ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)

ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ

Д.В.Сокольский атындағы «Жанармай,
катализ және электрохимия институты» АҚ

ХАБАРЛАРЫ

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
электрохимии им. Д.В. Сокольского»

NEWS

OF THE ACADEMY OF SCIENCES
OF THE REPUBLIC OF KAZAKHSTAN
JSC «D.V. Sokolsky institute of fuel, catalysis
and electrochemistry»

SERIES
CHEMISTRY AND TECHNOLOGY

5 (437)

SEPTEMBER - OCTOBER 2019

PUBLISHED SINCE JANUARY 1947

PUBLISHED 6 TIMES A YEAR

ALMATY, NAS RK

Clarivate
Analytics

NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

«ҚР ҰҒА Хабарлары. Химия және технология сериясы».
ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)
Меншіктенуші: «Қазақстан Республикасының Ұлттық ғылым академиясы» Республикалық қоғамдық бірлестігі (Алматы қ.)
Қазақстан республикасының Мәдениет пен ақпарат министрлігінің Ақпарат және мұрағат комитетінде 30.04.2010 ж. берілген **№1089-Ж** мерзімдік басылым тіркеуіне қойылу туралы куәлік

Мерзімділігі: жылына 6 рет.
Тиражы: 300 дана.

Редакцияның мекенжайы: 050010, Алматы қ., Шевченко көш., 28, 219 бөл., 220, тел.: 272-13-19, 272-13-18,
http://chemistry-technology.kz/index.php/en/arhiv

Типографияның мекенжайы: «Аруна» ЖК, Алматы қ., Муратбаева көш., 75.

«Известия НАН РК. Серия химии и технологии».
ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)
Собственник: Республиканское общественное объединение «Национальная академия наук Республики Казахстан» (г. Алматы)
Свидетельство о постановке на учет периодического печатного издания в Комитете информации и архивов Министерства культуры и информации Республики Казахстан **№10893-Ж,** выданное 30.04.2010 г.

Периодичность: 6 раз в год
Тираж: 300 экземпляров

Адрес редакции: 050010, г. Алматы, ул. Шевченко, 28, ком. 219, 220, тел. 272-13-19, 272-13-18,
http://chemistry-technology.kz/index.php/en/arhiv

Адрес редакции: 050100, г. Алматы, ул. Кунаева, 142,
Институт органического катализа и электрохимии им. Д. В. Сокольского,
каб. 310, тел. 291-62-80, факс 291-57-22, e-mail:orgcat@nursat.kz
Адрес типографии: ИП «Аруна», г. Алматы, ул. Муратбаева, 75

News of the National Academy of Sciences of the Republic of Kazakhstan. Series of chemistry and technology.
ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)
Owner: RPA "National Academy of Sciences of the Republic of Kazakhstan" (Almaty)
The certificate of registration of a periodic printed publication in the Committee of Information and Archives of the Ministry of Culture and Information of the Republic of Kazakhstan N 10893-Ж, issued 30.04.2010

Periodicity: 6 times a year
Circulation: 300 copies

Editorial address: 28, Shevchenko str., of. 219, 220, Almaty, 050010, tel. 272-13-19, 272-13-18,
http://chemistry-technology.kz/index.php/en/arhiv

Editorial address: Institute of Organic Catalysis and Electrochemistry named after D. V. Sokolsky
142, Kunayev str., of. 310, Almaty, 050100, tel. 291-62-80, fax 291-57-22,
e-mail: orgcat@nursat.kz

Address of printing house: ST "Aruna", 75, Muratbayev str, Almaty

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2019.2518-1491.60**
Volume 5, Number 437 (2019), 100 – 107

UDK 543.429

A.A. Bakibaev[1], K.B. Zhumanov[2], S.Yu. Panshina[1,3],
S.I. Gorbin[1,3], V.S.Malkov[1,3], D.V. Khrebtova[1], O.V. Ponomarenko[4],
I.G. Tsoy[2], G. K. Matniyazova[2], E.A.Baybazarova[2]

[1]Tomsk National Research State University, Tomsk, Russia;
[2]M. Kh. Dulati Taraz State University, Taraz, Kazakhstan;
[3]Tomsk National Research Polytechnic University, Tomsk, Russia;
[4] L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan
bakibaev@mail.ru, Zhumanovkb@mail.ru, janim_svetatusik@mail.ru, gorbinsergey@gmail.com,
khrebtova.darya@yandex.ru, malkov.vics@gmail.com, oksana.ponomarenko.88@mail.ru,
tsoyirinagen@mail.ru, evisko_87_87@mail.ru, gulsim.matniyazova@mail.ru)

NMR SPECTRA OF PHOSPHORYLATED CARBAMIDE-CONTAINING HETEROCYCLES: PECULIARITIES OF CHEMICAL SHIFTS FROM THE VALENCE STATE OF THE PHOSPHORUS AND THE SIZE OF THE CYCLE

Abstract. The article discusses the results of using NMR spectroscopy to study the structure and flexibility of the skeleton of the analyzed molecules of phosphaze compounds and the electronic environment of nitrogen and phosphorus atoms. The authors carried out a cumulative system analysis of chemical shifts in the ^{31}P and ^{13}C NMR spectra of 89 phosphorus derivatives of carbamidecontaining heterocycles, which differ in the valence state of the phosphorus atom, the size of the cycle and the method of cycle junction.

Key words: heterocyclic compounds, NMR spectroscopy, phosphazo compounds, phosphorylated carbamide containing heterocycles (PCCH), 3-coordinated phosphorus atom, 5-coordinated phosphorus atom.

