ELECTROCHEMICAL BEHAVIOUR AND ESR SPECTRA
OF NITRO SUBSTITUTED MONO-
AND DIBENZOYLMETHYLENEBENZTHIAZOLINES
AND SELENAZOLINES*

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Compounds of the type of 2-(4′-nitrobenzoyl)methylene-3-ethylbenzothiazoline (*I*) and 2-bis-(*p*-nitrobenzoyl)methylene-3-ethylbenzothiazoline (*II*) were studied polarographically and by ESR spectroscopy to obtain informations about their electrochemical and follow-up reactions and their conformation. Whereas with compounds of the type *I* the conjugation in their molecules is preserved, with type *II* the coplanarity of the molecules is disturbed, which is manifested in the values of the splitting constants of the ESR spectra and a slow electron transfer between both nitrophenyl substituents. These conclusions are supported by NMR spectroscopic studies.

Substances exemplified by compounds of the type
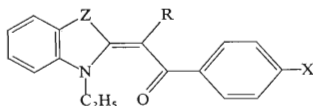
were studied from the point of view of their sensibilation effect and the relation between their structure and spectral properties[1,2]. A number of derivatives of the mentioned type was studied in recent years by NMR spectroscopy and a transfer of the effect of X and R substituents on the electronegativity of the heterocyclic nitrogen was stated as determined from the internal shift of NMR signals of the ethyl group bound to the heterocyclic nitrogen[3]. There was a substantial difference in the transfer of this effect between compounds where the substituent R was hydrogen and those where R was a (substituted) benzoyl group.

Since some of the studied substances could be considered as derivatives of nitro-benzene, the polarographic method and ESR spectroscopy appeared suitable for a further study of the mentioned effects[4]. In this way the following derivatives were studied:

Ia: R = H, Z = S, X = NO$_2$, 2-(4'-nitrobenzoyl)methylene-3-ethylbenzothiazoline;

Ib: R = H, Z = Se, X = NO$_2$, 2-(4'-nitrobenzoyl)methylene-3-ethylbenzoselenazoline;

IIa: R = —CO—C$_6$H$_4$-p-NO$_2$, Z = S, X = NO$_2$, 2-bis(p-nitrobenzoyl) methylene-3-ethylbenzothiazoline;

IIb: R = —CO—C$_6$H$_4$-p-NO$_2$, Z = Se, X = NO$_2$, 2-bis(p-nitrobenzoyl)methylene-3-ethylbenzoselenazoline.

EXPERIMENTAL

Chemicals

Compounds *Ia—IIb* were furnished by Dr A. Mistr (Research Institute of Pure Chemicals, Lachema, Brno)[3]. Dimethylformamide (DMF) used as solvent was from USSR; it was purified by azeotropic distillation with water and benzene and rectified on a column under reduced pressure. Water residue were removed by standing for several days with a molecular sieve Calsit 5A. Tetraethylammonium bromide (TEABr) used as supporting electrolyte was of reagent grade (Lachema, Brno); it was purified by recrystallization from a warm solution in DMF and fractionated precipitation from this solution with benzene, the crystals were sucked off and washed with benzene. The solutions were deaerated with nitrogen which was lead through a BTS catalyst column (Fluka) to remove traces of oxygen and then through a molecular sieve Nalsit 4A column to remove traces of water. Other chemicals were commercial products of reagent grade.

Polarography

Polarographic curves were recorded on a Radelkis OH 102 polarograph with a three-electrode system. An aqueous calomel reference electrode was separated from the measured solution by two fritted glass discs between which a supporting electrolyte solution in DMF was placed; this was exchanged before every measurement. The counter-electrode was a platinum foil in a supporting electrolyte solution separated from the measured one by fritted glass. The concentration of the supporting electrolyte was 0·1M, that of the depolarizer about 0·001M. The reversibility of the polarographic waves was checked by means of a Kalousek switch with an operating frequency of 7·5 and 12 Hz. The corresponding curves were recorded with the mentioned polarograph in a two-electrode mode. The auxiliary potential was set in the region of the limiting current of the waves under study.

