A COMPARISON OF THE ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF THE ANION RADICALS OF PIAZTHIOLE AND PIAZSELENOLE AND THEIR α,β-DICHLORO DERIVATIVES

S. P. Solodovnikov and Z. V. Todres

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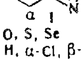
It has been shown by a comparison of the EPR spectra of the anion radicals of piazthiole and piazselenole and their α,β-dichloro derivatives that the density of the unpaired electron in the anion radical of piazthiole is highest at the α carbon atom.

We have previously [1] studied the EPR spectra of the anion radicals of arene-2,1,3-X-diazoles (where X = O, S, Se). To obtain the anion radicals, we reduced the corresponding heterocyclic compounds with potassium, or electrochemically. On the basis of an analysis of the hyperfine structure of the spectra (hfs) it was concluded that the O, S, and Se atoms of these compounds definitely participated in conjugation. We confirmed these conclusions by calculations of spin densities using the molecular orbital method. The results that we obtained agreed basically with those of Strom and Russell [2]. The magnitudes of the hfs constants of the protons in the α and β positions of the anion radical of piazselenole (I, X = Se, Y = H) proved to be equal and those in the anion radicals of benzofurazan (I, X = O, Y = H) and piazthiole (I, X = S, Y = H) proved to be different. Atherton and Ockwell [3] have also recently found some difference (0.83 G) in the hfs constants from the α and β protons in the anion radical of piazselenole. The authors connect this result with the better resolution in the spectra that they achieved [3] and with the difference in the methods of obtaining anion radicals as compared with that of Strom and Russell [2].

Orbital calculations were carried out for all three cases [1–3] and greater values of the spin densities were assigned to the α positions of the corresponding anion radicals of compounds of series (I).



