^{1}H and ^{31}P nuclear spin-lattice relaxation in C-phosphorylated oximes

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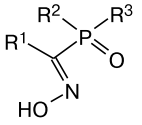
The ^{1}H spin-lattice relaxation times of the proton-bearing groups and the ^{31}P spin-lattice relaxation times in C-phosphorylated oximes $R^1C(=NOH)P(=O)R^2R^3$ (R^1 = Ph, $R^2 = R^3$ = OMe; R^1 = Ph, R^2 = OMe, $R^3 = OCH_2CH_2Br$; $R^1 = PhCH_2$, $R^2 = R^3 = OCHMe_2$) and dioxime $R_2P(=O)C(=NOH)(CH_2)_4C(=NOH)P(=O)R_2$ (R = OMe) in DMSO-d_6 were measured. The characteristic reorientation times of the whole molecules were estimated using the measured values of the ^{1}H relaxation times and the results of semiempirical PM3 quantum chemical calculations of the molecular geometries. The reorientation times were used to identify the contributions of different relaxation mechanisms to the rate of ^{31}P spin-lattice relaxation. The anisotropy of the chemical shielding of ^{31}P nuclei was evaluated from the difference between the ^{31}P relaxation rates measured at 101.27 and 161.92 MHz.

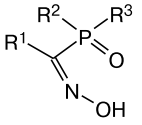
Key words: nuclear magnetic resonance, nuclear magnetic relaxation, spin-lattice nuclear relaxation, oxime, C-phosphorylated oximes.

Oximes are widely used in synthetic, analytical, and coordination chemistry as pharmaceuticals and antidots, plant growth regulators, sources of iminoxyl free radicals, *etc*.[1—6] Among various groups of oximes, an important role is played by phosphorus-containing oximes. Increasing interest in these compounds is due to the extension of synthetic potential provided by phosphorus-containing substituents (see, *e.g.*, Ref. 5) and to the fact that many of them are biologically active (insecticides, phosphonocefems, *etc*.).[4]

Phosphorylated oximes are of particular interest because the iminoxyl radicals generated from them show the interaction of the phosphorus atom with the radical center,[6—8] which depends on their mutual arrangement. In this connection, considerable attention was paid to studies of the molecular and electronic structures of C-phosphorylated oximes.[9—14] It was shown that these, like other types of oximes, can exist in solutions as $E_{C=N}$- and $Z_{C=N}$-isomers irrespective of the nature of substituents in the phosphorus-containing and carbon fragments. Usually, $Z_{C=N}$-isomers of the α-phosphorylated oximes are stabilized by the intramolecular hydrogen bond P=O···HO. This results in flattening of the phosphoryl imine oxime fragment of the molecule and to an increase in the barrier to internal rotation about the =C—P= bond (an increase in the "rigidity" of the phosphoryl hydroxyimine fragment).



E-Isomer



Z-Isomer

Parameters of the ^{31}P, ^{13}C, and ^{1}H NMR spectra of the isomers are noticeably different.[9—14] The most stereodependent are the direct ($^{1}J_{P,C}$), geminal ($^{2}J_{P,C}$), and vicinal ($^{3}J_{P,C}$) spin-spin coupling constants.

Application of nuclear magnetic relaxation spectroscopy to the solution of structural chemistry problems allows one to assess not only the molecular structure and conformations, but also the dynamics of the whole molecule and its fragments. In the present work, we report the results of a study on the mechanisms of ^{31}P and ^{1}H nuclear spin-lattice relaxation and on the parameters of their mag-

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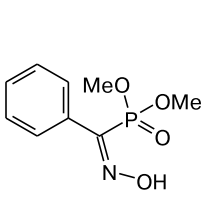

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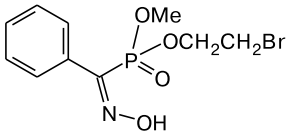

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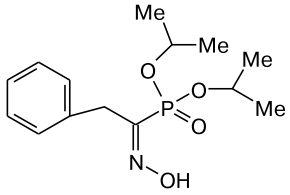

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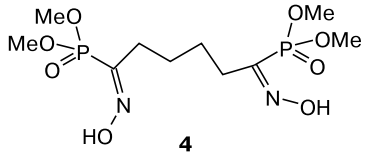

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netic interactions resulting in relaxation in dilute solutions. Measurements were carried out for dimethyl hydroxyiminobenzylphosphonate (**1**), 2-bromoethyl methyl hydroxyiminobenzylphosphonate (**2**), diisopropyl (1-hydroxyimino)-2-phenylethylphosphonate (**3**) with different environments of the phosphorus atom, and for tetramethyl 1,6-bishydroxyiminohexane-1,6-diyldiphosphonate (**4**) in which the phosphoryl groups are separated by the C_6 spacer.

