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Synthesis and NMR Study of Cyclohexylphosphonates

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Abstract—Cyclohexyl-, 2-chlorocyclohex-1-yl and cyclohexen-1-ylphosphonic acids chlorides and fluorides were synthesized and studied by the ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR methods with the use of correlation spectroscopy and quantum-chemical calculations.

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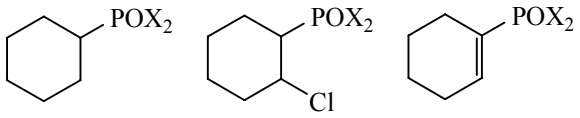
Phosphorus-substituted derivatives of cyclohexane remain virtually unexplored compounds as concerns of the methods for their synthesis, chemical properties, and the spatial structure. Meanwhile the compounds of this class are of great practical use, in particular, 1-(butyl-amino)cyclohexylphosphonic acid dibutyl ester (trake-fon, buminafos) is applied as phytohormone [1, 2], and phosphorus-containing derivative of cyclohexene, 3-(pentyl-3-hydroxy)-4-acetylamino-5-aminocyclohexen-1-ylphosphonic acid ammonium salt (tamiphosphor), is the antiviral drug [3, 4].

The aim of this work is the synthesis of the simplest phosphorus derivatives of cyclohexane and their examination by means of NMR spectroscopy to determine the spectroscopic characteristics, which are necessary of the study of the related more complicated structures.

Unfortunately, the use of the proton magnetic resonance spectroscopy to study the cyclohexane compounds has limitations related to the fact that the signals are located in a narrow spectral region, and the spectra are difficult for interpretation due to the complex spin-spin interactions. Much the same applies to the ^{13}C NMR spectroscopy.

In this regard, the spectral analysis of phosphorus-containing cyclohexane derivatives is of particular interest because of the possibility of obtaining additional spectroscopic parameters and application of heteronuclear spectroscopy. In this study the cyclohexane derivatives such as cyclohexyl- (**I**, **IV**), 2-chlorocyclohexyl- (**II**, **V**) and cyclohexen-1-ylphosphonic acids (**III**, **VI**) dichlorides and difluorides were synthesized and studied.

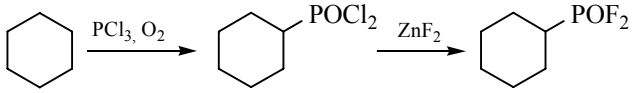


I, IV **II, V** **III, VI**

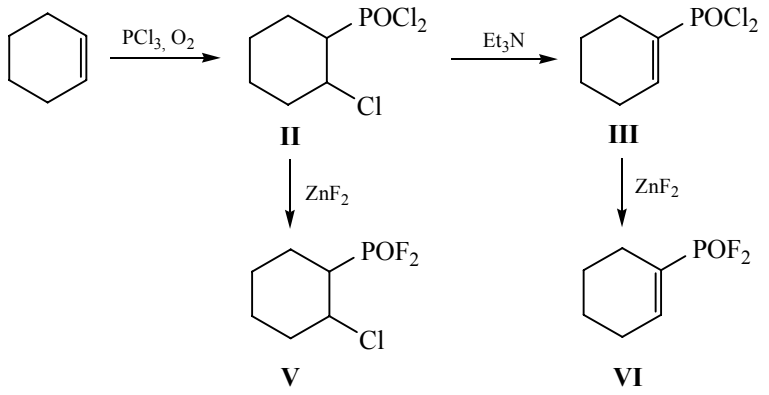
X = Cl (**I, II, III**), F (**IV, V, VI**).

Methods of the synthesis of cyclohexane derivatives with a C–P bond are limited. The sufficiently effective method is based on the addition reaction of hydrophosphoryl compounds to the C=O bond of cyclohexanone and its derivatives, which has been recently modified by O.O. Kolodyaznaya and O.I. Kolodyazhnyi [5].

Use of cyclohexyl-containing Grignard reagents [3] has the limitations of organometallic synthesis. Cyclohexylphosphonate was obtained starting from cyclohexane via the reaction of oxidative chlorophosphorylation [6]. Although this method is ineffective for processing because of the considerable consumption of phosphorus trichloride in a parallel reaction of oxidation to the oxychloride, it is sufficiently convenient for the syntheses for research purposes, because it allows to obtain phosphonic acids dichlorides, the suitable synthons for subsequent conversion into other derivatives, through one stage using the available materials.



