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L. S. DEGTYAREV, L. N. GANYUK, A. M. GOLUBENKOVA,

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Abstract

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L. S. DEGTYAREV, L. N. GANYUK, A. M. GOLUBENKOVA,
Corresponding Member of the Academy of Sciences of the USSR A. I. BRODSKII

E.P.R. SPECTRA AND TRANSMISSION OF SUBSTITUENT EFFECTS IN ANION-RADICALS OF PARA-NITRODIPHENYLS

The present work was undertaken to elucidate the effect of introducing a second benzene ring on the distribution of electron densities in radicals of substituted para-nitrobenzene, as a function of the nature of the substituent. Until now, only symmetrical diphenyls with identical substituents in both para positions have been studied by the e.p.r. method: CH_3 ([1]), $N(CH_3)_2$ ([2]), NO_2 ([5,7]). We investigated the polarograms and e.p.r. spectra of the anion-radicals of a series of substituted para-nitrodiphenyls NO_2 $C_6H_4C_6H_4X$ with substituents X in the para position, listed in Table 1.

Table 1

Splitting constants ([1]), total spectral width (ΔH), and polarographic half-wave potentials ($E_{1/2}$) of substituted para-nitrodiphenyls

No.	X	$E^{5}_{1/2}$	ΔH^{7}	a_N	a^{3}_H	a_2
1	NH_2	0.119	29.5	11.1	3.6	
2	CH_3	1.109	28.4	10.6	3.6	
3	H	1.096	26.9	9.8	3.6	
4	F	0.094	28.0	(10.1)[1]	3.7	5.6[6]
5	Cl	1.062	25.9	9.6	3.3	
6	Br	1.053	54.4	9.4	3.3	
7	$COOCH_3$	0.901	24.0	8.9	3.1	
8	$COCH_3$	0.888	25.4	8.7	4.0	
9	NO_2	0.867	20.8	3.6[2]	1.3[4]	0.3[4]

[1] Interpolated from Fig. 3.
[2] Two equivalent N.
[3] Two equivalent H.
[4] Four equivalent H.
[5] In volts relative to the n. v.-c. e.

Fig. 1. EPR spectrum of 4-nitro-4′-chlorobiphenyl

Figure 1: Fig. 1. EPR spectrum of 4-nitro-4′-chlorobiphenyl

[6] Splitting on F.
[7] Between the centers of the outermost lines.

The substances had melting points coinciding with the literature data. Polarograms were recorded at concentrations of about 0.002 N in acetonitrile, with the addition of 0.1 N tetraethylammonium bromide, relative to a saturated aqueous calomel electrode at 15°. For all substances a clear potential $E_{1/2}$ of the first half-wave was obtained, corresponding to a one-electron transition with formation of the anion-radical. For the differences $E_{3/4} - E_{1/4}$, values from 52 to 70 mV were obtained, corresponding to a reversible electrode reaction ([3]). To obtain the e.p.r. spectra, the anion-radicals were generated by electrolysis of the same solutions in which the polarograms were recorded, at potentials approximately 0.1 V higher than the found $E_{1/2}$. The construction of the electrolyzer, with a capillary side arm lowered into the resonator of the spectrometer and with a drop of mercury at its bottom as the cathode, was similar to that described earlier ([4]). At a current of 7–8 μA, after 1/2 hour from the start of electrolysis, the concentration of radicals was sufficient to obtain intense e.p.r. spectra.

Para-nitrobiphenyl with substituents $X = \mathrm{NH_2}, \mathrm{CH_3}, \mathrm{H}, \mathrm{Cl}$, and Br gave identical, well-resolved spectra consisting of three triplets $(1:2:1):(1:2:1):(1:2:1)$, corresponding to splitting by N^{14} and by two equivalent H atoms in the ortho positions to the nitro group, on which the greater part of the unpaired-electron density is shifted (Fig. 1). The splitting by ortho-H also agrees with the quantum-mechanical calculation ([5]). The spectral lines have a width of 4.0–4.5 Oe, apparently owing to unresolved finer splitting by other protons, whose magnitude, according to other data ([6]), may be estimated at approximately 1 Oe.

This additional splitting is not very clearly detected in the spectra with $X = \mathrm{NH_2}, \mathrm{CH_3}$, and Cl. For unsubstituted para-nitrobiphenyl, an analogous spectrum had previously ([6]) been obtained with $a_N = 9.84$ Oe and $a_H = 3.60$ Oe (two equivalent H atoms), likewise with unresolved finer structure.

Fig. 1. EPR spectrum of 4-nitro-4′-chlorobiphenyl

The spectra of nitrobiphenyls with $X = \mathrm{COOC_2H_5}$ and $\mathrm{COCH_3}$ likewise consist of 9 lines with intensities $(1:2:1):(1.5:3:1.5):(1:2:1)$ and $(1:2:1):(2:4:2):(1:2:1)$. Their interpretation remains the same. The increased intensity of the middle triplet is apparently explained by the superposition of an additional, incompletely resolved splitting from both ortho-H atoms of the second ring bearing the substituent X, with a splitting constant comparable to a_H.

Such splitting is caused by an increase in the unpaired-electron density on this

Fig. 2. EPR spectrum of the anion-radical of 4,4′-dinitrobiphenyl. Below: the central line at high resolution

Figure 2: Fig. 2. EPR spectrum of the anion-radical of 4,4′-dinitrobiphenyl. Below: the central line at high resolution

ring, owing to the acceptor properties of the substituent.