Experimental

In the present work, we used the same samples of oximes **1—4** as those previously used[7] in an EPR study of iminoxyl radicals generated from them. The spectroscopic and other physicochemical characteristics of the samples of oximes **1—4** agreeed with the published data.[7,13—15] The concentrations of the oximes in solutions in DMSO-d_6 were 3 mass % for **1**, **3**, and **4** and 5 mass % for **2**. The low concentrations of the oximes **1—4** are due to their poor solubilities. DMSO-d_6 (Isotope Joint Stock Company, Russia; degree of substitution 99.5%) was used as purchased. Samples were placed in standard 5-mm tubes, degassed under high vacuum using the freeze—pump—thaw cycle, and then sealed.

The ^{1}H nuclear spin-lattice relaxation rates were measured on a conventional Bruker WM-250 NMR spectrometer at 250 MHz using the inversion—recovery technique (π—t—$\pi/2$ pulse sequence) under broadband noise-modulated suppression of the ^{31}P NMR spectrum. The ^{31}P nuclear spin-lattice relaxation rates were determined with Bruker WM-250 and MSL-400 NMR spectrometers operating at 101.27 and 161.92 MHz, respectively, using the same pulse sequence under broadband noise-modulated suppression of proton lines. The recovery time of the nuclear polarization between the pulse sequences was ~10T_1. The

Table 1. Experimental rates of ^{1}H spin-lattice relaxation (R_1/s^{-1}) of proton-containing groups in *Z*-isomers of oximes **1—4**

Compound	C_6H_5			CH_2	CH_3	=NOH
	ortho	*meta*	*para*			
1	0.36±0.02	0.36±0.02	0.36±0.02	—	0.38±0.02	5.00±0.25
2	0.43±0.02	0.43±0.02	0.43±0.02	—[a]	0.40±0.02	1.33±0.10
3	0.34±0.02	0.34±0.02	0.33±0.02	2.00±0.10[b]	0.63±0.03	2.00±0.15
4	—	—	—	2.51± 0.1	0.36±0.02	2.94±0.15

[a] Not determined.
[b] ^{1}H nuclear spin-lattice relaxation rate of hydrogen atoms in the CH_2 group of the benzyl fragment.

Table 2. Characteristics of ^{31}P nuclear relaxation in the *Z*-isomers of oximes **1—4**

Compound	$R_1(^{31}P)^a/s^{-1}$		$\tau_c{}^b \cdot 10^{11}$/s	$R_{1dd}(^{31}P)^c \cdot 10^2/s^{-1}$	$R_{1\sigma}{}^d/s^{-1}$		$\Delta R_1{}^e/s^{-1}$	$\Delta\sigma^f$, ppm
	ν_1	ν_2			ω_1	ω_2		
1	0.27(0.01)	0.31(0.01)	6.00(0.32)	4.88(0.24)	0.03(0.01)	0.08(0.01)	0.19(0.02)	103.5(5.6)
2	0.40(0.03)	0.59(0.02)	7.18(0.39)	5.70(0.29)	0.12(0.01)	0.31(0.04)	0.22(0.03)	181.8(12.2)
3	0.29(0.02)	0.48(0.01)	6.50(0.24)	4.32(0.22)	0.12(0.01)	0.31(0.04)	0.13(0.02)	171.9(13.2)
4	0.48(0.03)	0.52(0.02)	9.33(0.31)	6.05(0.42)	0.03(0.01)	0.07(0.01)	0.39(0.04)	62.1(6.1)

[a] ^{31}P nuclear relaxation rates at the resonance frequencies ν_1 = 101.27 and ν_2 = 161.92 MHz.
[b] Correlation times.
[c] ^{31}P nuclear relaxation rates due to the dipole-dipole interaction with protons.
[d] ^{31}P nuclear relaxation rates due to the interaction with the anisotropy of the chemical shift $R_{1\sigma}(\omega_1)(\nu_1$ = 101.27 MHz) and $R_{1\sigma}(\omega_2)(\nu_2$ = 161.92 MHz).
[e] The total contribution of the scalar and spin-rotational mechanisms of ^{31}P nuclear relaxation $\Delta R_1 = R_1 - (R_{1\sigma} + R_{1dd})$.
[f] Parameter of anisotropy of the ^{31}P chemical shielding in *Z*-isomers of oximes **1—4**.

recovery time of signals between the π and π/2 pulses increased to $5T_1$. The average error in measurements of the ^{1}H and ^{31}P nuclear relaxation rates was about 5%. In the course of measurements, the temperature of the samples was maintained at 295 K using the standard temperature accessories.