We have shown previously [7] that the formation of the C–P bond via the oxidative chlorophosphorylation of unsaturated hydrocarbons begins with a chlorine radical attack on the double bond that determines the regioselectivity of this process. This method is used in the present work for the synthesis of compounds **II–IV**.



The structure and individuality of the obtained cyclohexylphosphonic dichlorides and difluorides were proved by the ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectroscopy (Table 1).

Chemical shifts of the phosphorus nuclei of compounds **I–VI** are characteristic of the corresponding saturated and unsaturated derivatives. In the spectra of difluorides **IV** and **VI** the phosphorus resonates as a triplet signal with the characteristic constants $^{1}J_{PF} \approx 1000$ Hz. Accordingly, the ^{19}F nuclei signals are doublets with the constant $^{1}J_{PF}$ of the same value. In contrast to these compounds the ^{31}P NMR spectrum of chlorocyclohexyl derivative **V** contains two doublets, which indicates some non-equivalence of the fluorine nuclei. This may be due to the predominance of conformation which is unsymmetrical relative to the cyclohexane ring with respect to the C–P bond. Accordingly, the ^{19}F NMR spectrum of compound **V** contains two signals of the fluorine nuclei, which are the doublets of doublets due to the spin-spin coupling of nuclei ^{19}F–^{31}P and ^{19}F–^{19}F. The vicinal constant $^{2}J_{FF}$ in such systems ^{19}F–^{31}P–^{19}F was apparently first obtained. Its value is 108.4 Hz.

To verify these data, we performed quantum-chemical calculations for compounds **IV–VI** by RB3LYP/6-31+G(d) method using full geometry optimization. These calculations showed that the predominant conformation of the cyclohexane derivatives **IV** and **VI** is the *chair* conformation with the equatorial location of C–P bond, while in all compounds the minimum energy corresponds to a skewed-staggered conformation of difluorophosphoryl group relative to this bond. This leads to the fluorine atoms non-equivalence. In the spectra this non-equivalence is detected only in the case of 2-choro derivative **VI**, where the rotation of the difluorophosphoryl

Table 1. Parameters of the ^{31}P, ^{13}C, and ^{19}F NMR spectra for compounds **I–VI**

Comp. no.	δ_P, ppm (J_{PF}, Hz)	δ_F, ppm (J_{PF}, Hz)	δ_C, ppm (J_{CP}, J_{CF}, Hz)
I	56.94		25.24 d ($^{3}J_{CP}$ 4.63), 25.82 d ($^{2}J_{CP}$ 10.17), 50.95 ($^{1}J_{CP}$ 93.11)
II	49.93		26.06 d ($^{3}J_{CP}$ 4.29), 35.87 d ($^{2}J_{CP}$ 11.02), 57.45 d ($^{1}J_{CP}$ 77.71)
III	36.08		21.46 d ($^{3}J_{CP}$ 12.68), 23.41 d ($^{3}J_{CP}$ 11.93), 26.19 d ($^{2}J_{CP}$ 20.74), 134.10 d ($^{1}J_{CP}$ 135.63), 146.81 d ($^{2}J_{CP}$ 9.06)
IV	25.67 t ($^{1}J_{PF}$ 1156.01)	99.87 d ($^{1}J_{FP}$ 1156.01)	32.89 d.t ($^{1}J_{CP}$ 139.16, $^{2}J_{CF}$ 15.10)
V	21.69 t ($^{1}J_{PF}$ 1146.8)	99.93 d ($^{1}J_{FP}$ 1146.8) 104.63 d ($^{1}J_{FP}$ 1146.8)	23.66 d ($^{3}J_{CP}$ 15.75), 25.72 d ($^{3}J_{CP}$ 4.93), 36.41 d ($^{2}J_{CP}$ 14.19), 43.16 d ($^{1}J_{CP}$ 143.54, $^{2}J_{CF}$ 15.90), 55.50 d ($^{2}J_{CP}$ 6.84)
VI	11.71 t ($^{1}J_{PF}$ 1101.09)	100.92 d ($^{1}J_{FP}$ 1101.09)	21.23 d ($^{3}J_{CP}$ 11.93), 23.44 d ($^{3}J_{CP}$ 10.32), 26.36 d ($^{2}J_{CP}$ 21.14), 121.11 d.t ($^{2}J_{CP}$ 193.71, $^{3}J_{CF}$ 25.16), 151.90 d ($^{1}J_{CP}$ 9.51)

moiety around the C–P bond is apparently more hindered.

