	C ₁₂ H ₁₀ N ₂ O (198·2)	121—122	72·71	5·08	14·13	
		116 ²¹	72·62	5·18	14·12	
<i>Ig</i>	C ₁₂ H ₉ N ₂ OCl (232·7)	169—172	61·95	3·90	12·04	15·24
		169—171 ^b	61·60	3·97	12·03	14·31
<i>Ih</i>	C ₁₅ H ₁₄ N ₂ O ₃ (270·3)	125—126	66·65	5·22	10·36	
		127—128 ^d	66·39	5·28	10·32	
<i>Ii</i>	C ₁₂ H ₉ N ₃ O ₃ (243·2)	261—262	59·26	3·73	17·28	
		250—255 ^e	59·18	3·87	17·45	
<i>IIb</i>	C ₁₉ H ₁₇ N ₂ O ₂ Cl (340·9)	203—206	66·96	5·03	8·22	10·40
		—	66·99	5·17	7·92	10·49
<i>IIc</i>	C ₂₀ H ₁₉ N ₂ O ₂ Cl (354·9)	224—226	67·69	5·40	7·89	10·00
			67·47	5·50	7·81	10·10
<i>IIId</i>	C ₂₀ H ₁₉ N ₂ OCl (339·7)	239—242	70·89	5·65	8·27	10·46
			70·80	5·67	8·28	10·46
<i>IIe</i>	C ₂₁ H ₂₀ N ₃ O ₂ Cl (381·9)	200—210 ^f	—	—	—	—
<i>IIIf</i>	C ₁₉ H ₁₇ N ₂ OCl (324·8)	240—243	70·26	5·28	8·63	10·92
			70·42	5·24	8·75	11·36
<i>IIg</i>	C ₁₉ H ₁₆ N ₂ OCl ₂ (359·3)	216—219	63·52	4·49	7·80	19·74
			63·30	4·49	7·77	19·34
<i>IIh</i>	C ₂₂ H ₂₁ N ₂ O ₃ Cl (396·9)	203—206	66·58	5·33	7·06	8·94
			66·53	5·34	7·35	9·17
<i>IIIi</i>	C ₁₉ H ₁₆ N ₃ O ₃ Cl (369·7)	224—227	61·71	4·36	11·36	9·59
			61·56	4·56	11·20	9·60

TABLE I
(Continued)

Compound	Formula (M.w.)	M.p., °C	Calculated/Found			
			% C	% H	% N	% Cl
<i>IIIb</i>	C ₁₉ H ₁₈ N ₂ O ₂ (306.4)	132—135	74.48	5.92	9.14	
			72.37	5.90	8.94	
<i>IIIc</i>	C ₂₀ H ₂₀ N ₂ O ₂ (320.4)	129—132	74.98	6.29	8.74	
			72.48	6.17	8.49	
<i>III d</i>	C ₂₀ H ₂₀ N ₂ (304.4)	98—100	78.92	6.62	9.20	
			76.45	6.48	8.87	
<i>III f</i>	C ₁₉ H ₁₈ N ₂ O (290.4)	75—79	78.58	6.25	9.65	
			75.91	6.26	9.41	
<i>III g</i>	C ₁₉ H ₁₇ N ₂ OCl (324.9)	120—123	70.23	5.27	8.62	
			67.93	5.26	8.44	
<i>III h</i>	C ₂₂ H ₂₂ N ₂ O ₃ (362.4)	105—108	72.91	6.12	7.73	
			70.95	5.96	7.31	

^a Ref.^{2,2}; ^b ref.^{2,3}; ^c ref.^{2,4}; ^d ref.⁶; ^e ref.⁸; ^f compound without further purification.