The measured ^{1}H and ^{31}P nuclear spin-lattice relaxation rates $R_1 \equiv T_1^{-1}$ for oximes **1**—**4** are listed in Tables 1 and 2, respectively.

Results and Discussion

In a system comprising two different nuclei with the spins $I = 1/2$ and $S = 1/2$, the change in the longitudinal magnetization is described by the system of coupled differential equations[16]:

$$dI_z/dt = -R_1^I(I_z - I_z^T) - r_1^{IS}(S_z - S_z^T),$$

$$dS_z/dt = -R_1^S(S_z - S_z^T) - r_1^{SI}(I_z - I_z^T), \quad (1)$$

where I_z^T and S_z^T are the equilibrium values of I_z and S_z at the temperature T; R_1^I and R_1^S are the rates of longitudinal relaxation that is due to all types of interactions of the spins I and S, respectively; and r_1^{IS} and r_1^{SI} are the rate constants for cross-relaxation due to the dipole-dipole interaction between the spins I and S, respectively.

Under resonance saturation of a spin system (*e.g.*, I), the multiplet spectrum of the spin system S disappears and the cross-relaxation contribution to the spin-lattice relaxation of the spin system S vanishes. Recovery of the longitudinal magnetization after application of the pulse sequence π—t—π/2 is described by the exponential function

$$S_z = S_{z\eta}^T[1 - 2\exp(R_1^S t)], \quad (2)$$

where $S_{z\eta}^T$ is the enhanced value of the longitudinal magnetization. In addition, saturation of a spin system causes the cross-relaxation contribution to the relaxation of the other spin system to vanish and removes the spin-spin splitting of spectral lines.

In the highly dilute solutions studied in the present work, the molecules of oximes **1**—**4** are at rather long distances from one another and surrounded by a layer of DMSO-d_6 molecules containing deuterium nuclei. The hydroxyl groups of the oxime fragments of the *Z*-isomers are involved in intramolecular hydrogen bonds and (weakly) in association through intermolecular hydrogen bonds. Therefore, the contribution of intermolecular dipole-dipole interactions to the ^{1}H and ^{31}P nuclear relaxation can be neglected and the measured ^{1}H and ^{31}P nuclear relaxation rates are due to intramolecular magnetic interactions.

The room-temperature ^{31}P and ^{1}H NMR spectra showed that the solutions of oximes **1**—**4** in DMSO-d_6 mainly contain *Z*-isomers. For instance, the *Z*/*E* ratio for the oxime **2** is 67 : 33. Similar *Z*/*E* ratios were found for the other oximes studied. According to semiempirical PM3 calculations,[17] the *Z*-configuration of the oxime molecule whose hydroxyl group is involved in the formation of an intramolecular hydrogen bond with an adjacent group is energetically more preferable. The barrier to rotation about the double bond C=N in oximes is estimated[17—19] from 30 to 140 kJ mol^{-1}. This suggests no free interconversion of *Z*- and *E*-isomers at room temperature and was confirmed by the test ^{1}H NMR spectra. Based on the aforesaid, all measurements and discussion in the present work are concerned only to the *Z*-isomers of oximes **1**—**4**.

From the standpoint of the problems posed, oximes **1**—**4** have complex molecular structures. They contain hydroxyl, phenyl, methyl, and methylene groups. The methyl groups are involved in internal rotation about the corresponding axes of symmetry while protons of the hydroxyl groups are involved in proton exchange. In addition, the molecules of oximes **1**—**3** have asymmetrical structures and their rotational motions are anisotropic and characterized by three components of rotational diffusion. The measured ^{1}H and ^{31}P nuclear spin-lattice relaxation rates are insufficient for the determination of parameters of anisotropic reorientations of the whole molecule and internal motions of particular atomic groups. However, the "rigidity" of the oximes under study is enhanced by the formation of intramolecular hydrogen bond P=O···HO in their *Z*-isomers and by hindered internal rotation of the benzene ring in oximes **1** and **2** owing to conjugation. Therefore, in the experiments we will restrict ourselves to a simplified analysis, *viz.*, the determination of the characteristic time of molecular reorientation and identification of possible ^{31}P nuclear relaxation mechanisms.