The ^{1}H NMR spectra of cyclohexylphosphonic dichlorides and difluorides **I** and **II** correspond to the symmetric structure of the ring. The proton spectrum of dichloride **I** (700 MHz) (Fig. 1) contains a well-separated signals of the protons H_a^1, $H_a^{2,6}$, $H_e^{2,6}$, $H_a^{3,5}$, $H_e^{3,5}$, H_a^4 and H_e^4. All signals are in the range of 1–2.5 ppm (~1000 Hz when the spectra are recorded at 700 MHz). The assignment is done based on the analysis of the chemical shifts and spin-spin coupling constant with accounting for the ring geometry in a *chair* conformation with an equatorial location of dichlorophosphonate group in the position 1. The integral intensity is somewhat distorted because of the overlap of closely located signals. However, in general it is in agreement with the given assignement.

As is known, the value of vicinal spin–spin coupling constant depends essentially on the value of the dihedral angle HCCH. For cyclohexane derivatives, in general and according to the quantum-chemical calculations, the dihedral angle H_aCCH_a is close to 180º, so that this constant is maximal. Accordingly, the constants H_aCCH_e and H_eCCH_e should be small since the corresponding dihedral angles are close to 60º. Consequently, it is expected that the signals of axial protons must be better resolved in the spectrum. In the spectrum of compound **I** (Fig. 1) the proton signal H_a^1, which is a quartet of triplets, is more resolved. Obviously, the signal type corresponds to equal spin–spin coupling constants this nucleus with the protons $H_a^{2,6}$ and with the ^{31}P nucleus: $^3J_{1a,2(6)a} = {}^2J_{1a,P} = 12.3$ Hz, $^3J_{1a,2(6)e} = 3.1$–3.2 Hz.

A similar analysis of the axial proton signal in position 4 indicates the equality of proton–proton constants: $^3J_{4a,3(5)a} = {}^2J_{4a,4e} = 12.8$ Hz, $^3J_{4a,3(5)e} = 3.4$ Hz.

Assignment of the signals of axial protons in positions 2,6 and 3,5 can be made on the basis of the analysis of their multiplicity. The $H_a^{3,5}$ proton signal located as expected in a stronger field contains four main peaks separated by 6.12 Hz from each other, indicating that these protons are neighboring to the proton H_a^4 and the approximate equality of the two vicinal and one geminal constants [$^3J_{4a,3(5)a} \approx {}^3J_{2(6)a,3(5)a} \approx {}^2J_{3(5)a,3(5)e} \approx 12.6$ Hz].

In contrast, the signal of the protons $H_a^{2,6}$ contains 5 main peaks separated also by 12.6 Hz. The increase in the multiplicity is clearly associated with the vicinal spin–spin coupling with ^{31}P nucleus in the equatorial position with approximately the same value of the constant: $^3J_{2(6)a,3(5)a} \approx {}^3J_{2(6)a,1a} \approx {}^2J_{2(6)a,2(6)e} \approx {}^3J_{2(6)a,Pe1} \approx 12.6$ Hz. The interaction of these protons with the vicinal equatorial protons leads to a triplet splitting of each of the major peaks ($J \approx 3.4$ Hz).

The proton H_e^4 signal (Fig. 1d) consists of a main doublet with the splitting ~12.6 Hz, due to, obviously, the spin-spin coupling with the geminal proton H_a^4. Each of the components of the doublet is a multiplet (apparently, close to quintet) due to the interaction with the axial and equatorial protons in positions 3 and 5, with approximately equal coupling constants (~3 Hz), which is consistent with the mentioned above analysis of the axial protons signals.