I

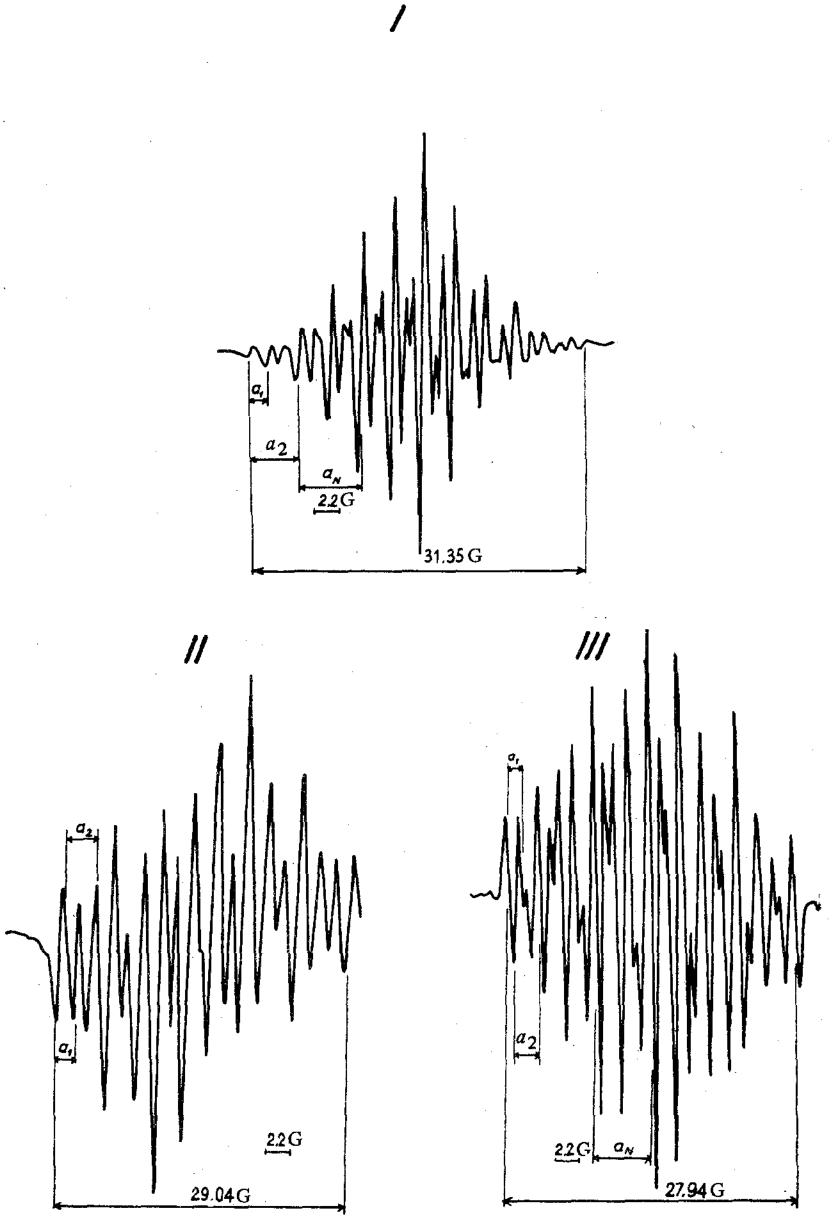
X = O, S, Se
Y = H, α-Cl, β-Cl

However, in the results obtained by these authors [2, 3] and also in our own [1] we find some indefiniteness. It consists in the fact that the calculation of the distribution of spin densities at various values of the Coulomb integral α_X and the exchange integral β_{NX} of the key heteroatoms O and S gives in some cases the inequality $\rho_\alpha > \rho_\beta$ and in other case $\rho_\beta > \rho_\alpha$. In the case of the inequality $\rho_\alpha > \rho_\beta$, we have a kind of spin density distribution analogous to that of the anion radical of naphthalene [4]. This inequality is observed at $\beta_{NX} = \beta_{CC}$ and $\beta_{NX} = 1.5\,\beta_{CC}$, i.e., in a model which permits the participation of the heteroatom in conjugation. If, however, we take $\beta_{NX} = 0.5\,\beta_{CC}$ or $\beta_{NX} = 0$, which corresponds to the weakening or even the absence of conjugation through the key heteroatom, then when α_X or α_N is changed (in the case in which $\beta_{NX} = 0$) there are regions where the inequality $\rho_\beta > \rho_\alpha$ is valid. In this latter case, the spin density distribution already approximates to the type of o-benzosemiquinone [5].

The values of the molecular orbital parameters are known only approximately, and they change for different types of compounds, while the calculations themselves are approximate. Consequently, the theoretical assignment of the spin densities found experimentally to the α and β positions requires additional confirmation. This confirmation is also important for judging the correctness of the views put forward on the participation of the key heteroatoms in conjugation.

With this aim, we turned our attention to the EPR spectra of the anion radicals of the α- and β- chloro derivatives of piazthiole and piazselenole (I, X = S, Se; Y = Cl). A study of the EPR spectra of the anion radicals of the chloro derivatives of p-benzoquinone [6], nitrobenzene [7], and some other compounds has shown that changes in the spin density distribution in these anion radicals as compared with the anion radicals from the corresponding unsubstituted molecules are small. The chlorine nucleus has a magnetic moment 3.5 times smaller than the magnetic moment of a proton. The spin of the chlorine nucleus is 3/2 and the spin of the proton 1/2. As a result, splitting at the chlorine atom is 1/10 of the splitting at a proton at the same value of the spin density in the nucleus. Consequently, splitting due to chlorine atoms is frequently not observed in the spectra. The replacement of a hydrogen atom in the molecule by a chlorine atom leads to the elimination of one of the proton splittings, and this changes the shape of the spectrum correspondingly. The nature of the changes mentioned depends on the position in the molecule of the proton that is being replaced by a chlorine atom. These changes can be used as additional arguments for assigning the hfs constants to one or other position in the unsubstituted molecule. The change in the other constants of the spectrum that may be observed on passing to the chloro derivative are generally insignificant.

