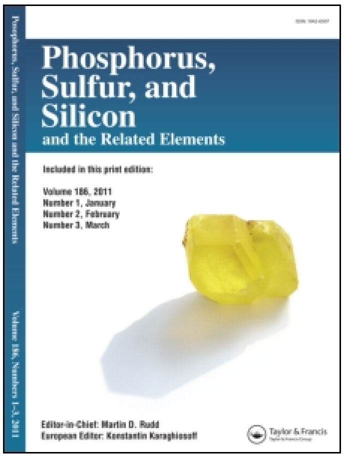

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NMR AND ESR STUDY OF PHOSPHORYLATED OXIMES AND IMINOXY RADICALS

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Abstract E,Z-isomeric forms of phosphorylated oximes were established by NMR ^{1}H, ^{13}C, ^{31}P spectroscopy. Stereospecifity of phosphorus-carbon coupling is shown to be suitable criteria for distinction of spatial isomers. The new type of phosphoniminoxy radicals was generated from these oximes and spin distribution dependencies upon phosphorus environment and spatial structure of the molecules were established.

Key words: *Phosphorylated oximes, iminoxy, structure, magnetic resonance*

INTRODUCTION

Phosphorus containing oximes and iminoxy free radicals are of great interest because of their important specific properties and biological activities. It became obvious to clarify the peculiarities of their electronic structure, the character of inter- and intramolecular interactions in this type of organophosphorus compounds. New type of iminoxy radicals with one and two phosphorus atom to unpaired electron localization center P-C=N-O were firstly described in papers.[1,2].

RESULTS AND DISCUSSION

NMR ^{1}H, ^{31}P, ^{13}C and IR-spectroscopy studies showed that phosphorylated oximes exist in solution in the form of Z- and E-isomers, and particular isomeric forms are stabilized by intramolecular interaction.[3] The chemical shifts, spin couplings ^{1}H - ^{31}P, ^{13}C - ^{31}P as well as nuclear relaxation times of ^{1}H, ^{13}C, ^{31}P strongly depend upon geometrical factors of the molecules and phosphorus atom surrounding. Typical features of NMR ^{13}C spectrum of phosphonoxime and it parameters are shown on Figure 1. Stereospecifity of phosphorus-carbon coupling in NMR spectra is clear to be a suitable criteria for distinction of spatial isomers of phosphorylated oximes.

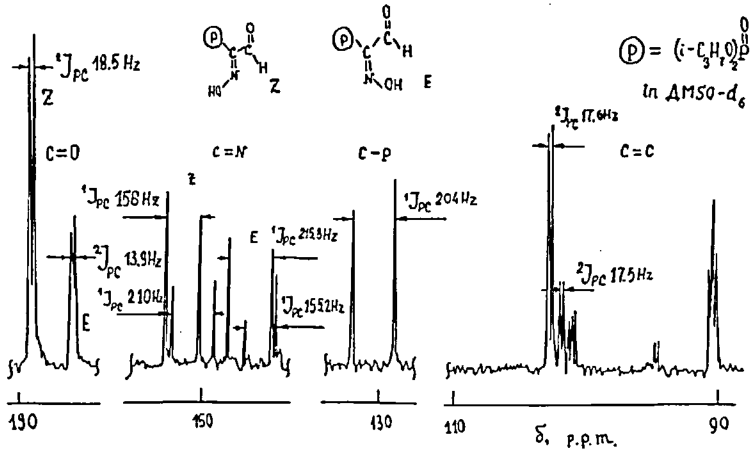

FIGURE 1. ^{13}C NMR spectra of diisopropoxyphosphoryl-α-oximinoacetaldehyde in DMSO-d^6

Iminoxyls are σ-type of free radicals with a paramagnetic fragment C=N-O·. It is known[2,3] that like the original oximes iminoxy radicals exist in two isomeric forms *Z* and *E* , marking the transition from one to the other form practically impossible. Phosphorus-containing iminoxy radicals of the $XP(O)(OR)_2C=NO\cdot$ and $[P(O)(OR)_2]_2C=NO\cdot$ types, described for the first time in [1], were produced as secondary products in the photolysis of a solution of 2-methyl-2-nitrosopropane in the presence of alkyl esters of phosphinoyliodo(bromo) acetic acid.

ESR studies showed that, like other iminoxy radicals, phosphorus-containing iminoxyls exist in two stable isomeric *syn* and *anti* forms with markedly differing values of the hyperfine coupling constants of the phosphorus atom. Iminoxy radicals with a phosphorus atom bound directly to a CNO· group have typical spectra due to hyperfine coupling of with ^{14}N and ^{31}P nuclei in two isomeric *syn* and *anti* forms of radicals (Figure 2). Parameters of ESR spectra of iminoxyl are given on Figure 3. It follows from the data obtained that the hyperfine coupling constants of the atom of the substituent at the imino carbon atom are stereospecific.