Electrochemical Generation of Radicals

For the measurement of ESR spectra the radicals were generated outside the resonator cavity in a previously described cell[4]. The working electrode was a mercury pool, the reference was aqueous saturated calomel electrode with a salt bridge filled with the supporting electrolyte, and the counter-electrode was a platinum sheet. The anode compartment was separated by fritted glass of density 1 and filled also with the supporting electrolyte. Electrolyses were carried out potentiostatically at the potentials of the limiting currents of the individual waves found

polarographically, and were followed polarographically. Samples for the measurement of ESR spectra were taken during electrolysis.

Electron Paramagnetic Resonance Spectra

These spectra were measured on an EPR spectrometer of the type ER-9 (Carl Zeiss, Jena) at room temperature or in some cases at a lower temperature while the resonator cavity was cooled by means of a Temperature Variator of the firm Zeiss.

Quantum-Chemical Calculations

Molecular calculations were carried out on a Minsk 22 computer with the use of the standard HMO procedure. Spin densities were calculated according to McLachlan with the common value of $\lambda = 1.2$. The following values of correction parameters h_X of the coulombic and k_{XY} of the resonance integral were used:

NO₂ group: $\quad\alpha_N = \alpha + 2.2\beta, \quad \beta_{CN} = 1.2\beta,$
$\quad\quad\quad\quad\quad\quad\quad\alpha_O = \alpha + 1.4\beta, \quad \beta_{NO} = 1.67\beta;$
CO group: $\quad\alpha_O = \alpha + \beta, \quad \beta_{CO} = \beta;$
heterocyclic N: $\quad\alpha_N = \alpha + 1.5\beta, \quad \beta_{CN} = 0.8\beta;$
heterocyclic S: $\quad\alpha_S = \alpha + \beta, \quad \beta_{CS} = 0.7\beta;$
heterocyclic Se: $\quad\alpha_{Se} = \alpha + 0.9\beta, \quad \beta_{CSe} = 0.6\beta.$

The ethyl group was simulated in the calculations by the heteroatomic model X: $\alpha_X = \alpha + 2\beta$, $\beta_{XN} = 0.7\beta$. With the derivatives IIa and IIb, the influencing of both benzene rings was expressed by a change of the parameters for carbon atoms in the interaction ($C_{14,15,28,29}$): $\alpha_{Ci} = \alpha + h_{Ci}\beta$, where h_{Ci} was changed in the range from 0 to -0.2. A disturbance of the conjugation in the molecule was expressed by a change of the corresponding resonance integral as shown in Tables II—IV. The calculation of simulation spectra was carried out on a Minsk 22 computer with the use of a program furnished by Dr K. Pilař, Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague.

RESULTS

Polarography

In polarography in anhydrous DMF, the compounds Ia and Ib exert the same behaviour, their polarograms consist of three waves (Fig. 1, curve *1*) whose half--wave potentials are given in Table I. A comparison of the wave height with that of *p*-nitrophenol reveals that the first two waves correspond to one-electron reductions. A logarithmic analysis of the individual waves gave the respective slopes of 59, 70, and 73 mV. Their heights are directly proportional to the depolarizer concentration and to the square root of the height of mercury column, their temperature coefficients are in the range $0.8—1.3\%/K$. Experiments with the Kalousek switch showed that the reduction in both the first and second waves is reversible.

The compounds IIa and IIb behave polarographically also in the same manner; their polarograms consist of four waves (their $E_{1/2}$ values are given in Table I) and a maximum at -2.43 V (Fig. 2, curve *1*). The height of all four waves is directly

proportional to the depolarizer concentration and to the square root of the height of mercury column except for the fourth wave whose height is little dependent on the column height. Logarithmic analysis of these waves gave the respective slopes of 60, 58, 75, and 66 mV, their temperature coefficients are in the range $0.8-2.4\%/K$. Experiments with the Kalousek switch showed these waves to be reversible.