Thus, the ^{1}H NMR spectrum data (700 MHz) along with the results of quantum-chemical calculations indicate the existence of cyclohexylphosphonic dihalides in a sufficiently rigid *chair* configuration with an equatorial location of the phosphonate group.

The ^{1}H NMR spectrum of difluoride **IV** (400 MHz) is generally similar to that of dichloride, except for the presence of an additional triplet splitting of the signal components of the proton in position 1 due to the spin-spin coupling with the nuclei ^{19}F ($^3J_{HF}$ 3.04 Hz).

Unfortunately, the ^{13}C NMR spectra of these compounds (50.3 and 100.5 MHz for difluoride **IV** and dichloride **I**, respectively) (Fig. 2) do not allow us to obtain the characteristics of the carbon atoms resonance due to the proximity of the signals (within 0.5 ppm) of all the carbon nuclei except for the *ipso*-carbon. The signal of *ipso*-carbon of dichloride **I** is a doublet at δ_C 50.95 ppm ($^1J_{CP}$ 93.11 Hz). In the spectrum of difluoride **IV** the signal of the *ipso*-carbon atom is shifted upfield (δ_C 32.89 ppm, $^1J_{CP}$ 139.16, $^2J_{CF}$ 15.10 Hz). The signals of other carbon atoms of compounds **I** and **IV** are located in a narrow region δ_C from 24.5 to 25.2 ppm.

The correlation NMR spectrum ^{1}H–^{13}C HMQC-2 (Jeol 400/100 MHz spectrometer) also did not possess significant information because of the proximity of signals of all the carbon atoms except the *ipso*-carbon. By the cross-peaks only the accordance of the *ipso*-carbon and the proton connected to it can be identified. The parameters of ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectra of **I** and **IV** are shown in Tables 1 and 2, the ^{13}C NMR spectra of compounds **I** and **IV** are shown in Fig. 2.

In contrast to the compounds **I** and **IV**, the quantum-chemical calculations of geometry of cyclohexen-