TABLE II
Electronic (in nm) and NMR (in ppm) spectra of compounds *I*

Compd.	λ_{\max}	NH	H-2 ^a	H-6 ^a	H-4 ^a	H-5 ^a	Aromatics	
<i>Ia^b</i>	330	10.11	9.08 s	8.73 d	8.27 d	— ^c	7.53	6.67
<i>Ib^d</i>	289	10.20	9.28 s	8.73 d	8.26 d	— ^c	7.55	6.80
<i>Ic^e</i>	287	10.31	9.12 s	8.76 d	8.30 d	7.60 dd	7.72	6.98
<i>Id^f</i>	285	10.33	9.10 s	8.72 d	8.28 d	7.55 dd	7.66	7.15
<i>Ie^g</i>	294	10.45	9.10 s	8.72 d	8.26 d	— ^c	7.76—7.54	
<i>If^h</i>	283	10.40	9.11 s	8.76 d	8.26 d	7.58 dd	7.80	7.33
<i>Ig</i>	269	10.57	9.13 s	8.78 d	8.29 d	7.57 dd	7.83	7.42
<i>Ihⁱ</i>	288	10.73	0.12 s	8.80 d	8.30 d	7.61 dd	7.95	
<i>Ii</i>	317	10.96	9.13 s	8.78 d	— ^c	7.60 dd	8.30—8.05	

^a Pyridine protons; ^b 3.32 q (CH₂), 1.08 t (CH₃); ^c signal under aromatic protons; ^d 9.10 (OH); ^e 3.80 s (OCH₃); ^f 2.30 s (CH₃); ^g 10.48 (NH), 2.92 s (CH₃); ^h 7.14 dd (H₄); ⁱ 4.31 q (CH₂), 1.33 t (CH₃).

1-Benzyl-N-(4'-X-Phenyl)-3-aminocarbonylpyridinium Chlorides (*IIa*–*IIIi*)

The quaternary salts were synthesized¹⁰ from respective pyridines *I* and benzyl chloride. The resulting compounds were recrystallized from ethanol. We did not succeed in obtaining compound *IIe* in analytically pure form, however, it afforded a satisfactory half-wave potential on platinum electrode. Melting points and elemental analyses of compounds *IIa*–*IIIi* are summarized in Table I, their absorption and NMR spectra in Table III.

1-Benzyl-N-(4'-X-Phenyl)-3-aminocarbonyl-1,4-dihydropyridines (*IIIa*–*IIIi*)

1,4-Dihydropyridines *III* were synthesized from quaternary salts *II* by dithionite reduction¹¹. Starting salt *II* (0.6 mmol) was dissolved under stirring in 25 ml H₂O by heating to 50°C. A mixture of sodium dithionite and sodium carbonate solutions was prepared from their aqueous solutions (3 mmol in 8 ml H₂O) and kept at 50°C during 15 min solution of *II* was added dropwise. The reaction mixture was then stirred another 10 min at 50°C. During the whole procedure the reaction mixture was kept in dark. Formation of dihydropyridine was followed by TLC (Silufol, ethanol). Melting points and elemental analyses of compounds *IIIa*–*IIIi* are summarized in Table I, their electronic and NMR spectra in Table IV.

Electrochemical Experiments

Polarographic and voltammetric measurements were effectuated with a three electrode circuit. A dropping mercury electrode with an outflow velocity equal to 0.75 mg s⁻¹ (and with controlled drop time) was applied as a working electrode for the polarographic reductions and a rotated platinum disc electrode (1 500 min⁻¹) for the voltammetric oxidations, respectively; a platinum foil served as a counter electrode and a jacketed 0.5M calomel electrode was the reference electrode