TABLE I

Values of $E_{1/2}$ ($-V$ against S.C.E.) for Compounds Investigated

Compound	1st wave	2nd wave	3rd wave	4th wave
Ia	0.880	1.46	2.55	—
Ib	0.875	1.44	2.51	—
IIa	0.720	0.93	1.27	1.63
IIb	0.715	0.92	1.27	1.60

FIG. 1

Polarographic Curve and Course of Electrolysis for Compound *Ia*

$c = 9.5 \cdot 10^{-4}$M, 0.1M-TEABr in anhydrous DMF; S.C.E. *1* Original solution; *2* after 4 min electrolysis at -1.70 V (limiting current of the second wave). For spectrum see Fig. 3; *3* after 2h electrolysis.
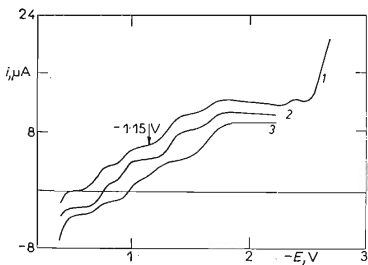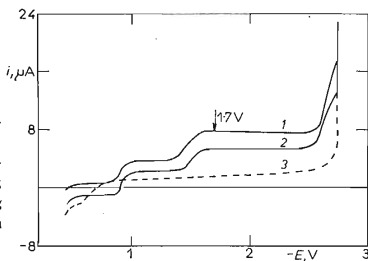

FIG. 2

Polarographic Curve and Course of Electrolysis for Compound *IIa*

$c = 9.8 \cdot 10^{-4}$M, 0.1M-TEABr in anhydrous DMF; S.C.E. *1* Original solution; *2* after 20 min electrolysis at -1.15 V (limiting current of the second wave); *3* after 2.5 h electrolysis.

Electron Spin Resonance Spectra

The compounds *Ia,b* give after electrolysis at the potential of the limiting current of the first wave $(-1\cdot1\ \mathrm{V})$ a spectrum with a hyperfine structure (Fig. 3). After electrolysis at the potential of the limiting current of the second wave $(-1\cdot70\ \mathrm{V})$ a spectrum identical with the preceding one was obtained if the time of electrolysis was shorter than would correspond to a complete reduction (Fig. 1, curve 2). After complete
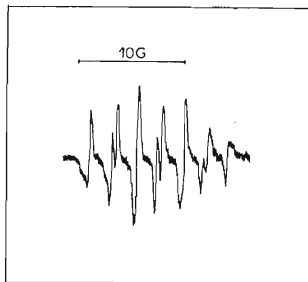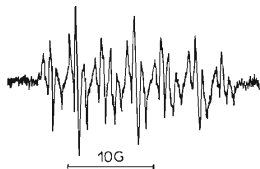

◄   FIG. 3

ESR Spectrum of Radical Anion of Compound *Ia*

   The radical was generated by electrolysis on a dropping mercury electrode at $-1\cdot1\ \mathrm{V}$ (S.C.E.) in the medium of $0\cdot1\text{M-TEABr}$ in anhydrous DMF.

FIG. 4

ESR Spectrum of Radical of Compound *IIa*

   The radical was generated by electrolysis on a dropping mercury electrode at $-0\cdot8\ \mathrm{V}$ (S.C.E.) (limiting current of the first wave) in the medium of $0\cdot1\text{M-TEABr}$ in anhydrous DMF.
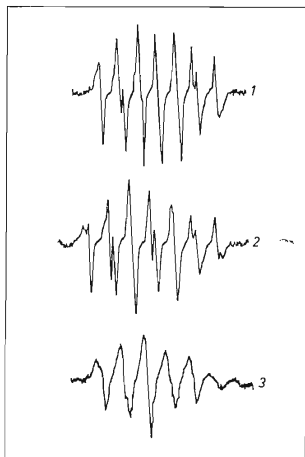
FIG. 5

Temperature Dependence of ESR Spectrum of Compound *IIb*

   The radical was generated as in the case of Fig. 4. The spectra were measured at the following temperatures: *1* 50°C; *2* 0°C; *3* −50°C.

electrolysis (Fig. 1, curve 3) no ESR signal was obtained. Spectra obtained during electrolysis of solutions of compounds IIa and IIb are almost identical. During electrolysis at the potential of the limiting current of the first wave a spectrum is obtained which with respect to its assymetry is apparently formed by two overlapping spectra (Fig. 4); lowering of the temperature enhances the intensity of the lines of the originally less intense overlapped spectrum (Fig. 5). A change of the supporting electrolyte cation influences the spectrum: replacing the tetraethylammonium bromide by sodium perchlorate causes a marked broadening of the lines and the central line of the more intense spectrum splits to a quartet (Fig. 6).