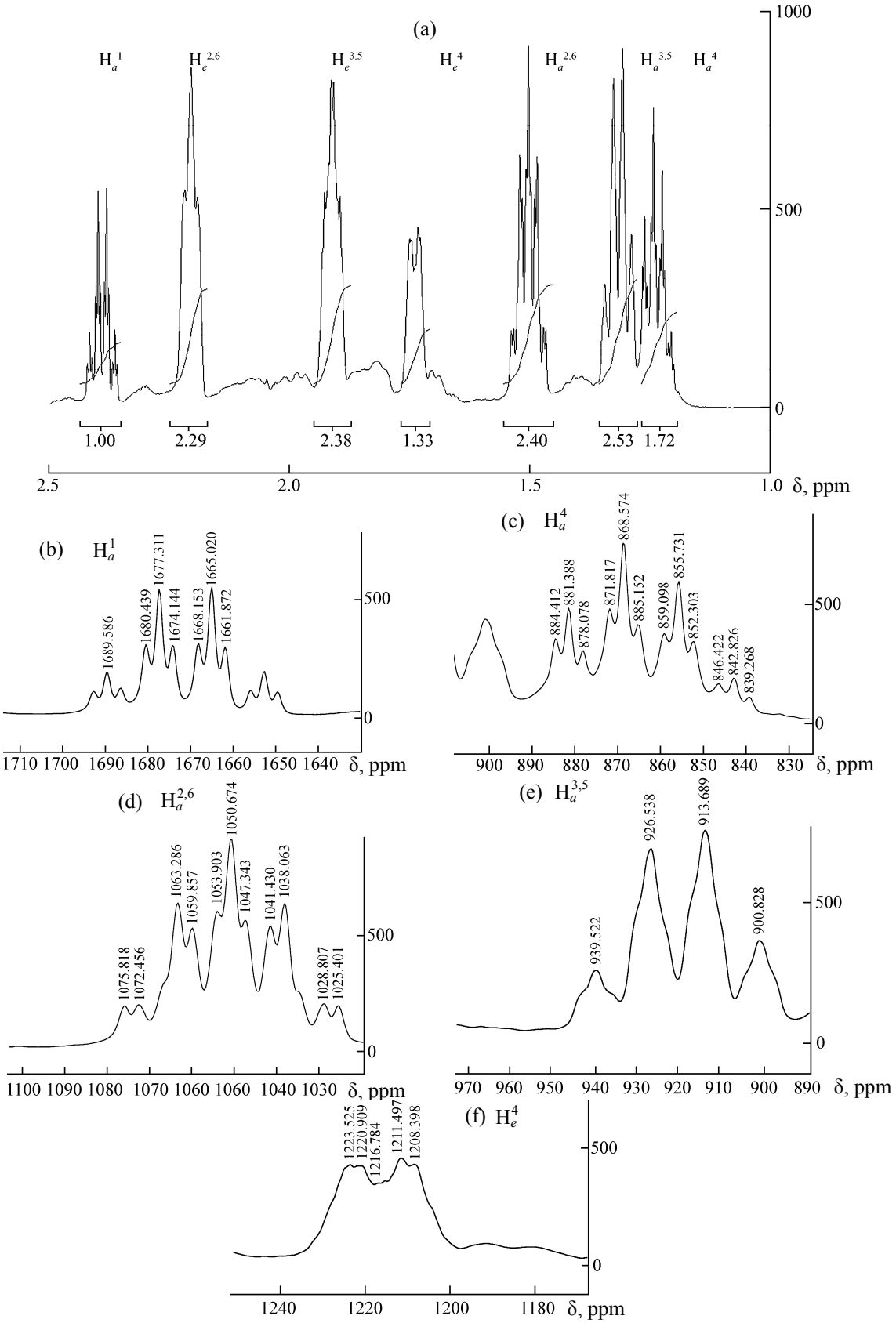


Fig. 1. (a) ^{1}H NMR spectrum of dichloride **I** (700 MHz, $CDCl_3$) and (b–f) its components on an enlarged scale.

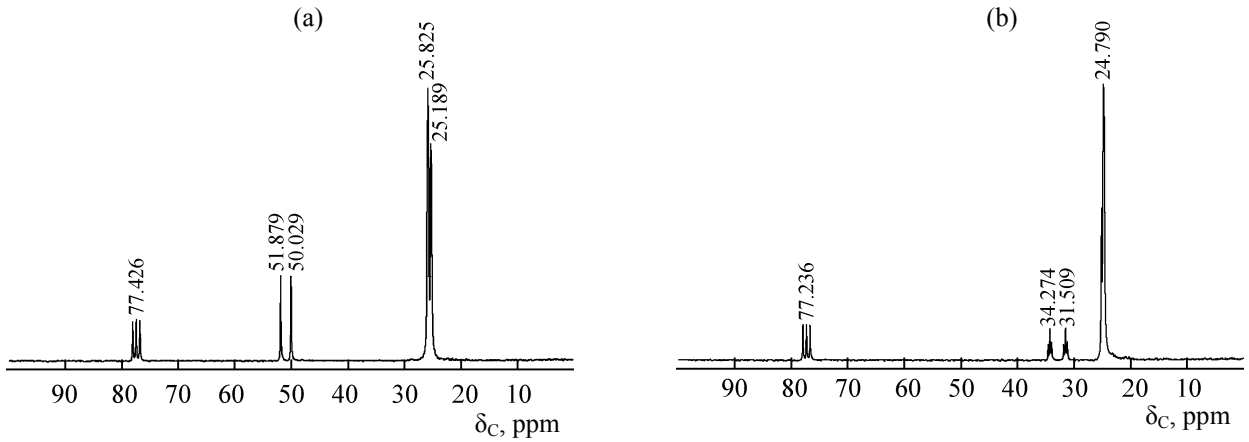


Fig. 2. ^{13}C NMR spectrum of (a) dichloride **I** and (b) difluoride **IV** (50 MHz, $CDCl_3$).