In order to obtain anion radicals from chloropiazthioles and chloropiazselenoles, we reduced these compounds at a mercury electrode at from −10 to −20° C in dimethylformamide solution. As conducting support we used $(n\text{-}C_3H_9)_4N\cdot ClO_4$. The reduction was carried out in cells similar to those described previously [1].



EPR spectra of the anion radicals of: I) piazthiole, $a_1 = 1.6$, $a_2 = 2.9$, $a_N = 5.6$ G; II) β-chloropiazthiole, $a_1 = 1.55$, $a_2 = 2.97$ G; III) α-chloropiazthiole, $a_1 = 1.43$, $a_2 = 1.76$, $a_N = 5.28$ G.

This gave rise to paramagnetic particles the EPR spectra of which differed from the EPR spectra of the anion radicals of piazthiole and piazselenole. The extensions of the EPR spectra of the anion radicals from β- and α-chloropiazselenoles were the same at 31 G. This agrees with the equivalence of the hfs constants from the β and α protons in the anion radical from unsubstituted piazselenole recorded in the literature [1, 2]. According to Atherton and Ockwell [3], in the benzfurazan, piazthiole, and piazselenole series, the difference in the splitting constants $[a_{H\alpha} - a_{H\beta}]$ is least for the anion radical of piazselenole.

The EPR spectra of the anion radicals from piazthiole, β-chloropiazthiole (I, X = S, Y = β-Cl) and α-chloropiazthiole (I, X = S, Y = α-Cl) are shown in the figure. Without yet going into details of the analysis of the complex hyperfine structure of the spectra, we may point out the successive decrease in their total extension from 31.3 to 29.04 to 27.94 G, respectively. This decrease is connected with the replacement of the β or α hydrogen atom in the anion radical of piazthiole, which have different α_H constants, by a chlorine atom. As a result, the spectra of the chloro derivatives become narrower, this contraction being approximately equal to the values of the hyperfine splittings of the corresponding hydrogen atoms in the anion radical of piazthiole mentioned previously ($a_{H\beta} = 1.6$; $a_{H\alpha} = 2.9$ G) [1]. The result obtained independently confirms the conclusion drawn previously that an inequality of the type $\rho_\alpha > \rho_\beta$ is valid for the anion radical of piazthiole. Thus, we have succeeded in eliminating the indefiniteness mentioned above in the conclusion concerning the participation of the sulfur atom of piazthiole in the creation of a system of electrons delocalized over the molecule.

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Institute of Heteroorganic Compounds, AS USSR, Moscow

SYNTHESIS OF ESTERS OF THE FURAN SERIES

V. G. Glukhovtsev, S. V. Zakharova, and R. A. Karakhanov

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Five new esters of the furan series have been synthesized by the reaction of β-(5-methyl-2-furyl)propionyl chloride with 2-(3'-hydroxypropyl)-furan, 2-(3'-hydroxybutyl)tetrahydrofuran, and furfuryl, tetrahydrofurfuryl, and allyl alcohols in the presence of pyridine.

On being heated with saturated monohydric or polyhydric aliphatic alcohols or their alkoxides, the chlorides of furylalkanecarboxylic acids form the corresponding esters or chloro esters [1, 2]. Tetrahydrofuran and, particularly, furan derivatives in which the nuclei are not stabilized by electronegative substituents, are extremely sensitive to the action of acidic agents at high temperatures [3].

For this reason, in the reaction of β-(5-methyl-2-furyl) propionyl chloride (I) with furfuryl and tetrahydrofurfuryl alcohols and with their alkoxides, instead of the formation of the corresponding esters complete resinification of the reaction products takes place.

We have found that esters of the furan series can be obtained from I and acidophobic alcohols with a yield of ~70% if this reaction is carried out in pyridine.