During electrolysis of the compound IIa at the potential of the limiting current of the second polarographic wave we obtain at shorter electrolysis times (Fig. 2, curve 2) the same spectrum as during electrolysis at the potential of the first wave; after a longer electrolysis time (Fig. 2, curve 3) another spectrum is superimposed, which is better visible on pictures obtained during electrolysis at more negative potentials. During electrolysis at the limiting current of the third wave the same spectrum is obtained as during electrolysis at the limiting current of the second wave.

Fig. 6

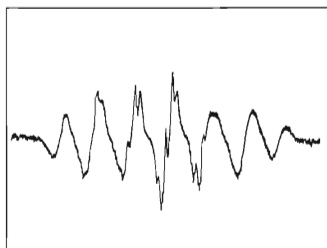ESR Spectrum of Radical of Compound IIa in Presence of Na$^+$ Ions

The radical was generated by electrolysis on a dropping mercury electrode at -0.8 V (s.c.e.) in the medium of 0·1M-NaClO$_4$ in anhydrous DMF.
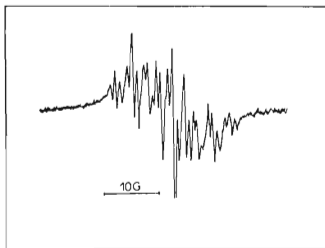

Fig. 7

ESR Spectrum of Biradical of Compound IIa

The radical was generated by electrolysis on a dropping mercury electrode at -1.80 V for 7 min in the medium of 0·1M-TEABr in anhydrous DMF.

10G

Finally, if we electrolyse at the limiting current potential of the fourth wave (-1.90 V), we obtain after shorter electrolysis times a new spectrum corresponding to that which appears as a new type of spectrum and masks the spectrum observable originally with the first wave during reduction at the potentials of the second and third waves (Fig. 7). After a longer electrolysis at the limiting current of the fourth wave (after complete reduction) the spectra vanish.

DISCUSSION

The individual atoms in the molecule will be numbered as follows:
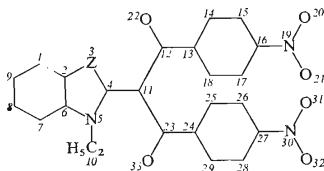
Compounds Ia,b have carbon 23 replaced by hydrogen and atoms of higher numbers are cancelled.

Our experimental data suggest that the compounds of type I are polarographically reduced in two one-electron reversible steps under the formation of an anion radical $R^{\mp}$ and a diamagnetic dianion R^{2-}. The appearance of the spectrum during reduction at the potential of the second wave can be ascribed to a reaction of the reduced particle with the original molecule (reaction (C)) and the overall reaction mechanism can be described as follows:

First wave: $M \quad + \quad e \quad \rightarrow \quad R^{\mp} ,$ (A)

Second wave: $R^{\mp} \quad + \quad e \quad \rightarrow \quad R^{2-} ,$ (B)

                          $R^{2-} \quad + \quad M \quad \rightarrow \quad 2\, R^{\mp} .$ (C)