1-ylphosphonic acid difluoride **VI** indicates the planar structure of the ring. The proton resonance spectrum of the corresponding dichloride **III** (Fig. 3) agrees with this conclusion. The spectrum contains a doublet signal with a chemical shift of 6.85 ppm, corresponding to the proton H^2 at the double bond with a spin–spin coupling constant $^2J_{HP}$ 29.21 Hz characteristic of the *cis*-proton-phosphorus interaction, with the intensity corresponding to one proton. The signal with an intensity of about 4 protons in the region of 2.13–2.14 ppm obviously corresponds to the resonance of 4 hydrogen nuclei in the allylic positions, H^3 and H^6. Two signals in the stronger field at δ 1.5 and 1.6 ppm probably correspond to the hydrogen atoms H^4 and H^5, which are the most distant from the double bond. We assign the most upfield signal to the proton H^5, which is the most distant from the phosphorus-containing group. But this correlation is ambiguous because of the proximity of the chemical shifts of nuclei H^4 and H^5. The signals are weakly split. The maximal value of the spin–spin coupling between the protons in this molecule is 4.4 Hz, i.e. there is no interaction of axial–axial type, which is consistent with the structure of the molecule, close to planar.

The ^{13}C NMR spectrum of dichloride **VI** contains 6 signals of the ring carbon atoms, of which 5 are split into doublets because of spin–spin interaction with the ^{31}P nucleus. Based on the analysis of chemical shifts, we assign these signals as follows:

Carbon atom	C^1	C^2	C^3	C^4	C^5	C^6
δ_C, ppm	134.10	146.81	23.40	20.58	21.47	26.19
J_{CP}, Hz	135.63	9.06	11.93	0	12.68	20.73

We failed to obtain reliable spectral characteristics for ^1H and ^{13}C nuclei of other compounds studied.

Thus, we synthesized and studied the structure of phosphorus-containing derivatives of cyclohexane: cyclohexyl- (**I**, **IV**), 2-chlorocyclohexyl- (**II**, **V**), and cyclohexen-1-ylphosphonic (**III**, **VI**) dichlorides and difluorides.

EXPERIMENTAL

The NMR spectra were recorded on spectrometers Bruker AC-200 [200.132 (^1H), 50.328 (^{13}C), 81.014 MHz (^{31}P)], Bruker AC-400 [400.133 (^1H), 376.506 MHz (^{19}F)], Varian S-700 [699.75 MHz (^1H)], and Tesla BS-497 [100 MHz, using the double magnetic resonance $^1H–\{^{31}P\}$]. The two-dimensional correlation spectra were recorded on a HMQC Jeol JNM-

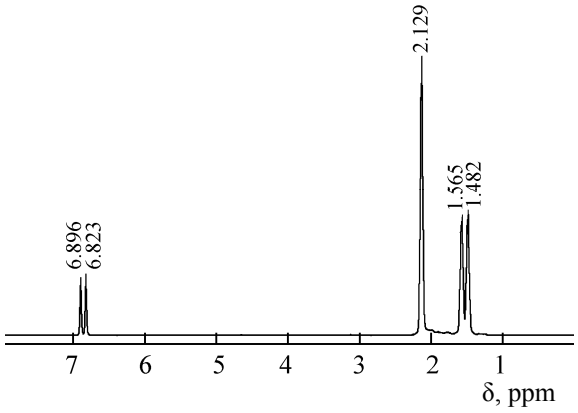


Fig. 3. ^1H NMR spectrum of dichloride **III** (400 MHz, $CDCl_3$).

Table 2. Signals assignment in the ^{1}H NMR spectrum (700 MHz) of **I**

Atom	δ, ppm	Geminal constants, ^2J, Hz	Vicinal constants, ^3J, Hz
H_a^1	2.39	$^2J_{1a,P}$ 12.3	$^3J_{1a,2(6)e}$ 3.1–3.2, $^3J_{1a,2(6)a}$ 12.3
$H_a^{2,6}$	1.50	$^2J_{2a,2e}$ 9.6	$^3J_{2a,3a}$ 12.4, $^3J_{2a,3e}$ 3.5, $^3J_{2a,P}$ 12.4
$H_e^{2,6}$	1.91	$^2J_{2a,2e}$ 9.6	$^3J_{2e,P}$ 13.1, $^3J_{2(6)e,1a}$ 3.1–3.2
$H_a^{3,5}$	1.32	$^2J_{3a,3e}$ 9.7	$^3J_{3a,2a}$ 12.4, $^3J_{3a,4a}$ 12.4
$H_e^{3,5}$	2.20	$^2J_{3a,3e}$ 9.7	$^3J_{3e,2a}$ 3.5, $^3J_{3e,4a}$ 3.4
H_a^4	1.24	$^2J_{4a,4e}$ 12.4	$^3J_{4a,3a}$ 12.4, $^3J_{4a,3e}$ 3.4
H_e^4	1.74	$^2J_{4a,4e}$ 12.4	