TABLE III
Absorption (in nm) and NMR (in ppm) spectra of compounds *II*

Compd.	λ_{\max}	NH	H-2 ^a	H-6 ^a	H-4 ^a	H-5 ^a	Aromatics ^b
<i>IIb</i> ^c	— ^d	11.14	10.00 s	9.33 d	9.17 d	8.30 dd	7.65–6.82
<i>IIc</i> ^e	269	11.36	10.09 s	9.36 d	9.21 d	8.30 dd	7.72–6.98
<i>IId</i> ^f	266	11.20	10.00 s	9.30 d	9.17 d	8.29 dd	7.75–7.20
<i>IIe</i> ^g	254	11.28	10.03 s	9.31 d	9.18 d	8.28 dd	7.78–7.44
<i>IIf</i>	266	11.44	10.08 s	9.30 d	9.18 d	8.29 dd	7.89–7.18
<i>IIg</i>	266	11.70	10.09 s	9.36 d	9.22 d	8.30 dd	7.98–7.44
<i>IIh</i> ^h	286	11.63	10.52 s	9.33 d	0.15 d	8.32 dd	8.03–7.54
<i>IIIi</i>	318	12.16	10.12 s	9.32 d	9.20 d	— ⁱ	8.30–7.45

^a Pyridine protons; ^b 5.98 s (CH₂ benzyl); ^c 9.49 (OH); ^d diffusion maximum; ^e 3.76 s (OCH₃); ^f 2.30 s (CH₃); ^g 10.12 (NH), 2.96 s (CH₃); ^h 4.30 q (CH₂), 1.33 t (CH₃); ⁱ signal under aromatic protons.

The electrochemical measurements were carried out with the polarographic analyzer GWP 673 (G.D.R.) connected to an XY recorder ENDIM 602 02 or Bak-5-T. The scan rate for polarographic reductions was synchronized with the drop time (1.5 s, controlled by a time-beater) in the direction from 0.0 V to more negative potentials in 5 mV or 1 mV steps, respectively. Electrochemical oxidations were scanned from -0.5 V towards more positive potentials. The velocity of the scan was 0.1 V/min; for cyclic voltammetry curves the velocity was 0.250 V/s.

Polarographic and voltammetric data were obtained with solutions of the compounds *I*, *II* and *III* in non-aqueous dimethylformamide at 25°C, the concentrations of the depolarizer were $1.5 \cdot 10^{-3}$ (*I*) and $1.0 \cdot 10^{-3}$ (*II* and *III*) mol l⁻¹, respectively. As supporting electrolyte the 0.1 mol l⁻¹ (n-C₄H₉)₄N⁺PF₆⁻ was used. Before recording the *i*-*E* curve the investigated solutions were first deaerated by a stream of argon; during recording the curve the inert gas was led above the solution (reduction). Solutions of the compounds *III* were protected from light.

The cyclic voltammetric measurements were carried out with a hanging mercury electrode on a platinum electrode at a scan rate 0.25 V s⁻¹.

The half-wave potentials $E_{1/2}$ of compounds *I* and *II* were obtained either by directly evaluating the *i*-*F* curves or from the logarithmic plots ($\log i/(I_d - i) = f(E)$) of the secures. Similarly treated were oxidations of *III*. The values $E_{1/2}$ obtained by this procedure are given in Tables V—VII; the Tables V—VII also include the values of the slopes $RT/\alpha nF$ bearing relation to the reversibility of the electrode process followed in this paper. The correlations (*I*) using the substitution constants^{12,13} were evaluated by regression analysis.

RESULTS AND DISCUSSION

Reduction of Compounds II in Anhydrous Dimethylformamide

All examined depolarizers *II* exhibit an analogous polarographic behaviour. For the case that a dropping mercury electrode was used, two wave types were detected in the potential range 0—2.2 V: anodic prewaves A in the more positive region ($E_{1/2}$ around

TABLE IV
Absorption (in nm) and NMR (in ppm) spectra of compounds *III*

Compd.	λ_{\max}	NH	H-2 ^a	H-6 ^a	H-5 ^a	H-4 ^a	Aromatics ^b
<i>IIIb</i> ^c	360	8.58	7.14 s	5.97 d	4.68 dd	3.12 d	7.40—6.65
<i>IIIc</i> ^d	354	8.70	7.17 s	5.97 d	4.69 dd	3.12 d	7.51—6.85
<i>III d</i> ^e	360	8.75	7.19 s	5.97 d	4.70 dd	3.12 d	7.50—7.05
<i>III f</i>	368	8.82	— ^f	5.98 d	4.71 dd	3.12 d	7.61—6.98
<i>III g</i>	362	8.98	— ^f	5.97 d	4.72 dd	3.12 d	7.66—7.24
<i>III h</i> ^g	376	9.18	— ^f	5.98 d	4.74 dd	3.12 d	7.86—7.31