Therefore, the spectrum on the second wave is formed only when the electrolysis did not proceed to the end, and it is identical with the spectrum obtained on the first wave. For the equilibrium constant of reaction (C), we calculated from the difference of the $E_{1/2}$ values of the first and second wave the value of $K = 4 . 10^9$. From the analysis of ESR spectra of compounds of type I follows a splitting to a triplet from a nucleus with the spin 1 (N_{19}) and to two triplets from two couples of equivalent nuclei $(H_{C_{14}}, H_{C_{18}}, \text{ and } H_{C_{15}}, H_{C_{17}})$. Each line is further splitted to an ill-separated doublet from a nucleus with the spin 1/2 $(H_{C_{11}})$. The assignment of the splitting constants was done on the basis of the calculation of spin populations;

owing to the fact that ESR spectroscopy is a sensitive method for the determination of electron delocalization and thus for the determination of steric effects in the molecule, on which the HMO parameters depend, the calculations were carried out with respect to possible prolonging or torsion of the bonds $C_{11}\text{---}C_{12}$ and $C_{12}\text{---}C_{13}$ with various values of the resonance integrals for these bonds (Table II). The calculated spin populations were used to calculate the splitting constants according to the following relations:

$$a_N(NO_2) = 99.0\varrho_N - 71.6\varrho_0 \,, \tag{1}$$

$$a_H^i = Q_{CH}^H |\varrho_{C_i}| = 27.0|\varrho_{C_i}| \,. \tag{2}$$

The constant for the $\sigma - \pi$ spin polarization Q_{CH}^H was determined as follows: For p-substituted nitrobenzene derivatives, the sum of the splitting constants of protons in $ortho$ and $meta$ positions is constant[5,6]. A change of the β-integral of the $C_{12}\text{---}C_{13}$ bond is analogous to an exchange of the substituent in p-position. Hence, we can write for n values of this integral (Table II):

$$Q_{CH}^H = (a_H^0 + a_H^m)/\left[(1/n)\sum_{1=1}^{n}(\varrho_0 + \varrho_m)_i\right] \,. \tag{3}$$

The value of $Q_{CH}^H = -27.0$ G thus obtained lies in the range $23 - 28$ G given for anion radicals of substituted aromatic hydrocarbons.

TABLE II

Calculated Splitting Constants and $E_{1/2}$ Values for Compound Ia at Different Values of Resonance Integrals of $C_{11}\text{---}C_{12}$ and $C_{12}\text{---}C_{13}$ Bonds

Res. integral		Splitting constants				
$C_{12}\text{---}C_{13}$	$C_{11}\text{---}C_{12}$	a_H^0	a_H^m	a_H^{11}	$a_{N_2}^{NO}$	$-E_{1/2}$, V
0	1	3.82	1.30	0.00	9.34	1.07
0.4	1	3.22	0.91	0.13	7.42	0.94
0.45	1	3.10	0.82	0.15	7.04	0.91
0.5	1	2.98	0.72	0.15	6.16	0.87
1	1	1.80	0.50	0.08	3.45	0.48
1	0.5	1.27	1.19	0.26	2.28	0.26
1	0	1.01	1.47	0.00	1.78	0.13
Exp. values		3.13	0.83	0.21	6.96	0.88

The half-wave potential for the reduction of nitrobenzene derivatives in DMF can be correlated with the energy of the lowest unoccupied orbital[6]:

$$E_{1/2} = 0.85 - 4.83\varepsilon_{LFMO} . \tag{4}$$

The splitting constants for the compound *Ia* calculated for various values of the resonance integrals for the C_{11}—C_{12} and C_{12}—C_{13} bonds are compared with experimental values in Table II together with the $E_{1/2}$ values. It follows that the best agreement of the calculated splitting constants with the experimental values is obtained with the use of the values of the integrals $\beta(C_{11}$—$C_{12}) = 1$ and $\beta(C_{12}$—$C_{13}) = 0.45$. The simulated spectrum calculated on the basis of these values corresponds to the experimental one; the calculated $E_{1/2}$ value is also in a good agreement with the measurement.

