

NMR ^1H , ^{13}C , ^{31}P Interpretation of Phosphorylotropic Rearrangement in N,N' -(Bis)(Diisopropoxyphosphorylamidocarbonyl)-1,10-Diaza-18-Crown-6-Ester in DMSO Solution

F.Kh. Karataeva, S.V. Efimov*, and V.V. Klochkov

Kazan Federal University, Kazan, 420008 Russia

* e-mail: Sergej.Efimov@kpfu.ru

Abstract

Phosphorylotropic rearrangement in N,N' -(bis)(diisopropoxyphosphorylamidocarbonyl)-1,10-diaza-18-crown-6-ester dissolved in DMSO was investigated by ^1H , ^{13}C , and ^{31}P NMR spectroscopy. The transition from the amide form to the phosphorylotropic form was shown to cause a simultaneous signal modification of the NMR spectra of three mentioned isotopes in all structural elements of the molecule.

Keywords: NMR spectroscopy, 1,10-diaza-18-crown-6-ester, phosphorylotropic rearrangement, temperature changes, solvent effect

Funding Information

This work was supported by the Russian Science Foundation (project no. 18-73-10088). V.V.K. acknowledges the state assignment in the sphere of scientific activities (project no. 3.5283.2017/6.7).

Introduction

Studies of low-temperature ^1H , ^{13}C , and ^{31}P NMR spectra of N,N' -(bis)diisopropoxyphosphorylamidocarbonyl)-1,10-diaza-18-crown-6-ester (DA-18-C-6, see Fig. 1) dissolved in CDCl_3 , CD_2Cl_2 , and CD_3CN in the temperature range from 193 to 293 K revealed three reproducible intramolecular processes [1]:

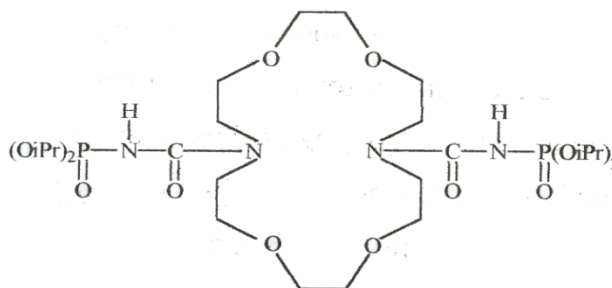
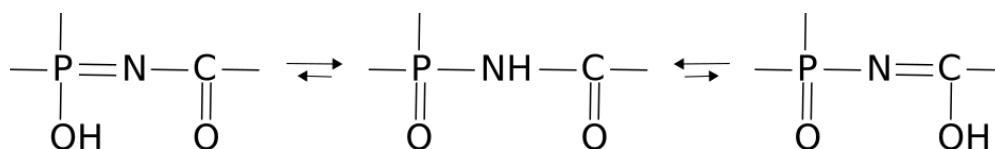


Figure 1. DA-18-C-6

- (1) Hindered rotation around the C–N bond leading to *trans*- and *cis*-rotamers (3 : 1, 248 K).
- (2) Triad prototropy in C–N–P (Scheme 1).
- (3) Macrocycle ring inversion. This process leads to appearing of two “frozen” conformations in the range of 298–223 K with the centrosymmetrical structure having the dominant *trans*-orientation of the substituents relative to the cycle symmetry plane (Fig. 2).



Scheme 1.

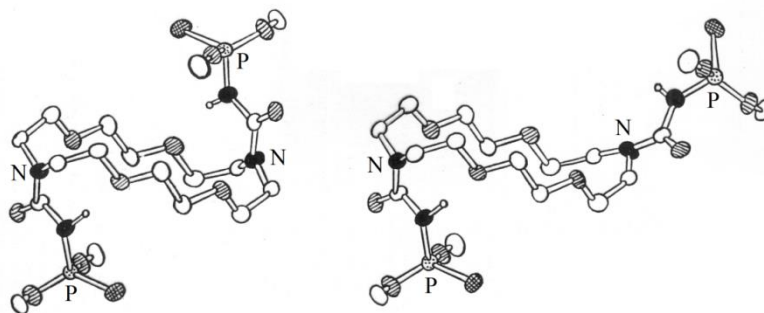


Figure 2. Two conformations of the central macrocycle

Phosphorylotropic form (B; see Fig. 3) was also observed in analogous crown esters containing P=S and C=S, P=S and C=O, or P=O and C=S bonds in amide substituents (O*i*Pr)₂P(X)NHC(Y)-. It arises due to the migration of the thiophosphoryl group to the heteroatom (O or S) at the carbon atom [2].