For fluorinated derivatives bearing strong electronegative substituents in aryl group spin density distributes to the fluorine atom as well. In this case it were found the small differences of fluorine hyperfine couplings in *E* and *Z* isomers. It was observed that the population of *syn* isomer exceeded the *anti* isomer one only for phosphoniminoxy with ortho-fluorine atom in aryl group. It is probably due to certain conformation position of aryl group to the unpaired electron location. In the case of bis-oximes separated by 3-6 methylene groups the usual free radical forming was established no exchange interactions being observed between radical centers.

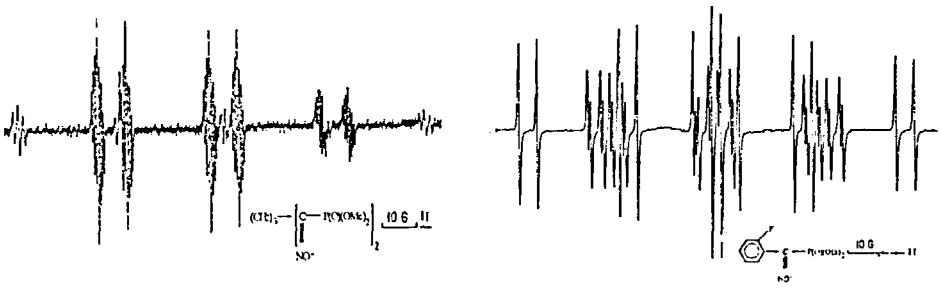

FIGURE 2. EPR spectra of the radicals in toluene, T=298K

The ratio of intensities of the ESR lines of *syn* and *anti* isomers of phosphoniminoxyl depends on the temperature, the intensities of the ESR lines of *anti* isomers decreasing with temperature, while *syn* isomers are more stable. The studies in the

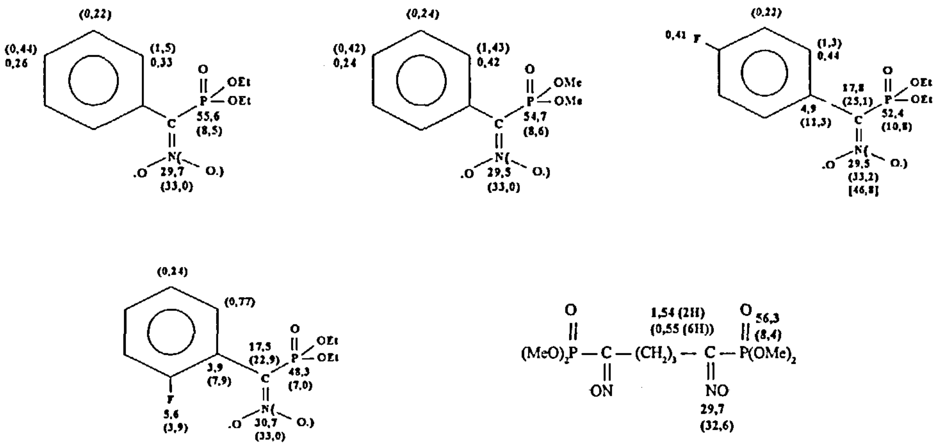

FIGURE 3. Hyperfine constants of radicals (in G). Numbers in parenthesis represent hyperfine constant for *syn*- isomer of each radical.

temperature range from -60 to +45^{o}C showed that the hyperfine coupling constants and g-factors belonging to each iminoxyl isomers do not change.

A specific feature of phosphoniminoxyls is the different relaxation characteristics that depend on the molecular geometry. For *anti* isomers of phosphoniminoxyls narrower absorption lines and longer spin-lattice relaxation times are observed compared to those of *syn* isomers. The differences in magnetic characteristics of geometric isomers of phosphoniminoxyls indicate that molecular geometry and intermolecular interactions influence significantly the ESR spectra of such systems.

In studies of spin density distribution in the series of phosphoniminoxyls[4] $R^1R^2P(O)\ CR^3=NO\cdot$ on successive substitution of groups $R^1 = R^2 = n$-BuO by n-Bu it was observed that in the *Z* isomer a^P significantly decreased (> 2 times). It should be noted that on replacement of R^1 by a less electronegativity group the stability of iminoxyls markedly decreases. A change in a^{31P} upon change in the nature of the substituent, was found also for the radicals $(R,OR)_2P(S)$-S-C -Ph_2.[5]

These new type of phosphoniminoxy radicals under investigation are certain to present the sensitive spin probes of solution parameters and conformation of surrounding molecules especially for the detection of order in biologocal tissues.

EXPERIMENTAL

The NMR ^1H, ^{13}C, ^{31}P were recorded on Bruker spectrometers WM-250 and MSL-400. Phosphoniminoxy free radicals were generated during chemical or electrochemical reactions in the special electrochemical cell.[2,6] ESR measurements of vacuumed solution of free radicals were carried out on Bruker ER 200 D spectrometer.

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