Introduction

Phosphazaheterocycles containing an urea fragment and a phosphoryl group in the cyclic skeleton are attractive because these links of molecules, acting as the key structural elements of these compounds, give them a skeleton of the structure and contribute to the formation of multifunctional reaction centers. The simultaneous combination of urea fragments and phosphoryl groups in a molecule makes it possible to impart specific physicochemical and practically useful properties to the target substance, the investigation of which is the subject of many studies, including and using NMR spectroscopy.

The use of NMR spectroscopy to study the structure of phosphaza compounds allows not only to identify the compounds, but also to judge the flexibility of the skeleton of the analyzed molecules and the electronic environment of nitrogen and phosphorus atoms. In addition, a generalized analysis of chemical shifts of an array of phosphazacycles helps to reveal their characteristics for the considered range of compounds. However, so far no attempts have been made of the cumulative analysis of an array of NMR spectral data of phosphorus-containing urea-containing heterocycles.

In order to fill this gap, we carried out a cumulative system analysis of chemical shifts in the 31P and 13C 89 NMR spectra of phosphorus-containing urea-containing heterocycles, which differ in the valence state of the phosphorus atom, the size of the cycle and the method of junction cycles.

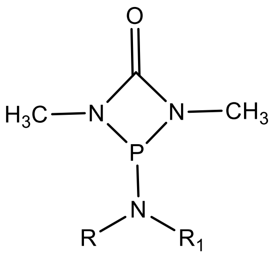
In a number of works [1–14] devoted to the synthesis of the corresponding phosphazacycles, the ^{31}P NMR spectroscopy data was used to identify a larger number of different phosphorylated carbamide containing heterocycles (PCCH). This paper summarizes the intervals of changes in chemical shifts (CS) of PCCH in the ^{31}P NMR spectra, which are illustrated by the data given depending on the valence state of phosphorus, the size of the cycle and the method of junction.

Results and discussion

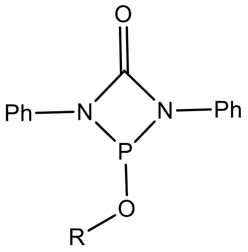
CHEMICAL SHIFTS OF 3-COORDINATED PHOSPHORUS ATOM IN PCCH NMR SPECTRA

Analyzed PCCH containing 3 valence phosphorus atom are represented by 4-membered phosphazacycles (diazaphosphetidinediones 1-6), 5-membered phosphazacycles (diazaphospholidinediones 7-10) and 6-membered phosphazacycles (triazaphosphorinandiones 11-25).

A comparative analysis of CSphosphetidinediones1-2 [1] and 3-6 [2] shows that, for all other equal structural parameters, the electronegativity of the substituent, directly attached to the phosphorus atom,has a decisive influence on CS. In other words, in the series of phosphetidinediones1-6 alkoxy groups (compounds 3-6) cause pronounced disshielding of the phosphorus atom (10 ppm), rather than amino groups (compounds 1-2)



1-2



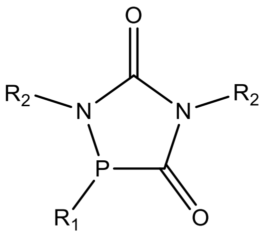
3-6

1 - R_1=Me, R=Ph (83.6);
2 - R_1=Me, R=циклогексил (81.9);
3 - R=Me (95.2);
4 - R=Et (93.1);
5 - R= i-Pr (92.3);
6 - R=n-Bu (93.1)

As one can see from the above data, the formation of N, N-P-N and N, N-P-O units in the 4-membered PCCH cycle of the compounds 1-6 contributes to the appearance ofCSof phosphorus atoms in the positive spectral region in the interval 81.9-95.2 ppm.

The CS values of 5-membered PCCH 7-10 [3] correspond to the interval from 24.2 to 38.3 ppm, which indicate a significant screening of the phosphorus atom in the diazaphospholidinediones 7-10 compared to the 4-membered phosphetidinones1-6. In this case, the strong-field shift of phosphorus atoms in compounds 7–10 compared with phosphazacycles 1–6 is due to the isolation of the second urea nitrogen atom by the carbonyl group at the 5th position of the cycle, which excludes its direct electronegative effect on the phosphorus atom. At the same time, a similar effect of the carbonyl group, as can be seen from the comparison of CS, is not comparable with the influence of the nitrogen atom.

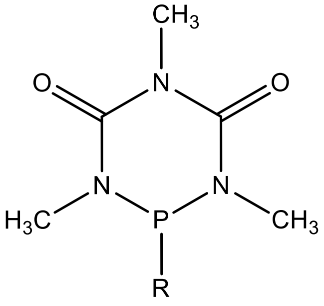
Thus, the formation of the N, C-P-C = O link in PCCH 7-10, compared with FCSG 1-6, causes a significant strong-field shift (by 50 ppm) of phosphorus.



7-10

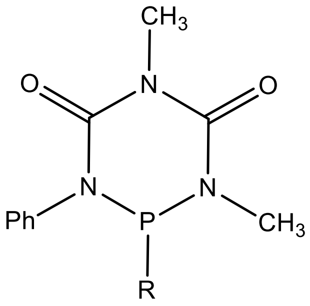
7 - R_1=R_2=Me (30.7);
8 - R_1=Me, R_2= n-Bu (24.2);
9 - R_1=i-Pr, R_2=Me (30.8)
10 - R_1= CH_3, R_2 = C_6H_5 (38.3)

Turning to the 6-membered PCCH 11-25 [4-6], it should be noted that the influence of substituents (R) in the N, N> P-R unit on the CS of the ^{31}P nucleus appears in the interval of 66.7-106.9 ppm.