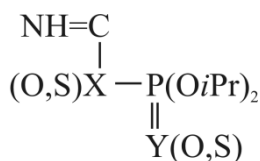


Figure 3. Form B

The fraction of this form was small (2–4%) in all cases and was temperature-independent.

Phosphorylotropic rearrangement in *N,N'*-(bis)diisopropoxythiophosphorylamidocarbonyl)-1,10-diaza-18-crown-6-ester (**II**) dissolved in DMSO was studied earlier by ¹H, ¹³C, and ³¹P NMR [3]. The choice of the solvent is justified by the possibility to increase significantly the upper limit of the temperature range (up to 373 K) and its high dielectric permittivity $\epsilon = 49$ as compared to CCl₄, CD₃CN, or (CD₃)₂CO ($\epsilon = 2.24$ –37.5). Moreover, using a more polar solvent might shift the A \rightleftharpoons B equilibrium to the right [4]. Indeed, comparative analysis of experimental data showed that the molecule experiences almost total transition from the amide form A to the phosphorylotropic form B when the solution is heated to 373 K.

Experimental

¹H (300 MHz), ¹³C (75.43) and ³¹P (121.42 MHz) NMR spectra were acquired on a Varian UNITY-300 spectrometer at different concentrations and temperatures of the solution. 10–15° pulses were used to obtain ³¹P spectra; the delays *RD* between the pulses were set to 1–2 s. Spectral width *SW* was 100 ppm; number of scans *NT* varied from 10 to 100; no digital filtering was used. 10–15° pulses were typically used in ¹³C experiments. Wideband proton decoupling was used; *SW* = 200 ppm; *NT* was in the range from 400 to 1000. Digital exponential filtering with the broadening parameter *LB* = 2–4 Hz was applied.

The solutions were prepared with the concentration of 3–5 wt % for ¹H spectroscopy and 10–15 wt % to record ¹³C and ³¹P spectra. The chemical shift referencing was made using an internal standard dissolved in the samples.

Results and Discussion

Allowing for the transition from the form A to B mentioned in the Introduction, we analyzed the changes occurring in the high-temperature ¹H, ¹³C, and ³¹P NMR spectra of *N,N'*-(bis)(diisopropoxyphosphorylamidocarbonyl)-1,10-diaza-18-crown-6-ester in DMSO. All obtained spectra show that a simultaneous transformation of the signals of corresponding structural elements occurs upon the rearrangement. First of all, this applies to the phosphorus nucleus and its closest environment: NH, O*i*Pr, and C=O groups. The NH proton signal (δ 8.0–7.94 ppm) becomes severely broadened and disappears due to the exchange in the range from 298 to 373 K. The absence of an individual signal of the =NH proton in the form B may be due to the similarity of the chemical shifts of NH and =NH protons or to a possible signal broadening as was observed for compound (**II**).

The signals of OCH protons at 293 K are two multiplets belonging to the amide (δ 4.75) and phosphorylotropic (δ 4.6 ppm) forms with the integral intensity ratio of 88.7 : 11.3 % (Fig. 4). The average value of

the scalar coupling ${}^3J_{\text{POCH}}$ is ~ 6.3 Hz. In the range of 298–373 K, the content of the form B increases to 71%, and continues to grow at 298 K after heating (85%). Thus, the phosphorylotropic rearrangement is irreversible, like in the case of *N,N'*-(bis)diisopropoxythiophosphorylamidocarbonyl)-1,10-diaza-18-crown-6-ester [3].