For the compound *Ib*, the following results were obtained on the basis of the same values of $\beta(C_{11}$—$C_{12})$ and $\beta(C_{12}$—$C_{13})$ as above:

Split. const.	$a_N(NO)_2$	a_H^0	a_H^m	a_H^{11}	$E_{1/2}$, V
Calculated	6.80	3.00	0.77	0.25	0.89
Experimental	6.79	3.00	0.77	0.25	0.875

It follows from the comparison of the results for compounds *Ia,b* that replacement of the S atom by Se in the heterocyclic part of the molecule does not influence (in contrast to the derivatives studied by us previously[7]) their electrochemical behaviour — the reaction center for electron acceptance is here localized in the *p*-nitrobenzoyl part of the molecule, and only a small part of the density of the unpaired electron comes to C_{11} as evidenced by the low value of the splitting constant for hydrogen bonded in this place as well by theoretical calculation. The necessity of a lower value of the integral (0.45) to describe the C_{12}—C_{13} bond implies a decrease of the conjugation between both parts of the molecule. This lowering of the resonance integral can be interpreted as a prolongation of the bond, which facilitates the equilibration of the nitrophenyl. A prolongation of this bond can be expected already on the basis of results of calculations for the corresponding benzoyl derivative with the use of standard values of all C—C resonance integrals leading to a low value of the bond order (0.387). The equilibrium of phenyl can elucidate also the equivalence of the splitting constants of H atoms in *ortho* position among themselves and of H atoms in *meta* position among themselves, whereas in the case of nitrobenzaldehyde these H atoms are not equivalent owing to interaction with oxygen of the CO group[8].

Polarographic reduction of type *II* compounds proceeds in both cases similarly regardless of the replacement of S by Se atom in the heterocyclic part of the mole-

cule. The polarographic curve consists of four one-electron steps, at least the first three of which are reversible (experiments with the Kalousek switch) and their height is controlled by diffusion of the depolarizer to the electrode. The acceptance of an electron in the first wave leads to the formation of an anion radical as evidenced with the ESR spectrum (Fig. 4). This is a superposition of two spectra, as already mentioned; the character of the splitting and the splitting constants of the more intense one were experimentally evaluated (Table III). Here the splitting to a triplet from a nucleus with a spin 1 (nitrogen) and double splitting from two nonequivalent nuclei with a spin 1/2 (H atoms) is apparent. The calculations give spin populations delocalized to two nitrophenyl groups, whereas experiments suggest a splitting that can be interpreted only on the basis of an interaction between an unpaired electron and nuclei of one nitrophenyl group. The spectrum showed further the nonequivalence of both protons in *ortho* position with respect to the NO_2 group. This implies a disturbance of the conjugation of both benzene rings which deviate from the plane of the remaining conjugated part of the molecule. Therefore, doubled values of the evaluated spin populations on one nitrophenyl group were taken for the calculation of the splitting constants. A possible mutual influencing of both these parts was taken into account by changing the coulombic integrals of the adjacent C atoms and one of the O atoms of the nitro group. It follows from Table III that the best agreement with the experiments (substantiated also by the simulation of the spectrum) is attained for

TABLE III

Calculated Splitting Constants and $E_{1/2}$ Values for Different HMO Parameters (compound *IIb*) and Experimental Values

Parameters				Splitting constants					
$\beta_{C_{12}-C_{13}}$ $\beta_{C_{23}-C_{24}}$	$\beta_{C_{11}-C_{12}}$ $\beta_{C_{11}-C_{23}}$	$h_{C_{14,15}}$ $_{28,29}$	$h_{O_{21,31}}$	$a_N^{NO_2}$	a_H^{14}	a_H^{15}	a_H^{17}	a_H^{18}	$-E_{1/2}$, V
0	1	0	1.40	9.34	1.30	3.82	3.82	1.30	1.07
0.4	1	0	1.40	6.09	0.59	2.77	2.77	0.59	0.82
0.45	1	0	1.40	5.58	0.43	2.60	2.60	0.43	0.77
0.55	1	−0.2	1.40	5.11	0.30	2.47	2.11	0.29	0.75
0.55	1	−0.1	1.40	4.84	0.09	2.36	2.20	0.20	0.70
!!0.55	1	−0.2	1.37	4.47	0.37	2.40	2.02	0.22	0.72!!
0.6	1	0	1.40	4.23	0.07	2.10	2.10	0.07	0.60
0.97	0.94	0	1.40	2.03	1.35	1.15	1.15	1.35	0.20
1	0	0	1.40	1.78	1.47	1.01	1.01	1.47	0.13
1	0.94	0	1.40	1.75	1.59	1.00	1.00	1.59	0.13
Exp. values				4.60	—	2.50	2.05	—	0.72