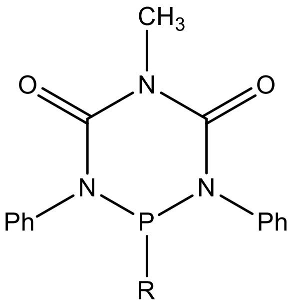
11-18

11 - R=NMe_2 (82.7 ppm);
12 - R=NEt_2 (80.1 ppm);
13 - R=NPh_2 (66.7 ppm);
14 - R=$NHCH_2CH_2Cl$ (70.6 ppm);
15 - R=$N(CH_2CH_2Cl)_2$ (82.3 ppm);
16 - R=OMe (90.6 ppm);
17 - R=$OSi(Me)_2$ (90.6 ppm);
18 - R=$N(CH_3)CH_2CH_2N(CH_3)_2$ (81.0 ppm);



19-21

19 - R=Me (80.5 ppm);
20 - R=Cl (106.9 ppm);
21 - R=Ph (68.4 ppm);



22-25

22 - R=Me (79.9 ppm);
23 - R=Ph (68.7 ppm);
24 - R=Cl (101.6 ppm);
25 - R=NMe_2 (79.3 ppm)

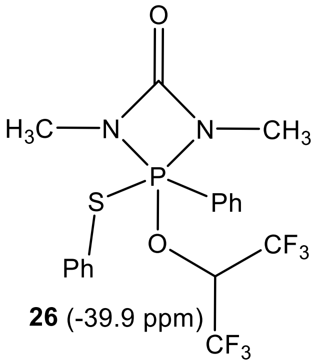
At the same time, in the series of triazaphosphorinandiones of the general formula 11-25 CS of the phosphorus atom bound to the R group, depending on the nature of the substituent in the P-R link, shifts to a weaker field in the series: P-C (compounds 19, 21-23 [6]) <P-N (Compounds 11-15 [6], 18 [4], 25 [6]) <P-O (compounds 16, 17 [5]) - P-Cl (compounds 20, 24 [6]). The established order of CS change in phosphazacycles 11-25 is in accordance with the electronegativity of the substituent R, directly attached to the phosphorus atom. The displacement of electrons by the R substituent from the phosphorus atom in these compounds contributes to the localization of the lone electron pair at the skeletal carbamide nitrogen atoms, thereby causing an additional contribution to the weak-field shift of phosphorus atoms.

From the CS data presented, it is clear that the effect of the distribution of electrons in the carbamide unit of the heterocyclic fragment of molecules 11–25 is worse than the direct displacement of electrons within the P – R sigma bond in the considered phosphazocycles. It is quite well established that CS of the three-coordinated phosphorus atom in PCCH 1-25 locate in the positive spectral region within 24.2-106.9 ppm and in the given corridor, the CS values depend on the chemical environment of the phosphorus atom.

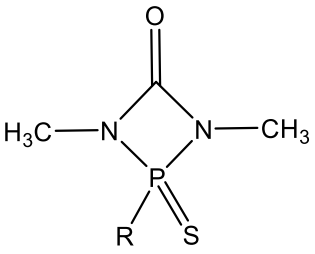
CHEMICAL SHIFTS OF THE 5-COORDINATED PHOSPHORUS ATOM IN PCCH NMR SPECTRA

A general analysis of the changes in ^{31}P CS in PCCH shows that 3-coordinated phosphazacycles 1–25 exhibit CS in the positive spectral region, whereas for 5-coordinated phosphazacycles this property is mixed. In other words, CH for 5-coordinated phosphazacycles 26–49 [7, 8] is characteristic both in the positive spectral region and in the negative region with a clear tendency toward the latter.

The change in cholesterol ^{31}P CS in a series of thiylateddiazaphosphophetidinone derivatives 26-49 is very interesting. So, if thionic phosphetidinones 27-34 [7] exhibit ^{31}P CS in the positive spectral region (58.5–83.1 ppm), regardless of the nature of the R substituent, then thiylatedchlorophosphetidinones 35-46 (-44.0; -49.6 ppm) and alkoxyphosphetidinone 26, (-39.9 ppm) show negative CS values [8].

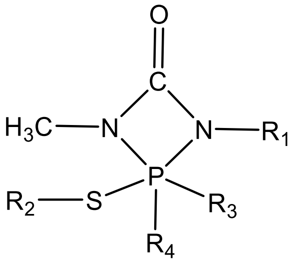


26 (-39.9 ppm)



27-34

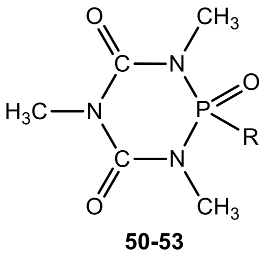
27 - R=Cl (59.20 ppm);
28 - R=NMt$_2$ (64.4 ppm);
29 - R=Net$_2$ (65.2 ppm);
30 - R=$(CH_2)_4$ (58.5 ppm);
31 - R=OMe(67.5 ppm);
32 - R=SMe$_2$ (83,1 ppm);
33 - R=NPh$_2$ (58.5 ppm);
34 - R=N-(циклогексил)$_2$ (58.8 ppm)