The spectrum of 4,4′-dinitrobiphenyl ($X = NO_2$) is well resolved (Fig. 2) and consists of 17 lines with further quintet splitting of each of them. This spectrum corresponds to a quintet with $a_N = 3.6$ Oe from both N^{14} atoms, with quintet splitting $a_{H_1} = 1.3$ Oe from four ortho-H atoms, and further quintet splitting $a_{H_2} = 0.3$ Oe from four meta-H atoms. Reconstruction of the spectrum with the indicated splitting constants agrees satisfactorily with the observed intensity ratios of the 17 main lines (instead of 25 because of the overlap of coincident frequencies): $1 : 4 : 6 : 3 : 6 : 11 : 4 : 7 : 15$.... According to data ([7]), in acetonitrile $a_N = 3.45$, $a_{H_1} = 1.34$, $a_{H_2} < 0.2$. In dimethylformamide, respectively, 2.69, 1.23, and 0.20 ([5]) were obtained.

The spectrum of 4-fluoro-para-nitrobiphenyl consists of 5 poorly resolved components. If one takes $a_N = 10.1$ Oe according to Fig. 3, then with $a_F = 5.6$ Oe and $a_H = 3.7$ Oe (for two equivalent H atoms) a spectrum similar to the observed one is obtained.

Fig. 2. EPR spectrum of the anion-radical of 4,4′-dinitrobiphenyl. Below: the central line at high resolution

Table 1 compares the values of $E_{1/2}$, a_N, a_H, and the total width ΔH of the EPR spectrum.

The values of $E_{1/2}$ correlate well with the Hammett equation $E_{1/2} = \rho\sigma$ with the value of σ taken from ([6]), according to Beckwith' s comparisons ([8]) (Fig. 3). In this case two straight lines are obtained with $\rho = 0.119$ for the electron-acceptor $X = COOC_2H_5, COCH_3, NO_2$ and 0.143 for the others. The values a_N, which fall on one common straight line with $\rho =$

$= 3.653$ (Fig. 3)*. The equations of these straight lines were calculated by the least-squares method and are given in Fig. 3.

The charge density of the unpaired electron is displaced toward the nucleus bearing substituent X to a greater extent, the stronger its electron-acceptor ability. This explains the successive decrease in the splitting constant a_N, and the similarly clearly expressed decrease in a_H (for H in the ortho position to NO_2) with increasing electronegativity of substituent X. In the same sequence, the total width ΔH of the spectrum decreases, owing to the increase in the weight of structures of the type

$$^{-}O\backslash N^{+} = \leftrightarrows = \leftrightarrows = X^{-}$$

$^{-}$O/

which partially withdraw the charge of the unpaired electron from the nuclei.

Fig. 3. Correlation of the polarographic half-wave potentials and the EPR splitting constants on nitrogen according to the Hammett equation for $NO_2C_6H_4C_6H_4X$.
I $-E^X_{1/2} = 1.094 - 0.143\,\sigma_X$.
II $-E^X_{1/2} = 0.950 - 0.119\,\sigma_X$.
III $-a^X_N = 10.32 - 3.656\,\sigma_X$.
The numbering of the substituents X corresponds to Table 1.

From comparison of the EPR spectra it is seen that, with electron-donor substituents, the density of the unpaired electron is concentrated mainly on the nitrophenyl group. With acceptor substituents it is transferred, to an increasing degree, partially to the second group; and in symmetrical dinitrodiphenyl it is distributed equally between both halves of the molecule. At the same time, the splitting constants a_N and a_H decrease not by a factor of 2, but by a factor of 2.5-3, which can be explained by the formation of the quinoid structures indicated above. They are especially favored by the symmetrical arrangement of both para-NO_2 groups.

A decrease in the values of a_N and a_H by several times on going from nitro- to para-dinitro derivatives of benzene was observed earlier ([5,6]). As was to be expected, for benzene compounds it is much more strongly expressed than for diphenyl compounds.

Comparison of the a_N values for para-nitrodiphenyls with those obtained by Maki and Geske ([6]) for para-nitrobenzenes makes it possible to estimate the weakening of transmission of substituent influence upon inclusion of a second benzene ring in the chain. The values a_N for para-nitrodiphenyls as a function of the value a'_N for para-nitrobenzenes with the same substituents fit well on the straight line

$$a_N = 5.61 + 0.424\,a'_N,$$

whence it follows that $\rho/\rho' = 0.42$. A similar comparison for the polarographic $E_{1/2}$ gives $\rho/\rho' = 0.24$. These data are close to those obtained earlier ([11]) for the dissociation constants of the acids $X \cdot C_6H_4 \cdot COOH$ and $X \cdot C_6H_4 \cdot C_6H_4 \cdot COOH$ (0.37) and for the rates of alkaline hydrolysis of the corresponding ethyl esters (0.24), and also ([12]) for hydrogen exchange in the CH_3 group of ketones $X \cdot C_6H_4 \cdot CO \cdot CH_3$ and $X \cdot C_6H_4 \cdot C_6H_4CO \cdot CH_3$ (0.25).

Thus, for different types of reactions, as well as for electron transfer during cathodic reduction and for the displacement of the density of the unpaired elec-

tron, inclusion of a second benzene ring in the conjugation chain decreases the transmission of substituent influence to similar values: by a factor of 2.5–4.

* An equally good correlation is obtained with the σ values according to Jaffé ([9]), if for NO_2 one takes the value 1.27, corresponding to NO_2 conjugated in the benzene ring with groups in the para position to it ([10]). In both scales, for NO_2 in dinitrodiphenyl, the doubled $a_N^{NO_2}$ is taken, corresponding to the two NO_2 groups in the molecule.

Further details and a quantum-mechanical calculation of the splitting constants in the EPR spectra of the compounds studied will be given in a more detailed publication.

Institute of Physical Chemistry named after L. V. Pisarzhevsky
Academy of Sciences of the Ukrainian SSR

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Note: Figure translations are in progress. See original paper for figures.