DISTRIBUTION OF THE ELECTRON DENSITY IN ANION-RADICALS CONTAINING TRIARYLPHOSPHAZO GROUPS

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Preceding investigations [1-3] have established the existence of a single π-conjugation system in anion-radical phosphazoarenes of the type $(n\text{-}RC_6H_4)_2(n\text{-}R'C_6H_4)P=NC_6H_4NO_2\text{-}n$ with $R=R'=H$. In principle, such a system should be sensitive to the nature of R and R'. In the present work a study was made of the effect of the substituents R and R' on the distribution of the spin density in anion-radicals of phosphazoarenes I-VIII (see Table 1).

As is evident from the splitting constants in the electron paramagnetic spectra of anion-radicals I-V (a typical paramagnetic resonance spectrum is shown on Fig. 1), the introduction of the electron-donor substituents R and R' does not break down the π-electron system characteristic for compound IX; in all cases there is splitting in the P^{31} nucleus. In this case, however, it decreases appreciably in comparison with anion-radical IX, and attains a minimal value in the anion-radicals IV and V, where the overall electron-donor effect of the substituents in an atom of phosphorus is strongest. This effect is not additive; comparison of the electron paramagnetic resonance spectra for the anion- radicals II-V, IX, and $[n\text{-}(CH_3)_2NC_6H_4]\cdot(C_6H_5)_2P=NC_6H_4NO_2\text{-}n$ ($a_P = 3.4$ Oe [2]) shows that only with the replacement of one phenyl ring by a stronger electron-donor group is there a drop in the value of a_P. We assume that precisely this group is included in the overall system of a π conjugation in place of a substituted phenyl ring, since the coordinated mesomeric effect of the groups $R'=N(CH_3)_2$, OCH_3, and CH_3, and of the positively charged phosphorus makes possible a direct polar conjugation between these centers, and makes preferential the inclusion of the $n\text{-}R'C_6H_4P=$ group in the π system. In view of the low values of the splitting constants at the protons of the aryl groups for an atom of phosphorus (around 0.2 Oe [2]) and, obviously, of the still smaller splitting constants at N^{14} of the amino group with $R'=N(CH_3)_2$, we have not been able to verify this assumption. With an increase in the number of electron-donor groups, the value of a_P does not change, but the value of a_N rises successively, which argues for an increasing supply of spin density to the nitro group.

The hyperfine splitting in the P^{31} nucleus in the anion-radicals of phosphazo compounds, in the opinion of the authors, cannot be explained on the basis of any mechanism other than a $d_\pi-p_\pi$ conjugation. In the anion-radical of 1-phospha-3,5-dioxa-4-(p-nitrophenyl)bicyclo[2.2.1]heptane [4], where there is no conjugation between the p-nitrophenyl group and the phosphorous-containing ring, the spin density is localized only in the anion-radical (the electron paramagnetic resonance spectrum contains 27 lines, and the splitting is of the type $3_1 \times 3_{1/2} \times 3_{1/2}$, where the lower number is the spin of the corresponding nucleus). Here the transfer of spin density to β nuclei by the mechanism of hyperconjugation [5] is excluded. The absence of splitting in the P^{31} atom in the anion-radical of triphenyl phosphazosulphenyl-p-nitrophenyl [1] makes improbable the mechanism of spin polarization with respect to nonbonding orbitals [6]. Finally, the fraction of $p_\pi p_\pi$ binding in four-coordinated phosphorus is obviously far less than the $d_\pi p_\pi$ binding, and cannot ensure transfers of spin density to the phosphorus; a calculation of the model compound $H_3PNC_6H_5$ using the Hofmann method showed that the 84% π population of the P=N bond is due to overlapping of the $2p_\pi$ orbital of nitrogen and the $3d_\pi$ orbitals of phosphorus.