At room temperature, the solvent DMSO-d_6 has high viscosity (2.473 P). In this case, a noticeable contribution of spin-rotational interactions to the rate of ^{1}H nuclear spin-lattice relaxation of proton-containing groups is unlikely. The relaxation mechanism due to the anisotropy of the chemical shift (ACS) is inefficient for protons. The major contribution to the proton nuclear relaxation of these groups comes from the dipole-dipole interactions. Under condition of the limiting narrowing of the NMR line ($\omega\tau_c << 1$), which is met in our experiments, the contribution of dipole-dipole nuclear interactions R_{1dd} is given by:

$$R_{1dd} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{\hbar^2}{n} \sum_{i \neq j} \alpha_{ij} \gamma_i^2 \gamma_j^2 \frac{1}{r_{ij}^6} \tau_c, \quad (3)$$

where μ_0 is the magnetic constant, the sybscripts i and j enumerate the nuclei, n is the number of nuclei involved in the interaction with the ith nucleus, τ_c is the effective correlation time of dipole-dipole nuclear interactions, α_{ij} is the factor equal to 3/2 for equivalent and 1 for non-

equivalent nuclei, γ_i and γ_j are the gyromagnetic ratios of the nuclei i and j, respectively, and r_{ij} is the internuclear distance. The internuclear distances were estimated from the molecular geometries using conventional bond lengths and bond angles as the initial values.[20—22]

The numerical values of internuclear distances necessary for evaluation of the effective correlation times of dipole-dipole interactions between protons and the ^{31}P nuclei using expression (3) were determined by optimization of the molecular geometry by the semiempirical PM3 method. According to calculations, protons and the phosphorus nuclei are at rather long distances from one another. The shortest distance r_{P-H} is 2.93 Å. This is much longer than the distance between neighboring methylene protons; that is why the contribution of the dipole-dipole interactions between the ^{31}P nuclei and protons to the ^1H nuclear relaxation of methylene groups appeared to be negligible. The correlation times of the phenyl and methylene protons are somewhat different (*e.g.*, $\tau_c(CH_2) = 7.4 \cdot 10^{-11}$ s and $\tau_c(Ph) = 5.7 \cdot 10^{-11}$ s for the *Z*-isomer of oxime **3**). Different $\tau_c(^1H)$ values may be attributed to the anisotropy of rotational motion of the molecule. This confirms our assumption of the rigid structure of the phosphorylhydroxyimine fragment in the molecules of the *Z*-isomers of oximes **1—4**. Four methylene groups in the *Z*,*Z*′-isomer of dioxime **4** are characterized by equal correlation times of the dipole-dipole interaction ($\tau_c(CH_2) = 9.3 \cdot 10^{-11}$ s). Thus, the correlation time of the dipole-dipole interactions of phenyl and methylene groups can be treated as the characteristic time of reorientation of the whole molecule. Because of this, the correlation times determined will be used for analysis of the ^{31}P nuclear spin-lattice relaxation. The τ_c values averaged over the correlation times of the phenyl and methylene protons are listed in Table 2.

The electron shell of the phosphorus atom is larger than that of the hydrogen atom. Therefore, not only the dipole-dipole interactions with protons, but also the interactions of the ^{31}P nuclear magnetic moment with the anisotropic chemical shift (or shielding), as well as the spin-rotational and scalar interactions can contribute to the ^{31}P nuclear magnetic relaxation. The ^{31}P nuclear relaxation rates measured at two resonance frequencies are listed in Table 2.

The ^{31}P nuclear spin-lattice relaxation rate can be represented by the sum of the contributions of different magnetic interactions:

$$R_1 = R_{1dd} + R_{1\sigma} + R_{1Sr} + R_{1Sc}, \quad (4)$$

where R_{1dd}, $R_{1\sigma}$, R_{1Sr}, R_{1Sc} are the contributions of the dipole-dipole interaction, the interaction between the nuclear magnetic moment with the ACS, the spin-rotational interaction, and the scalar interaction, respectively. These contributions would be separated using the results of variable-temperature measurements of the ^{31}P nuclear spin-lattice and spin-spin relaxation rates. Our experiments allowed us to estimate the contribution of the ACS mechanism.

As mentioned above, the distances between the phosphorus and the hydrogen atoms are rather long. Therefore, the contribution of the dipole-dipole interactions between the ^{31}P nuclei and protons to the ^{31}P nuclear relaxation estimated using expression (3) is small (see Table 2).

The contribution of the ACS mechanism can be estimated by measuring the ^{31}P nuclear spin-lattice relaxation rate at two resonance frequencies ω_1 and ω_2. Under the limiting narrowing conditions, the contribution of the ACS mechanism is given by

$$R_{1\sigma} = (2/15)\omega^2\Delta\sigma^2\tau_c. \quad (5)$$

Here ω is the resonance frequency and $\Delta\sigma$ is the anisotropy of the chemical shielding, defined[23] as

$$\Delta\sigma = \sigma_{zz} - 0.5(\sigma_{xx} + \sigma_{yy}), \quad (6)$$

where σ_{ii} are the principal components of the screening tensor in the molecular system of coordinates ($i = x, y, z$).