^a Pyridine protons; ^b 4.38 s (CH₂ benzyl); ^c 9.06 (OH); ^d 3.70 (OCH₃); ^e 2.22 s (CH₃); ^f signal under aromatic protons; ^g 4.41 q (CH₂), 1.30 t (CH₃).

–0.2 V) and diffusion-controlled cathodic one-electron waves B over the more negative potential region ($E_{1/2}$ around –1.0 V depending on substituent X). When a platinum foil was applied as a working electrode only waves B were detected within

TABLE V

Half-wave potentials of reductions, slopes of polarographic waves (from the log plot) of *Ia–Ih* in anhydrous dimethylformamide for $1.0 \cdot 10^{-3} \text{ mol l}^{-1}$ depolarizers, 0.1 mol l^{-1} $(n\text{-C}_4\text{H}_9)_4 \cdot \text{N}^+ \text{PF}_6^-$

Compd.	Substituent	$I_d \cdot 10^6$ A	$-E_{1/2}^a$ V	$-E_{1/2}^b$ V	$2 \cdot 303RT/(anF)^c$ mV
<i>Ia</i>	$\text{N}(\text{CH}_2\text{CH}_3)_2$	1.355	2.090	2.096	84
<i>Ib</i>	OH	1.223	2.046	—	—
<i>Ic</i>	OCH_3	1.346	2.010	2.006	85
<i>Id</i>	CH_3	1.280	2.000	1.999	83
<i>Ie</i>	NHCOCH_3	1.404	2.005	1.998	90
<i>If</i>	H	1.281	1.965	1.963	70
<i>Ig</i>	Cl	1.291	1.940	1.933	94
<i>Ih</i>	$\text{COOCH}_2\text{CH}_3$	1.276	1.860	1.861	93

^a Read from the *i–E* polarographic curve; ^b calculated from the log plot; ^c the values of slopes calculated from the log plot.

TABLE VI

Half-wave potentials of reductions, slopes of polarographic waves (from the log plot) of *Iib–Iii* in anhydrous dimethylformamide for $1.0 \cdot 10^{-3} \text{ mol l}^{-1}$ depolarizers, 0.1 mol l^{-1} $(n\text{-C}_4\text{H}_9)_4 \cdot \text{N}^+ \text{PF}_6^-$

Compd.	Substituent	$I_d \cdot 10^6$ A	$-E_{1/2}^a$ V	$-E_{1/2}^b$ V	$2 \cdot 303RT/(anF)^c$ mV
<i>Iib</i>	OH	1.228	1.026	1.027	45
<i>Iic</i>	OCH_3	1.400	0.995	0.997	44
<i>Iid</i>	CH_3	1.274	0.990	0.989	54
<i>Iie</i>	NHCOCH_3	1.169	0.978 ^d	—	—
<i>Iif</i>	H	1.004	0.995	0.997	51
<i>Iig</i>	Cl	1.690	0.963	0.962	52
<i>Iih</i>	$\text{COOCH}_2\text{CH}_3$	1.296	0.946	0.945	53
<i>Iii</i>	NO_2	1.194	0.890	0.890	66

^a Read from the *i–E* polarographic curve; ^b calculated from the log plot; ^c the values of slopes calculated from the log plot; ^d estimated from the *i–E* polarographic curve.

an identical potential range as for the dropping mercury electrode. Hence waves A should be attributed to the reaction of chloride anion proceeding from the quaternary depolarizer with mercury ions dissolved from the electrode in an anodic process.

The main one-electron waves B correspond then to pyridinium nucleus reduction. The B/A heights ratio remains in all cases constant and is approximately equal to one. In the case of derivative *IIIi* except the wave B with $E_{1/2} = -0.890$ V two waves are detected starting from -1.20 V towards the more negative potentials. Those waves correspond to the reduction of NO_2 substituent.