35 - R_1 = Ph, R_2 = CH_3, R_3 = Ph; R_4 = Cl (-44,3 ppm)
36 - R_1 = Ph, R_2 = Ph, R_3 = Ph; R_4 = Cl (-49,6 ppm)
37 - R_1 = Ph, R_2 = CH_3, R_3 = CH_3; R_4 = Cl (-44,0 ppm)
38 - R_1 = Ph, R_2 = Ph, R_3 = CH_3; R_4 = Cl (-46,2 ppm)
39 - R_1 = 4-$CH_3C_6H_4$, R_2 = CH_3, R_3 = CH_3; R_4 = Cl (-44,6 ppm)
40 - R_1 = 4-$CH_3C_6H_4$, R_2 = Ph, R_3 = CH_3; R_4 = Cl (-45,6 ppm)
41 - R_1 = 4-$CH_3C_6H_4$, R_2 = CH_3, R_3 = CH_2Cl; R_4 = Cl (-47,33 ppm)
42 - R_1 = 4-$CH_3C_6H_4$, R_2 = CH_3, R_3 = t-Bu; R_4 = Cl (-20,6 ppm)
43 - R_1 = 4-$O_2NC_6H_4$, R_2 = CH_3, R_3 = Ph; R_4 = Cl (-48,6 ppm)
44 - R_1 = 4-$O_2NC_6H_4$, R_2 = Ph, R_3 = Ph; R_4 = Cl (-50,9 ppm)
45 - R_1 = 4-$CH_3C_6H_4$, R_2 = CH_3, R_3 = Ph; R_4 = Cl (-43,8 ppm)
46 - R_1 = 4-$CH_3C_6H_4$, R_2 = Ph, R_3 = Ph; R_4 = Cl (-48,7 ppm)
47 - R_1 = CH_3, R_2 = Ph, R_3 = Ph; R_4 = 4-$O_2NC_6H_4$ (-54,1 ppm)
48 - R_1 = CH_3, R_2 = 4-$CH_3C_6H_4$, R_3 = t-Bu; R_4 = 4-$O_2NC_6H_4$ (-34,1 ppm)
49 - R_1 = CH_3, R_2 = 4-$CH_3C_6H_4$, R_3 = Ph; R_4 = 4-$O_2NC_6H_4$ (-53,9 ppm)

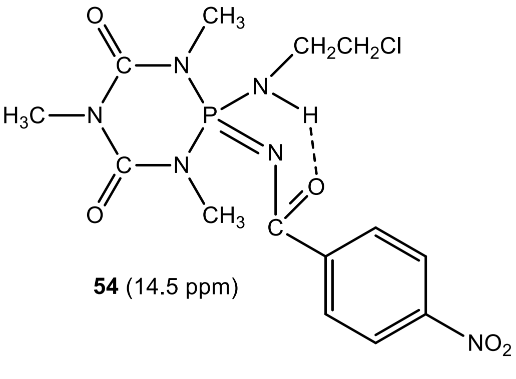
In the series of phosphetidinones 26-49 in the first approximation, the carbamide group of the heterocycle is equivalent in its effect on the phosphorus atom. Consequently, when comparing CS of the phosphorus atoms in these phosphazacycles, their positive shift is provided by the sp^2 hybridized state of the thionic group, and the negative shift of CS, along with other groups, is mainly due to the shielding effect of the thiol group, since chlorine atoms and alkoxy groups are present in all compounds 26–49.

One of the interesting features in the data analysis ^{31}P NMR spectra of phosphazacycles 50-53 [9] and 54-57 [10] is that the location of CS of phosphorus atom significantly depends on the hybridization of the P = X bond. So, for example, a distinct dependence of the CS shift to the negative region in the series P = N <P = O <P = S in compounds 50-57 is revealed.

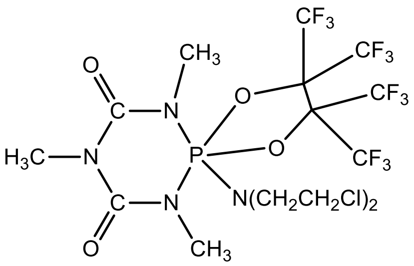


50-53

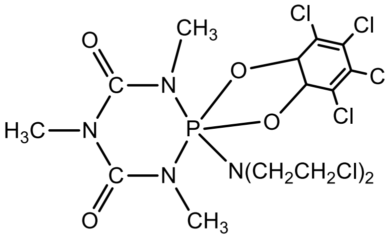
50 - R=$NHCH_2CH_2Cl$ (3.1 ppm);
51 - R=$N(CH_2CH_2Cl)_2$ (3.1 ppm)
52 - R=Cl (5.1 ppm);
53 - R=$N(CH_2CH_2)_2$ (4.2 ppm)



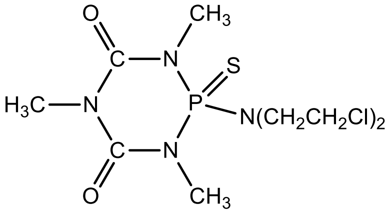
54 (14.5 ppm)



55 (-36.0 ppm)



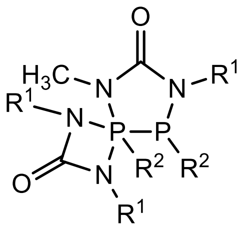
56 (-38.8 ppm)



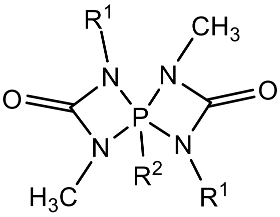
57 (-58.8 ppm)

The effect of other substituents at the phosphorus atom in these compounds on the screening of the P atom is not as obvious as the change of the heteroatom in the P = X fragment of the PCCH examined.