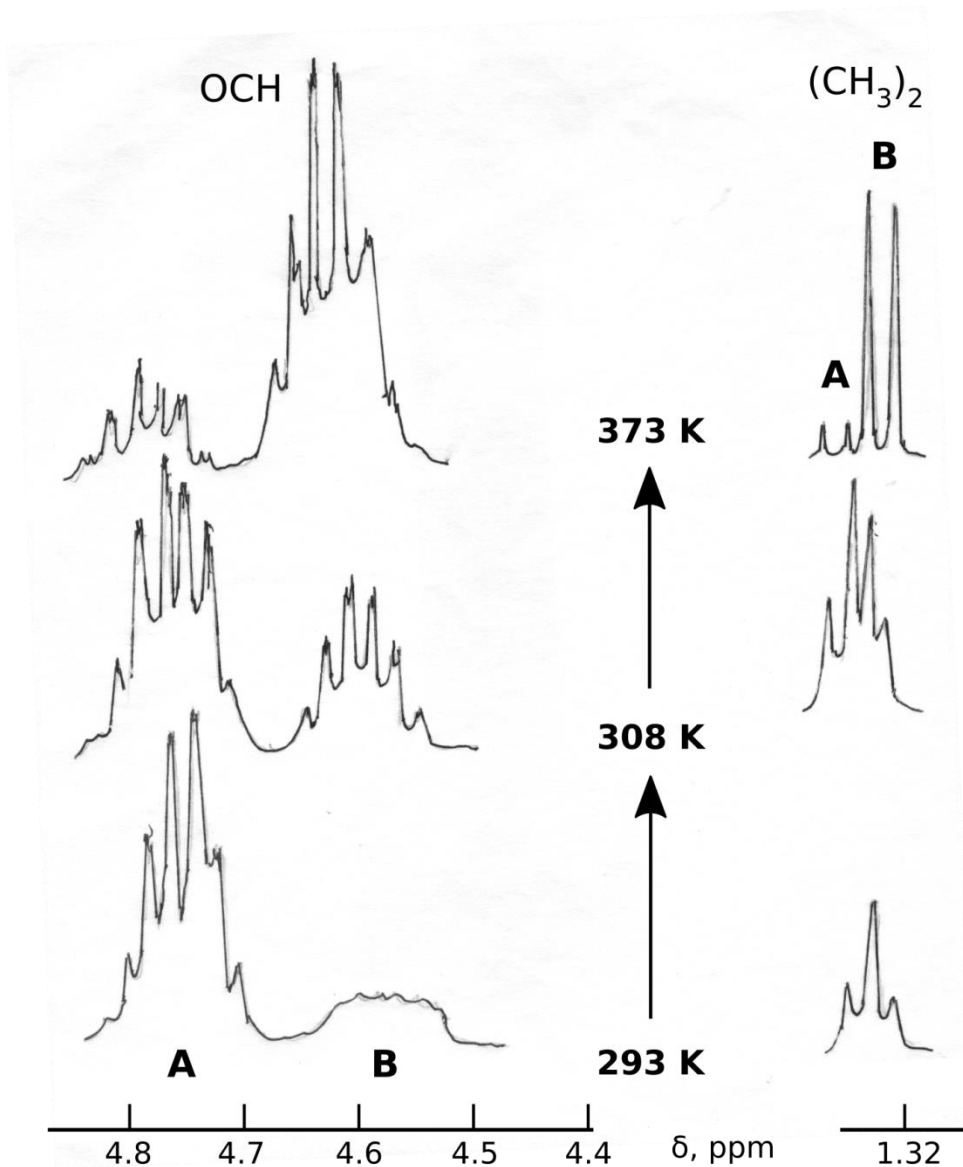


Figure 4. Temperature behavior of the ${}^1\text{H}$ NMR spectra of DA-18-C-6 (I)

The signals of methyl protons in isopropyl groups do not change their position, but show a shape transformation: from a broadened triplet at 293 K to two doublets at 373 K with the corresponding intensity ratio (Fig. 4).

Carbon signals experience corresponding changes. At 298 K the OCH ${}^{13}\text{C}$ NMR signal shows two doublets at δ 71.4 ppm with ${}^2J_{\text{POC}}$ 4.6 Hz (A) and δ 69.6 ppm (B), which have the intensity ratio of 85 : 15 %, respectively. The intensity of the doublet A decreases to 25% as the temperature grows to 373 K, and as the temperature is changed back to 293 K, the A : B ratio becomes opposite to the initial one. The methyl group signals experience similar modifications.

The key moment in the transition of *N*-(thio)phosphoryl(thio)amides from the amide form A to the phosphorylotropic form B is the appearance of the imine carbon NMR signal with a simultaneous decrease in the C=O signal intensity. The C=O signal is a doublet at 293 K with ${}^2J_{\text{PNC}}$ of 3.5 Hz, and its intensity decreases to 20% as the temperature rises. At the backward temperature change, the intensity of the C=N singlet (δ 156.78 ppm) grows.