Reduction of Compounds I in Anhydrous Dimethylformamide

Under the above conditions depolarizers *I* are reduced in a single one-electron wave (B) appearing in the potential region with $E_{1/2}$ around -2.0 V. The particular value of $E_{1/2}$ is influenced by the character of substituent X. The behaviour of the nitro derivative *IIi* is much more complicated by interference of the NO_2 group reduction waves. The first reduction step in this case is the reversible NO_2 group reduction to NO_2^- radical anion which causes a change in the electron distribution over the pyridine ring and this measurement cannot be therefore included into the series of remaining derivatives in Table V and Fig. 1.

Oxidation of Compounds III in Anhydrous Dimethylformamide

Experimental data are summarized in Table VII. From the table it follows that the oxidations proceed in a single irreversible wave C whose height corresponds to a two

TABLE VII

Half-wave potentials of oxidations, slopes of polarographic waves (from the log plot) of *IIIb* to *IIIh*, *IIIf*–*IIIh* in anhydrous dimethylformamide for $1.0 \cdot 10^{-3}$ mol l^{-1} depolarizers, 0.1 mol $\cdot \text{l}^{-1}$ $(\text{n-C}_4\text{H}_9)_4\text{N}^+\text{PF}_6^-$

Compd.	Substituent	$I_d \cdot 10^6$ A	$-E_{1/2}^a$ V	$-E_{1/2}^b$ V	$2.303RT/(nF)^c$ mV
<i>IIIb</i>	OH	8.39	0.585	0.590	117
<i>IIIc</i>	OCH_3	7.67	0.555	0.567	103
<i>III d</i>	CH_3	7.16	0.560	0.560	98
<i>III f</i>	H	9.26	0.600	0.594	99
<i>III g</i>	Cl	8.27	0.580	0.582	110
<i>III h</i>	$\text{COOCH}_2\text{CH}_3$	8.39	0.580	0.580	122

^a Read from the *i*-*E* polarographic curve; ^b calculated from the log plot; ^c the values of slopes calculated from the log plot.

electron consumption. The oxidation process includes the loss of a proton with the exception of *III*f in which $X = H$. Moreover, the half-wave potential of the two-electron anodic wave is not given by the transfer of a single electron only (as in *II*), but by a complicated loss of two electrons and of a proton. Half-wave potentials are ranging between 0.56 V and 0.60 V.

We tried to explain the insensitivity of half-wave potentials to different substitution and therefore we accomplished the quantum chemical EHT calculations¹⁴ of compounds *II*f and *III*f, respectively. Geometry was chosen according to ref.¹⁵. We found that in the case of *II*f the frontier molecular orbital LUMO is distributed over the quaternary pyridinium ring as well as over the carbamoyl group and the attached phenyl moiety. There is hence a possibility that substitution X on this phenyl influences polarographic reduction of the pyridinium ring. On the other hand when examining HOMO distribution of *III*f we found that it is distributed exclusively over the dihydropyridine and carbamoyl systems. Therefore the substitution of phenyl will not influence the oxidation of the 1,4-dihydropyridine and the insensitivity of half-wave potentials of compounds *III* oxidations to different substitution thus seems to be justified. The results are closely similar for planar as well as perpendicular arrangement of the attached phenyl group.