For the series of spiro compounds 58-75 with the nodal phosphorus atom CS ^{31}P become more characteristic. All PCCH with the nodal phosphorus atom in the spiro compounds 58-62 [11] and 63-75 [12] give only negative CS ^{31}P values (from -64.3 ppm to -79.9 ppm). For example, in phosphazacycles 58, 59 there are two CH ^{31}Ps (wherein in different valence states), however, CS of the nodal atom of phosphorus can be clearly recognized due to its strong negative shift (-64.3; -69.0 ppm), while the three-coordinated atom P gives positive CH in the region of 1.9-6.3 ppm.

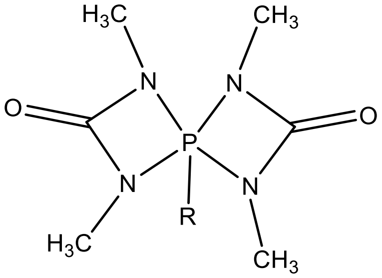


58 - R_2=Me, R_1=Ph (1.9; -69.0 ppm)
59 - R_1=R_2=Ph (6.3; -64.3 ppm)



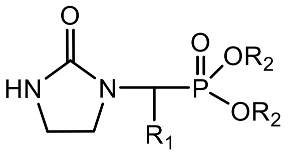
60 - R_1 = C_6H_4-CF_3-3, R_2 = C_6F_5 (-79.9 ppm)
61 - R_1 = Me, R_2 = Ph (-67.8 ppm)
62 - R_1 = Ph, R_2 = Ph (-68,5 ppm)

The intervals of CS ^{31}P changes for spiro compounds 63-75 [12] are largely determined by the direct influence of the substituents R at the phosphorus atom, and their oscillation range varies from -51.4 ppm to -119.1 ppm Attention is drawn to the fact that by varying halogen-containing substituents R for spirocycles 63-66 CS ^{31}P become more negative in the series: F <Cl <Br <I. The observed order of CS change of the nodal atom of phosphorus in compounds 63-66 is in full accordance with the electronegative properties of halogens. The phenyl group in the spirocycle 60-62, 70, 72 sensitively screens the phosphorus atom compared with the methyl derivatives 68, 69, 71, 73-75, which is most likely due to the anisotropic effect of the aromatic core.



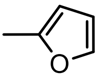
63 - R = Cl (-56.0 ppm);
64 - R = F (-51.4 ppm);
65 - R = Br (-73.3 ppm);
66 - R = I (-119.1 ppm);
67 - R = CN (-89.4 ppm);
68 - R = MeP($SiMe_3$) (-56.1 ppm);
69 - R = OMe (-57.0 ppm);
70 - R = OPh (-61.1 ppm);
71 - R = SMe (-56.0 ppm);
72 - R = SPh (-59.4 ppm);
73 - R = NMe_2 (-57.3 ppm);
74 - R = N_3 (-66.2 ppm);
75 - R = $NPMe_3$ (-71.0 ppm)

One of the factors affecting the location of CS ^{31}P in the PCCH is the possibility of molecular flexibility of a heterocycle that is not directly related to the phosphorus atom. So, in imidazolidone 76-85, this possibility leads to shielding, and for imidazolidones 86-89 – to unshielding of the phosphorus atom compared to phosphoric acid itself or its esters, as indicated by the significantly strong-field shift of cholesterol, observed on going to compounds 76-85 and weak-field shift on going to compounds 86-89.

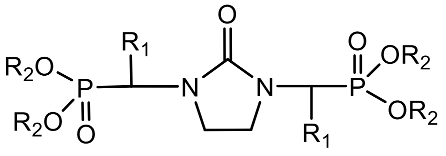


76-80

76 - R_1, $R_2 = C_6H_5$ (-12,4 ppm);

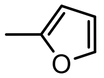
77 - R_1 =  , $R_2 = C_6H_5$ (-9,8 ppm);

78 - $R_1 = CH_3$, $R_2 = C_6H_5$ (-21,2 ppm);
79 - $R_1 = C_6H_5$, $R_2 = ClCH_2CH_2$ (-12,5 ppm)
80 - $R_1 = C_6H_5$, $R_2 = H$ (-16,4 ppm);

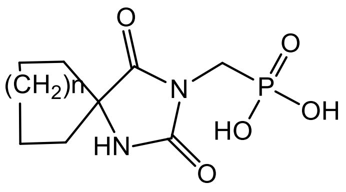


81-85

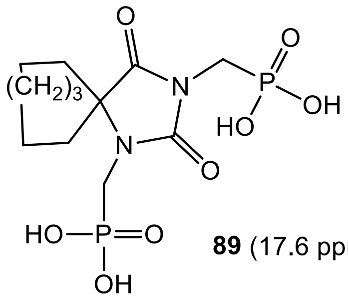
81 - R_1, $R_2 = C_6H_5$ (-11,6 ppm);

82 - R_1 =  , $R_2 = C_6H_5$ (-9,2 ppm);

83 - $R_1 = CH_3$, $R_2 = C_6H_5$ (-16,2 ppm);
84 - $R_1 = C_6H_5$, $R_2 = ClCH_2CH_2$ (-11,0 ppm)
85 - $R_1 = C_6H_5$, $R_2 = H$ (-15,8 ppm);



86 - n=0 (18.1 ppm, 20,6 ppm)
87 - n=1 (15.5 ppm, 19,4 ppm)
88 - n=2 (17.6 ppm, 20,0 ppm)



89 (17.6 ppm, 21,1 ppm)

Conclusion

Comparative consideration of CS of the phosphorus atom in PCCH with five-coordinated phosphorus shows that they undergo a negative shift, and their location mainly depends on the hybrid state of P atom in the cycle and the junction type of the cycles