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TABLE 1. Spectral Characteristics of the Anion-Radicals $(n\text{-}RC_6H_4)_2\ (n\text{-}R'C_6H_4)P=NC_6H_4NO_2\text{-}n$

Compound	R	R'	Splitting constants, Oe			
			a_{NO_2}	a_P	$a_{H_1}^*$	a_{H_2}
I	OCH_3	OCH_3	11,8	4,5	3,5	1,1
II	CH_3	CH_3	12,0	4,5	3,5	1,1
III	H	CH_3	11,6	4,5	3,5	1,1
IV	$N(CH_3)_2$	$N(CH_3)_2$	12,0	3,4	3,4	1,1
V	$N(CH_3)_2$	H	11,8	3,4	3,3	1,2
VI	Cl	Cl	11,7	5,7	3,3	1,1
VII	Cl	H	10,9	4,9	3,2	1,1
VIII	H	Br	11,7	4,6	3,6	1,0
IX	H	H	11,5	4,7	3,25	1,25†
X	H	CF_3	11,20	4,5	3,5	1,0†
XI	CF_3	H	10,9	5,2	3,2	1,0†
XII	CF_3	CF_3	12,20	—	3,37	1,12†

Accuracy of measurements ± 1 Oe, except for literature data.

* In the o-position to the nitro group.

† Data of [2] and [3]. In the spectrum of XII there is observed the split $a = 1.1$ Oe in a nucleus with the spin $J = 1$.

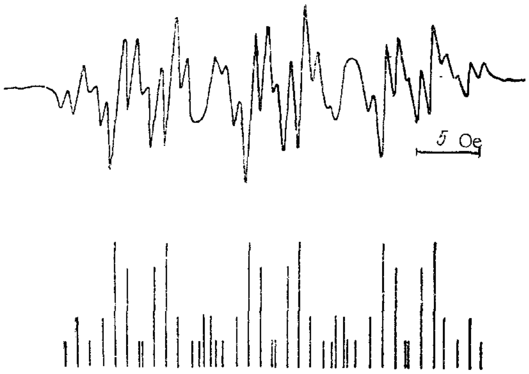

Fig. 1. Electron paramagnetic spectrum of anion-radical I in acetonitrile. Background 0.1 M solution of $(C_4H_9)Br$.

Splitting in the P^{31} nucleus is observed also in the case when p-halogen phenyl groups are located at the phosphorus atom (R, R' = Cl or Br, anion-radicals VI–VIII; these substituents are equivalent in their effect since their constants σ_Φ are practically identical [7]); the splitting increases with an increase in the number of groups, obviously the result of a growth of the positive charge on the atom of phosphorus, in accordance with an inductive mechanism. Accordingly, in the anion-radical VII there is a slight decrease in the constant a_N; both of these regularities have been observed earlier [3] with $R = CF_3$ (anion-radical XI). However, with R = R' = Cl, in distinction from anion-radical XII, breaking of the conjugate bond between P and N is not observed. This difference in the effects of the p-Cl and p-CF_3 groups can be explained by two factors: the weaker σ-acceptor character of the Cl group [8] and the presence in it of π-donor properties due to one of the unshared pairs. It is possible that, in the anion-radical state, when the ability of the 3d-orbitals of phosphorus to form conjugate bonds with all the substituents is high, this π-donor effect is found to be sufficient to maintain the total π conjugation of the system; correspondingly, the spin density in the nitro group and the constant a_N increase somewhat.

It would be of interest to follow the connection between the changes in a_P in the anion-radicals III–XI with the quantitative characteristics of the effect of the R groups. However, the values of a_P do not correlate either with the constants σ_Φ of C_6H_4R-p taken from [7], or with the constants σ^+, σ^-, or σ^0 [8]. It appears to us that the correlations of the constants of the hyperfine splitting in the nuclei P^{31} and N^{14} with the σ constants do not transmit to a sufficient degree the regularities of the π-electron interaction in anion-radicals of phosphazoarenes. However, the following qualitative explanation of these regularities may be put forward.