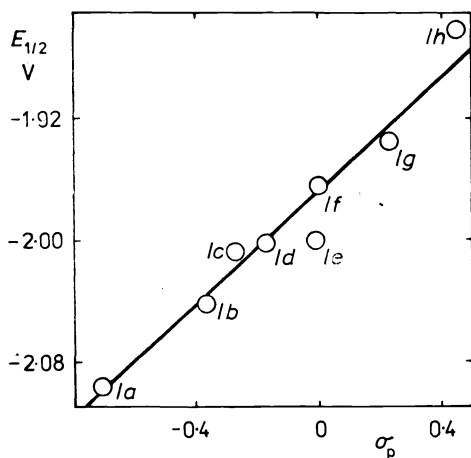


FIG. 1
Correlation of $E_{1/2}$ for the reduction of compounds *I* in anhydrous DMF with σ_p substituent constants of X

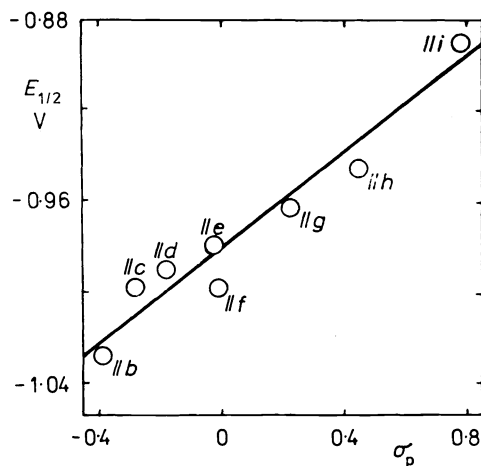
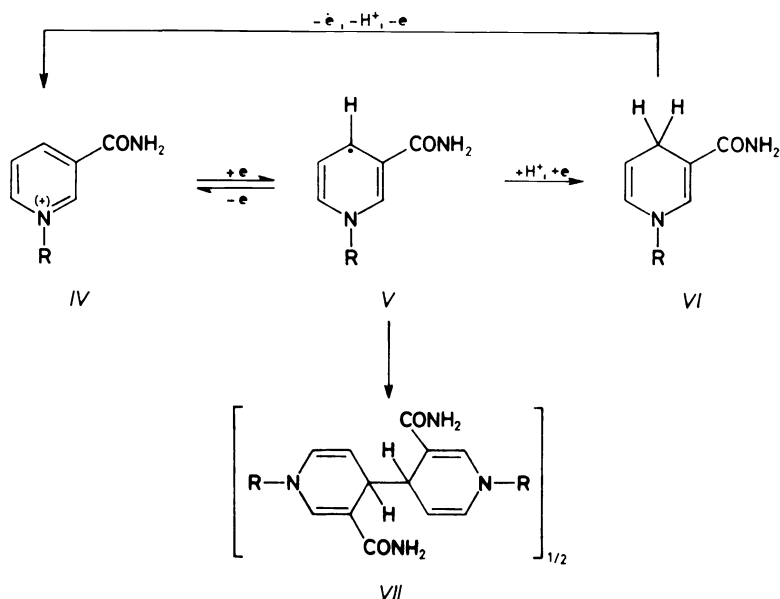


FIG. 2
Correlation of $E_{1/2}$ for the reduction of compounds *II* in anhydrous DMF with σ_p substituent constants of X

Cyclic Voltammetry

Cyclic voltammograms of compounds *I*, *II* and *III* exhibit in no case an anodic (cathodic) peak attributable to oxidation (reduction) of the primary product forming at wave B (or C). The only exception is the behaviour of the nitro derivative in the first reduction step.

We tried to interpret the above described electrochemical behaviour of compounds *I*, *II*, and *III* on the basis of mechanism depicted in Scheme 1 which is reasonably supported and documented in several cases¹⁶⁻²⁰.



SCHEME 1

Dihydropyridines *III* are irreversibly oxidized in a two-electron wave to the respective cation *IV*. The assumption of the cation formation is supported by cyclic voltammetry — a cathodic peak appears at -1.0 V which corresponds to the E_p^k value for the reduction of identically substituted derivative *II*.

In reductions the waves B correspond to the first reaction step in Scheme 1 which is an uptake of a single electron followed by the formation of a primary radical *V*. Polarographic data reveal indirect information about the fate of primarily formed radical *V*; its further reduction to dihydropyridine *VI* is impossible in the media where no proton is available. In the case of compound *II* reduction the fast follow-up combination of neutral radicals by bimolecular reaction $2 \text{V} \rightarrow \text{VII}$ is most probable and dimer *VII*, electrochemically inactive in given potential region, is thus formed^{16-19,21}.