An attempt to make a comparative analysis of CS of the carbonyl group (C = O) in PCCH did not reveal significant differences due to their changes in a narrow range of values (151-156 ppm), regardless of the valence state of the phosphorus atom in the cycle and the method of junction of cycles (for example, in the spiro compounds and bicycles 58-75). Only some shielding of C = O-group in PCCH compared with urea itself (159.5 ppm) [15] and the bicyclic bisurea of octane series - glycoluril (161.9 ppm) [15] is of interest. The observed effect appears to be determined by an increase in steric stresses (compression) in PCCH due to the limitations in the flexibility of their skeleton, and, as a consequence, by strengthening the order of the amide bond. The informational content of the NMR spectra analysis of PCCH is somewhat reduced due to the absence of CS data of the NH groups. But this circumstance is due to the fact that almost all synthesized and identified PCCH given in [1-14] contain substituents at the nitrogen atoms.

The dependences of chemical shifts on the structure of bicyclic bimocarbons and spiro compounds obtained can be used to study the properties of macromolecular nitrogen-containing systems, as shown by the example of some nitrogenous alkaloids [16].

ӘОЖ 543.429

**А.А. Бакибаев[1], К.Б. Жуманов[2], С.Ю. Паньшина[1,3], С.И. Горбин[1,3], Д.В. Хребтова[1],
О.В. Пономаренко[4], С.В. Мальков[1], И.Г. Цой[2], Г.К. Матниязова[2], Э.А. Байбазарова[2]**

[1]Ғылымизерттеу Томск мемлекеттік университеті, Томск, Ресей
[2]М.Х.Дулати атындағы Тараз мемлекеттік университет, Тараз, Қазақстан
[1]Ғылымизерттеу Томск политехникалық университеті, Томск, Ресей
[4]Л.Н. Гумилев атындағы Евразиялық ұлттық университет, Нұр-Сұлтан, Қазақстан

ФОСФОРИЛИРЛЕНГЕН КАРБАМИДҚҰРАМДЫ ГЕТЕРОЦИКЛДАРДЫҢ ЯМР СПЕКТРЛАРЫ: ФОСФОРДЫҢ ВАЛЕНТТІЛІК ҚҰРАМЫ МЕН ЦИКЛДАР ӨЛШЕМІНЕ БАЙЛАНЫСТЫ ХИМИЯЛЫҚ ҚОЗҒАЛЫСТАРДЫҢ ЕРЕКШЕЛІКТЕРІ

Аннотация. Мақалада талданып отырған фосфазақосылыстар молекулаларының құрылымы мен қаңқаларының иілгіштігін және азот пен фосфор атомдарының айналасындағы электрондарды зерттеуде ЯМР-спектроскопияны қолдану нәтижелері талқыланады. Авторлар 89 карбамидқұрамды гетероциклдардың фосфортуындыларын ЯМР ^{31}Р и ^{13}С спектрларындағы химиялық қозғалыстарды жүйелі талдау жүргізілген. Бұл қосылыстар бір-бірінен фосфор атомының валенттілік күйімен, циклдар өлшемімен және циклдардың бір-бірімен қосылу әдісі бойынша ерекшеленеді.

Түйін сөздер:гетероциклдықосылыстар, ЯМР-спектроскопия, фосфазоқосылыстар, фосфорилирленген карбамидқұрамды гетероциклдар (ФККГ), 3-координирленгенфосфор атом, 5-координирленгенфосфор атом.

УДК 543.429

**А.А. Бакибаев[1], К.Б. Жуманов[2], С.Ю. Паньшина[1,3], С.И. Горбин[1,3], Д.В. Хребтова[1],
О.В. Пономаренко[4], С.В. Мальков[1], И.Г. Цой[2], Г.К. Матниязова[2], Э.А. Байбазарова[2]**

[1]Национальный исследовательский Томский государственный университет
[2]Таразский государственный университет им. М.Х. Дулати
[3]Национальный исследовательский Томский политехнический университет
[4]Евразийский национальный университет имени Л.Н. Гумилева,

СПЕКТРЫ ЯМР ФОСФОРИЛИРОВАННЫХ КАРБАМИДСОДЕРЖАЩИХ ГЕТЕРОЦИКЛОВ: ОСОБЕННОСТИ ХИМИЧЕСКИХ СДВИГОВ ОТ ВАЛЕНТНОГО СОСТОЯНИЯ ФОСФОРА И РАЗМЕРА ЦИКЛА

Аннотация. В статье обсуждаются результаты применения ЯМР-спектроскопии для изучения структуры и гибкости скелета анализируемых молекул фосфазасоединений и электронногоокружения атомов азота и фосфора. Авторами проведен совокупный системный анализ химических сдвигов в спектрах ЯМР ^{31}Р и ^{13}С 89 фосфорпроизводных карбамидсодержащих гетероциклов, которые отличаются валентным состоянием атома фосфора, размером цикла и способом сочленения циклов.

Ключевые слова: гетероциклические соединения, ЯМР-спектроскопия, фосфазосоединения, фосфорилированные карбамидсодержащие гетероциклы (ФКСГ), 3-координированный атом фосфора, 5-координированный атом фосфора.