a change of the β-integrals of the C_{12}—C_{13} and C_{23}—C_{24} bonds to 0·55, a change of the α-integrals of the C atoms 14, 15, 28, and 29 by $-0·2\beta$, and a change of the α-integral of one of the O atoms of the NO_2 group to $\alpha + 1·37\beta$. Hence we obtain an exact idea about the space arrangement of this molecule: both nitrophenyl groups deviate by an angle of 57° ($\beta' = \cos \beta$) from the plane of the molecule, whereby the mentioned C atoms and O atoms of the nitro group get into interaction. This angle corresponds to a perpendicular distance of both benzene rings of 0·2 nm. These results obtained from the ESR spectra substantiate also that we have to do with the assumed *cis-cis* isomer. In the case of the *cis-trans* isomer, the interaction between both benzene rings could no occur, hence the nonequivalence of the hydrogen atoms in *ortho* position could not take place either. The $E_{1/2}$ value calculated from these parameters is also in accord with the measurement (Table III).

The existence of two overlapping spectra during the formation of a radical anion can be atributed to the existence of a free radical anion besides its ion pair. As seen from Fig. 6, the replacement of the tetraalkylammonium cation of the base electrolyte by sodium causes a change in the spectrum, the medium line shows a splitting to a quartet while other lines become broader, an evidence for an equilibrium formation of an ion pair with sodium with a nuclear spin of 3/2. We can assume analogously an equilibrium between an ion pair and a free radical anion also when the base electrolyte cation is $(C_2H_5)_4N^+$. A decrease of the temperature affects this equilibrium and causes an increase of the intensity of the weaker spectrum (Fig. 5). From the splitting constant of the sodium quartet ($a_{Na} = 0·46$) we obtain using the value of the $\sigma - \pi$ spin polarization $Q_{Na} = 316$ G (ref.[9]) a low spin density on the ion pair cation $\varrho_{Na} = 0·0015$. Hence it follows that the ion pair formation does not influence much the splitting constants of other atoms but is rather manifested by a change of the g factor leading to the observed asymmetry of the spectrum.

The fact that the spectrum obtained during electrolysis at the potential of the limiting current of the second wave is at shorter electrolysis times identical with that obtained during electrolysis at the potential of the first wave can be attributed as in the case of type *I* compounds to a reaction between the reduced and original molecules generating a radical anion. After a longer electrolysis time another spectrum appears, observable also during electrolysis at the limiting current of the third or fourth wave (Fig. 7), in the latter case only after shorter electrolysis time. This spectrum belongs to a biradical which is formed in the second wave but reacts with the original molecule to give a monoradical anion, whereas the radical formed in the third wave reacts with the original molecule to give both mono and biradical. The diamagnetic tetra-anion formed in the fourth wave reacts with the nonreduced molecule to give detectable radicals; at a suitable degree of conversion the biradical prevails in solution. Its spectrum shows a splitting similar to the spectra of compounds *Ia,b* (triplet 1 : 1 : 1 and two doublets 1 : 2 : 1), but with somewhat different

splitting constants as follows $\left(\Delta H_{1/2}\right.$ is the line width):

Split. const.	$a_N(NO)_2$	$a_H^{15,17(26,28)}$	$a_H^{14,18(25,29)}$	$\Delta H_{1/2}$
Compound *IIa*	7·40	3·00	0·83	0·58
Compound *IIb*	7·40	3·00	0·80	0·86

It follows from the analysis of this spectrum that the exchange integral in the spin hamiltonian is close to zero and the interaction of both electrons is negligible; the molecule is formed by wo relatively independent parts which are anion radicals. The nonequivalence of *ortho* and *meta* electron pairs was not observed, apparently because the acceptance of a further electron causes an acceleration of the libration to such an extent that the protons in each proton pair appear to be nonequivalent.

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