A clear indication of the rearrangement process is observed in ${}^{31}\text{P}$ NMR spectra. Two signals of the amide form A (δ 0.77 ppm) and the phosphorylotropic form B (δ 10.73 ppm) with the intensity ratio of 91.2 : 8.8 % are observed at 293 K. The intensity of the former peak decreases to 38% as the temperature changes in the range from

293 to 373 and back to 293 K, whereas the intensity of the latter increases to 62%. The triplet shape of the ^{31}P NMR signal of the amide form, obtained without proton decoupling, which does not change in the whole temperature range, together with broadening of NH signals in the ^1H NMR spectra indicate the exchange behavior of the molecule, which averages the geminal coupling $^2J_{\text{PNH}}$ to zero.

Note that a certain discrepancy in the relative ratio of the two forms obtained from different spectra is due to the difference in the relaxation times of the considered isotopes.

The structural rearrangement of the molecule leads also to modifications in ^1H and ^{13}C NMR spectra in the signal range of the macrocyclic atoms. Observed evolution of the signals upon heating and cooling of the samples (293–373–293 K) can only be interpreted in the slope of the transition from the amide to the phosphorylotropic form of the molecule.

Additional information on the behavior of the macrocycle in the high-temperature range is given by ^{13}C NMR spectroscopy. Broadened peaks are observed at 293 K, namely, the OCH_2 signal at δ_{C} 70.1 ppm and two NCH_2 signals of the forms A and B with the intensity ratio of 85 : 15 % at δ_{C} 48.6 and 46.4 ppm. The OCH_2 signal splits into two close signals of the forms A and B (15 : 85 %) in the temperature range from 293 to 373 K. The component in the NCH_2 signal corresponding to the minor form B also becomes larger.

Conclusions

Phosphorylotropic rearrangement in *N,N'*-(bis)(diisopropoxyphosphorylamidocarbonyl)-1,10-diaza-18-crown-6-ester dissolved in DMSO was investigated by ^1H , ^{13}C , and ^{31}P NMR spectroscopy. The following conclusion can be made based on the analysis of the spectral data: the molecule experiences a transition from the amide form into the phosphorylotropic form with the yield of 85% in the temperature range of 293–373–293 K. Spectral characteristics of this process were determined. The rearrangement is irreversible, as follows from the increase in the intensity of the signals of the phosphorylotropic form in the NMR spectra of three isotopes when the temperature decreases back to 293 K.

References

1. Karataeva, F.Kh., Galiullina, N.F., Aganov, A.V., Zabirov, N.G. (1998) Structure and intramolecular lability of N-(thio)phosphoryl(thio)amides. IV. ^1H , ^{13}C and ^{31}P NMR study of dynamic processes in solutions of *N,N'*-bis(diisopropoxythiophosphorylaminothiocarbonyl)-1,10-diaza-18-crown-6 ethers. *Russian Journal of General Chemistry*, 68(5), 743-747.
2. Karataeva, F.Kh. and Klochkov, V.V. (1999) Structure and intramolecular lability of N-(thio)phosphoryl(thio)amides: V. Dynamic properties of crown-containing *N,N'*-bis(thio)phosphoryl(thio)carbonylamides by ^1H , ^{13}C , and ^{31}P NMR spectroscopy. *Russian Journal of General Chemistry*, 69(7), 1131-1138.
3. Karataeva, F.Kh. (1999) Structure and intramolecular lability of N-(thio)phosphoryl(thio)amides: VI. ^1H , ^{13}C , and ^{31}P NMR interpretation of the phosphorylotropic rearrangement in the *N,N'*-bis(diisopropoxythiophosphoryl-aminocarbonyl)-1,10-diaza-18-crown-6 ether in DMSO solution. *Russian Journal of General Chemistry*, 69(7), 1139-1143.
4. Pudovik, A.N. and Zimin, M.G. (1983) Molecular rearrangements accompanied by the migration of phosphoryl groups between two nucleophilic centres. *Russian Chemical Reviews*, 52, 1036-1050. <https://doi.org/10.1070/RC1983v052n11ABEH002914>