The contributions of other relaxation mechanisms are independent of the resonance frequency, so one has

$$R_1(\omega_2) - R_1(\omega_1) = R_{1\sigma}(\omega_2) - R_{1\sigma}(\omega_1),$$

$$R_{1\sigma}(\omega_2)/R_{1\sigma}(\omega_1) = (\omega_2)^2/(\omega_1)^2. \quad (7)$$

If follows that

$$R_{1\sigma}(\omega_1) = [\omega_1^2/(\omega_2^2 - \omega_1^2)][R_1(\omega_2) - R_1(\omega_1)], \quad (8)$$

$$R_{1\sigma}(\omega_2) = R_1(\omega_2) - R_1(\omega_1) + R_{1\sigma}(\omega_1). \quad (9)$$

The $R_{1\sigma}(\omega_1)$ and $R_{1\sigma}(\omega_2)$ values determined using expressions (8) and (9) are listed in Table 2.

From these relationships it is clear that, using the known values $R_{1\sigma}(\omega_1)$ and $R_{1\sigma}(\omega_2)$, one would again estimate the correlation time τ_c, which characterizes the rotational motion of the molecule. However, the components of the tensor of the chemical shielding and, therefore, the anisotropy of the screening tensor for the ^{31}P nucleus in the oximes **1—4** are unknown. We thus use relationship (5) only for evaluation of the parameter $\Delta\sigma$ assuming that the correlation time τ_c is known.

Structurally, the phosphorus atom is in the rigid fragment of the molecule. As a consequence, the correlation time of the dipole-dipole interaction can be considered equal to that of the interaction between the nuclear magnetic moment and the anisotropic chemical shielding. In other words, the correlation time τ_c in expression (5) can be set equal to the effective correlation time of the

dipole-dipole interaction of protons calculated using expression (3). The $\Delta\sigma$ values thus determined are listed in Table 2.

From Eq. (4) it follows that the difference ΔR_1 between the experimental ^{31}P nuclear spin-lattice relaxation rate and the sum of the contributions $R_{1\sigma}$ and R_{1dd} equals the total contribution of the spin-rotational and scalar relaxation mechanisms. However, separation and identification of these contributions based on the results of this experiment is impossible. This task, as well as analysis of the contributions of these interactions will be done in the future.

The efficiency of the mechanism of anisotropy of the chemical shielding in nuclear magnetic relaxation increases in proportion to the squared magnetic field strength. We measured the rates of ^{31}P nuclear spin-lattice relaxation in oximes **1—4** in the magnetic fields with an induction of 5.9 and 9.4 T. As can be seen in Table 2, under these conditions the contribution of the ACS mechanism to the ^{31}P nuclear spin-lattice relaxation becomes comparable with that of the dipole-dipole interaction with protons.

At the same time, mention may be made that, owing to complexity of the molecular structure of oximes **1—4** and a complex character of motions, in determining the characteristic time of the rotational motion we restricted ourselves to a simple model, *viz.*, the model of isotropic rotational motion. This approximation is bound to be reflected in the values of the anisotropy of chemical shielding determined using the parameters of the motion. In this connection, one should compare the $\Delta\sigma$ values we have determined with the values obtained for other phosphorus-containing compounds.

In particular, this parameter was determined in an experimental study of the ^{1}H and ^{31}P longitudinal nuclear magnetic relaxation in quite a simple compound, the phosphorus-containing ion PHO_3^{2-} in an aqueous solution.[24] We found that the $\Delta\sigma$ value is in the range 115—123 ppm. The components of the tensor of the chemical shielding of the ^{31}P nucleus for phosphatidylethanolamine are[25] $\sigma_{zz} = 69$ ppm, $\sigma_{xx} = -67$ ppm, and $\sigma_{yy} = -13$ ppm. Using these values and expression (6), we found $\Delta\sigma = 110$ ppm. For dipalmitoylphosphatidylethanolamine, one has $\sigma_{zz} = 108$ ppm, $\sigma_{xx} = -81$ ppm, $\sigma_{yy} = -25$ ppm, and $\Delta\sigma = 161$ ppm.

The $\Delta\sigma$ values listed above and in Table 2 are close. This suggests that relaxation NMR spectroscopy can be as suitable as multipulse high-resolution NMR or NMR spectroscopy of single crystals and liquid crystals in the determination of this parameter.

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