Information about the authors

Bakibayev A.A. – Doctor of Chemical Sciences, Professor, Leading Researcher of the Laboratory of Organic Synthesis, National Research Tomsk State University, Lenin Avenue 36, Tomsk, Russia.ORCID: https://orcid.org/0000-0002-3335-3166

Zhumanov K.B. – PhD student, M.Kh. DulatiTaraz State University, Tole bi str., 60, Taraz, Kazakhstan. E-mail: Zhumanovkb@mail.ru. ORCID: https://orcid.org/0000-0002-1578-0623

Panshina S. – postgraduate student, Tomsk National Research Polytechnic University. ORCID: https://orcid.org/0000-0001-6824-2645

Malkov V.S. – candidate of chemistry sciences, associated professor, TomskNational Research State University, Lenin Prospect, 36.ORCID: https://orcid.org/0000-0003-4532-2882

Gorbin S. – Junior Researcher, National Research Tomsk State University, Lenin Avenue 36, Tomsk, Russia. ORCID: https://orcid.org/0000-0003-3948-8085

Khrebtova D.V. – Researcher, National Research Tomsk State University, Lenin Avenue 36, Tomsk, Russia.ORCID: https://orcid.org/0000-0002-6856-0894

Ponomarenko O.V. – PhD student, L.N. Gumilyov Eurasian National University,Nur-Sultan,Kazakhstan.ORCID: https://orcid.org/0000-0002-8172-5139

Tsoy I.G. – candidate of chemistry sciences, associated professor, M.Kh. DulatiTaraz State University, Tole bi str., 60, Taraz, Kazakhstan. ORCID: https://orcid.org/0000-0003-1705-6142.

Matniyazova G. K. – associated professor, doctor PhD, M.Kh. Dulati Taraz State University, Tole bi str., 60, Taraz, Kazakhstan. ORCID: https://orcid.org/0000-0002-6820-5219 .

Baybazarova E.A. – PhD student, teacher, M.Kh. Dulati Taraz State University, Tole bi str., 60, Taraz, Kazakhstan. ORCID: https://orcid.org/0000-0002-7059-9093.

REFERENCES

[1]Breker J., Wermuth U., Schmutzle R. (1990) Verbindungen mit dem 1,3-Dimethy 1-1,3-diaza-2-phosphetidin-4-on-Grundgerüst; Synthese von l,3-Dimethyl-2-thia-l,3-diaza-2 λ^4-phosphetidin-4-on-Derivaten, Zeitschrift für Naturforschung B.. Vol. 45. pp. 1398-1406

[2] Nikonorov K. V., Gurylev E. A., Antokhina L. A., Latypov Z. Ya. (1981). Reaction of phosphorus acid chlorides with diphenylurea Bulletin of the Academy of Sciences of the USSR, Division of chemical science. Vol. 30. No. 12. pp. 2330-2333

[3]Richter F. (2008). 1,4,2-diazaphospholidine derivatives, US20110207927A1.

[4] Kaukorat T., Neda I., Fischer A., Jones P. G., Schmutzler R. (1993). Verbindungen mit dem 1,3,5,2-Triazaphosphorinan-Grundgerüst: Synthese und Koordinationschemie neuartiger, N,N,N′-Trimethylethylendiamin-substituierter Verbindungen mit drei-und vierfach koordiniertem Phosphor. Chemische Berichte, Vol. 126, No. 6, pp. 1265–1270.

[5] Neda I., Farkens M., Schmutzler R. (1994). Zur Chemie der l,3,5-Triaza-2-phosphorinan-4,6-dione. Teil VII. Über die Synthese von 2-Methoxy- und 2-Trimethylsiloxy-l,3,5-trimethyl-1,3,5-triaza-2λ^3-phosphorinan-4,6-dion sowie 2-Chlor-l,3,5-trimethyl-1,3,5-triaza-2-oxo-2λ^4-phosphorinan-4,6-dion. Zeitschrift für Naturforschung B. Vol. 49b. pp. 165-170.

[6] Müller C., Meyer T. G., Farkens M., Sonnenburg R. und Schmutzler R. (1992). ZurChemie der 4,6-Dioxo-l,3,5,2 A3-triazaphosphinane. Teil II. Darstellung von 4,6-Dioxo-l,3>5,2 A3-triazaphosphinanen On the Chemistry of 4,6-Dioxo-l,3,5,2 A3-triazaphosphinanes. Part II. Preparation of 4,6-Dioxo-l,3,5,2A3-triazaphosphina Müller C., Meyer T. G., Farkens M., R alfSonnenburg, ReinhardSchmutzler. Z. Naturforsch. Vol. 47b. pp. 760 -766.

[7] BrekerJ., WermuthU., SchmutzleR. (1990). Verbindungenmitdem 1,3-Dimethy 1-1,3-diaza-2-phosphetidin-4-on-Grundgerüst; Synthesevonl,3-Dimethyl-2-thia-l,3-diaza-2 λ^4-phosphetidin-4-on-Derivaten // ZeitschriftfürNaturforschungB. Vol. 45. pp. 1398-1406

[8] Pinchuk V. A., Müller C., Fischer A., Thönnessen H., Jones P. G., Schmutzler R., Markovsky L. N., Shermolovich Y. G., Pinchuk A. M. (1995). Reactions of Sulfenamides with Compounds of Trivalent Phosphorus. Zeitschrift für anorganische und allgemeine Chemie. Vol. 621. No. 12. pp. 2001-2011

[9] Neda I., Farkens M., Schmutzler R. (1994). Zur Chemie der l,3,5-Triaza-2-phosphorinan-4,6-dione. Teil VII. Über die Synthese von 2-Methoxy- und 2-Trimethylsiloxy-l,3,5-trimethyl-1,3,5-triaza-2λ^3-phosphorinan-4,6-dion sowie 2-Chlor-l,3,5-trimethyl-1,3,5-triaza-2-oxo-2λ^4-phosphorinan-4,6-dion. Zeitschrift für Naturforschung B. Vol. 49b. pp. 165-170.