In derivative *I* reduction the radical-anion is formed by a one electron uptake, the formation of dimer *VII* is rendered impossible due to the same charge of both species.

Successive reactions of the radical *V* strongly influence reversibility of the process $IV \rightleftharpoons V$ as follows from the cyclic voltammetry results as well as from the calculated slope $2.303 RT/(nF)$; this value differs from the value 0.059 V derived for reversible processes. Similar behaviour was observed also in our previous communications^{2,4} for 1-benzyl- and 1-phenyl-3-aminocarbonylpyridinium cations.

From Figs 1 and 2 it is clear that half-wave potentials of wave B for the compounds *I* and *II* fulfill satisfactorily Hammett correlation (*I*) with the substitution parameters^{12,13} σ_p ($r = 0.977$ and $r = 0.966$ for *I* and *II*, respectively).

The slope $\rho_{\pi,R}$ in the Hammett plot equals 0.192 V (*I*) and 0.104 V (*II*), respectively, for anhydrous DMF and compares thus with this slope obtained with the 1-benzyl (0.127 V) and 1-phenyl (0.179 V) derivatives in our previous communications^{2,4}.

REFERENCES

1. Norris D. J.: Diss. Abstr. Int., B 1976, 6175; Chem. Abstr. 85, 127 278 (1976).
2. Kuthan J., Pavlíková-Raclová F.: Collect. Czech. Chem. Commun. 47, 2890 (1982).
3. Pavlíková-Raclová F., Kuthan J.: Collect. Czech. Chem. Commun. 48, 2273 (1983).
4. Krechl J., Mižaninová D., Volke J., Kuthan J.: Collect. Czech. Chem. Commun. 52, 1550 (1987).
5. Zuman P.: *Substituent Effects in Organic Polarography*. Plenum Press, New York 1967.
6. Pongratz A., Zirm K.: Monatsh. Chem. 88, 330 (1957).
7. Kushner S., Dalalian H.: J. Org. Chem. 13, 834 (1948).
8. Walker G., Klett M.: J. Med. Chem. 9, 624 (1966).
9. Meyer A., Graf F.: Chem. Ber. 61, 2205 (1928).
10. Chunoshin U., Denichi M., Shogo K.: J. Pharm. Soc. Jpn. 73, 111 (1953).
11. Mauzerall P., Westheimer F. J.: J. Am. Chem. Soc. 77, 2261 (1955).
12. Bray P. J., Barnes R. G.: J. Chem. Phys. 27, 551 (1957).
13. Jaffé H. H.: Chem. Rev. 53, 191 (1953).
14. Hoffmann R.: J. Chem. Phys. 39, 1397 (1963).
15. Pople J. A., Gordon M.: J. Am. Chem. Soc. 89, 4253 (1969).
16. Skála V., Volke J., Obáňka V., Kuthan J.: Collect. Czech. Chem. Commun. 42, 292 (1977).
17. Santhanam K. S. V., Elving P. J.: J. Am. Chem. Soc. 95, 5482 (1973).
18. Schmamel C. O., Santhanam K. S. V., Elving P. J.: J. Am. Chem. Soc. 97, 5083 (1975).
19. Carelli I., Cardinali M. E., Moracci F. M.: J. Electroanal. Chem., Interfacial Electrochem. 107, 391 (1980).
20. Blaedel W. J., Haas R. G.: Anal. Chem. 42, 918 (1970).
21. Volke J., Naarová M.: Collect. Czech. Chem. Commun. 37, 3361 (1972).
22. Pongratz A., Zirm K.: Monatsh. Chem. 93, 70 (1962).
23. Petyunin P., Kozhevnikov J.: Zh. Obshch. Khim. 33, 1261 (1963).
24. Kushner S., Dalalian H.: J. Org. Chem. 13, 834 (1948).

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