The experimental and calculated data of the present authors [2, 9], in accordance with general theoretical considerations, show that the π-electron system under consideration consists of five centers $RAr \cdots P \cdots N \cdots Ar \cdots NO_2$ ($Ar = C_6H_4$). It is obvious that in this system an atom of trivalent nitrogen may give up part of its electron density either to a nitrogen atom of the phosphorus, in accordance with the scheme of a $d_\pi - p_\pi$ conjugation, or to a p-nitrophenyl radical; the mobility of the π electrons of amine and imine nitrogen is well known. Since a phosphazo group in an aromatic ring has a donor character [10], direct polar conjugation between it and a nitro group may exist. Its existence is confirmed by an analysis of the values of the infrared frequencies $\nu^{as}_{NO_2}$ which, as is well known, are sensitive to the nature of the substituents. According to the data of [8, 11], the dependence of $\nu^{as}_{NO_2}$ on the value of σ_n for the substituents cannot always be well expressed by a linear function, since the value of σ_n itself is not constant, but is connected with the "indicator" group which is used to determine it by direct polar conjugation. In molecules of triarylphosphazo-p-nitrobenzenes, the frequency $\nu^{as}_{NO_2}$ is sharply lowered in comparison with the value of $\nu^{as}_{NO_2}$ for nitrobenzene, and even for p-nitroaniline; for example, in the infrared spectrum of I the value of $\nu^{as}_{NO_2} = 1488\ cm^{-1}$. Since R and R' are electron-donor groups, their electronic effect and the C effect of the phosphazo group are directed identically; it is impossible to separate the two effects. As a result, the electron density in the nitro group in anion-radicals I-V is increased in comparison to IX. With "liberation" of the electrons of the imine nitrogen, with their smaller participation in the P=N bond, the C effect should be reinforced. Therefore, in anion-radicals XII, the value of a_N rises in jumps since, with breaking of the system of conjugated bonds, there is nothing to prevent the transition of the electron density to the nitro group. In this case, the electron-acceptor properties of the p-$CF_3C_6H_4$ groups are not favorable to their interaction with the 3d orbitals of phosphorus since, in the anion-radical state, the latter can be partially populated. If R or R'=H, in a π system there must be the participation of the phenyl ring, as a donor group, and the changes in a_N and a_P will be mainly due to the increased electronegativity of the substituents at the phosphorus. Actually, in the anion-radicals VII and XI, the value of a is lower, and the value of a_P higher, than in IX.

EXPERIMENTAL

Previously known [12] and newly synthesized triarylphosphazo-p-nitrobenzenes were obtained by the action of tertiary phosphines on p-nitrophenylazide:

$$R_3P + N_3C_6H_4NO_2\text{-p} \xrightarrow[-N_2]{} R_3P{=}NC_6H_4NO_2\text{-p}$$

Triarylphosphazobenzenes (I, VI-VIII). To a solution of 0.001 g-mole tertiary phosphine in 5 ml of benzene was added 0.001 g-mole of p-nitrophenylazide. After the evolution of nitrogen had stopped, the solution was heated for 2-3 min up to 60-70°C, and the benzene was evaporated off in a vacuum. The oily residue was recrystallized by trituration with alcohol (I, VI, VII) or with an aqueous solution of alcohol (VIII).

Tri-p-chlorophenylphosphazo-p-nitrobenzene (VI). Yield 40%. mp 197-200° (dioxane + alcohol + water). Found, %: N 5.38; 5.31. $C_{24}H_{16}Cl_2N_2O_2P$. Calculated, %: N 5.58.

Di-p-chlorphenylphenylphosphazo-p-nitrobenzene (VIII). Yield 69%. mp 158-160° (dioxane + alcohol + water). Found, %: Cl 14.97; 14.93. $C_{24}H_{17}Cl_2N_2O_2P$. Calculated, %: Cl 15.20.

p-Bromophenyldiphenylphosphazo-p-nitrobenzene (VIII). Yield 65%. mp 108-110° (aqueous alcohol). Found, %: Br 16.68; 16.52. $C_{24}H_{18}BrN_2O_2P$. Calculated, %: Br 16.77.

Tri-p-methoxyphenylphosphazo-p-nitrobenzene (I). Yield 67%. mp 127-128° (dioxane + alcohol + water). Found, %: N 5.53; 5.55. $C_{27}H_{25}N_2O_5P$. Calculated, %: N 5.73.

The anion-radicals were generated by an electrochemical method in acetonitrile [1]; the back single-electron reduction of phosphazoarenes was established polarographically. The electron paramagnetic resonance spectra were recorded on RÉ-1301 and JES-EM-3BS instruments, and the infrared spectra in a UR-20 instrument in a solution of CCl_4. The authors thank L. N. Ganyuk for his help in recording the electron paramagnetic spectra, and É. S. Kozlov for supplying the 1-phospha-3,5-dioxa-4-(p-nitrophenyl)-bicyclo[2.2.1]heptane.

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