[10] Neda I., Farkens M., Fischer A., Jones P. G., Schmutzler R. (1993). Zur Chemie der 4,6-Dioxo-l,3,5,2-triazaphosphinane, Teil III. Darstellung von 4,6-Dioxo-1,3,5,2 λ^3-, 4,6-Dioxo-1,3,5,2 λ^4- und 4,6-Dioxo-1,3,5,2 λ^5-triazaphosphinanen. Zeitschrift für Naturforschung B. Vol. 48b. pp. 443-451.

[11] Roesky H. W., Ambrosius K., Sheldrick W. S. Darstellung und Struktur eines neuartigen spirobicyclischen Phosphorans mit einer λ^3P-λ^5P-Bindung // Chemische Berichte, Vol. 112, No. 4, 1979. pp. 1365-1371.

[12] Breker J., Jones P. G., Schmutzler R., Schomburg D. (1991). Chemie des 4-chlor-1,3,5,7-tetramethyl-1,3,5,7-tetraaza-4HHDFFHV-phosphaspiro[3.3]heptan-2,6-dions; Kristall- und molekulstruktur von halogen(F, Br)- und pseudohalogen(CN)-phosphoranen // Phosphorus, Sulfur, and Silicon and the Related Elements, Vol. 62, No. 1-4, pp. 139-153.

[13]Mikroyannidis J. A. (1982). Synthesis of substituted N-[(phosphonyl)methyl]-2-imidazolidinones AND N-[(phosphonyl)methyl]-2-pyrrolidinone // Phosphorus and Sulfur and the Related Elements. Vol. 12. No. 2. pp. 249–258.

[14] Naydenova E. D., Todorov P. T., Troev K. D. (2010). Synthesis and Characterization of Novel Cycloalkanespiro-5-Hydantoin Phosphonic Acids // Phosphorus, Sulfur, and Silicon and the Related Elements. Vol. 185. No. 7. pp. 1315–1320.

[15] Bakibayev A. A., Pan'shina S. YU., Ponomarenko O. V., Lyapunova M.V., Kotel'nikov O.A., Rubtsov K.V., Gorbin S.I., Mal'kov V.S. (2019). Questbook on IR and NMR spectroscopy of drugs and biologically active compounds [Zadachnik po IK- i YAMR- spektroskopii lekarstvennykh preparatov i biologicheski aktivnykh soyedineniy]. (In Russian).

[16] Nurkenov O. A., Seilkhanov T.M., Fazylov S. D., Issaeva A. Zh., Seilkhanov O.T., Zhaksybaeva G. Sh. **(2019)** Obtaining and research of the supramolecular complexes of alkaloid salsoline with cyclodextrins by NMR sprectoscopy // News of national academy of sciences of the Republic of Kazakhstan. Volume 1, Number 433 (2019), P.64-39. https://doi.org/10.32014/2019.2518-1491.9 ISSN 2224-5286 (Print).

Publication Ethics and Publication Malpractice in the journals of the National Academy of Sciences of the Republic of Kazakhstan

For information on Ethics in publishing and Ethical guidelines for journal publication see http://www.elsevier.com/publishingethics and http://www.elsevier.com/journal-authors/ethics.

Submission of an article to the National Academy of Sciences of the Republic of Kazakhstan implies that the described work has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis or as an electronic preprint, see http://www.elsevier.com/postingpolicy), that it is not under consideration for publication elsewhere, that its publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out, and that, if accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder. In particular, translations into English of papers already published in another language are not accepted.

No other forms of scientific misconduct are allowed, such as plagiarism, falsification, fraudulent data, incorrect interpretation of other works, incorrect citations, etc. The National Academy of Sciences of the Republic of Kazakhstan follows the Code of Conduct of the Committee on Publication Ethics (COPE), and follows the COPE Flowcharts for Resolving Cases of Suspected Misconduct (http://publicationethics.org/files/u2/New_Code.pdf). To verify originality, your article may be checked by the Cross Check originality detection service http://www.elsevier.com/editors/plagdetect.

The authors are obliged to participate in peer review process and be ready to provide corrections, clarifications, retractions and apologies when needed. All authors of a paper should have significantly contributed to the research.

The reviewers should provide objective judgments and should point out relevant published works which are not yet cited. Reviewed articles should be treated confidentially. The reviewers will be chosen in such a way that there is no conflict of interests with respect to the research, the authors and/or the research funders.

The editors have complete responsibility and authority to reject or accept a paper, and they will only accept a paper when reasonably certain. They will preserve anonymity of reviewers and promote publication of corrections, clarifications, retractions and apologies when needed. The acceptance of a paper automatically implies the copyright transfer to the National Academy of Sciences of the Republic of Kazakhstan.

The Editorial Board of the National Academy of Sciences of the Republic of Kazakhstan will monitor and safeguard publishing ethics.

Правила оформления статьи для публикации
в журнале смотреть на сайте:

www:nauka-nanrk.kz

http://chemistry-technology.kz/index.php/en/arhiv

ISSN 2518-1491 (Online), ISSN 2224-5286 (Print)

Редакторы: *М. С. Ахметова, Т. А. Апендиев, Аленов Д.С.*
Верстка на компьютере *А.М. Кульгинбаевой*

Подписано в печать 05.010.2019.
Формат 60х881/8. Бумага офсетная. Печать – ризограф.
9,0 п.л. Тираж 300. Заказ 5.

Национальная академия наук РК
050010, Алматы, ул. Шевченко, 28, т. 272-13-18, 272-13-19