ECX400A instrument. Hexamethyldisiloxane (HMDS) was used as an internal reference for ^{1}H NMR spectra. Phosphorus chemical shifts were determined relative to external 85% phosphoric acid (Bruker AC-200) and trimethylphosphate (Tesla BS-497). The ^{13}C spectra were taken relative to internal $CDCl_3$ and DMSO-d_6. The standard laboratory techniques were used to purify and dry the organic solvents and reagents [8–10].

A general procedure for the synthesis of dichlorides (I, II). A reactor was charged with a substrate and 5-fold excess of phosphorus trichloride. Dry oxygen was passed through the reaction mixture under stirring and cooling, while maintaining the temperature below 15°C. As the exothermal process completed, the formed $POCl_3$ was removed, and the residue was fractionated under the reduced pressure.

Cyclohexylphosphonic dichloride (I). Yield 21.6 g (45%), colorless liquid, bp 104–106°C (4 mm Hg). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ_H, ppm: 1.11–1.31 m (3H, H_a^4, $H_a^{3,5}$), 1.37–1.39 m (2H, $H_a^{2,6}$), 1.65–1.69 m (1H, H_e^4), 1.81–1.88 m (2H, $H_e^{2,6}$), 2.10–2.15 m (2H, $H_e^{3,5}$), 2.33 q.t (1H, H_a^1, $^2J_{HP}$ 11.60, $^3J_{HH}$ 2.80 Hz). ^{13}C NMR spectrum (50 MHz, $CDCl_3$), δ_C, ppm: 25.24 d ($C^{3,5}$, $^3J_{CP}$ 4.63 Hz), 25.82 d ($C^{2,6}$, $^2J_{CP}$ 10.17 Hz), 25.83 (C^4), 50.95 d (C^1, $^1J_{CP}$ 93.11 Hz). ^{31}P NMR spectrum (81 MHz, $CDCl_3$): δ_P 56.94 ppm.

2-Chlorocyclohexylphosphonic dichloride (II). Yield 30.1 g (42%), colorless liquid, bp 115–116°C (<1 mm Hg). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ_H, ppm: 1.34–1.38 m (2H, H^4), 1.64–2.02 m (4H, $H^{5,6}$), 2.69–2.85 m (1H, H^1), 4.23–4.30 m (1H, H^2). ^{13}C NMR spectrum (50 MHz, $CDCl_3$), δ_C, ppm: 23.49 (C^4), 23.73 (C^5), 26.06 d (C^3, $^3J_{CP}$ 4.29 Hz), 35.87 d (C^6, $^2J_{CP}$ 11.02 Hz), 56.42 (C^2), 57.45 d (C^1, $^1J_{CP}$ 77.71 Hz). ^{31}P NMR spectrum (81 MHz, $CDCl_3$): δ_P 49.93 ppm.

Cyclohex-1-enylphosphonic dichloride (III). To a solution of 10 g of **II** in 20 ml of anhydrous diethyl ether was added a solution of 5 g of triethylamine in 10 ml of anhydrous diethyl ether at cooling. The reaction mixture was kept for 0.5 h under cooling and 1 h at room temperature. Then triethylamine salt was filtered off, the filtrate was concentrated and fractionated. Fraction with bp 112–114°C (4 mm Hg) was collected. Yield 4.4 g (52%), colorless liquid, bp 82–84°C (<1 mm Hg). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ_H, ppm: 1.48–1.49 m (2H, H^4), 1.56–1.59 m (2H, H^5), 2.13–2.14 m (4H, $H^{3,6}$), 6.85 d (1H, H^2, $^2J_{HP}$ 29.21 Hz). ^{13}C NMR spectrum (50 MHz, $CDCl_3$), δ_C, ppm: 20.58 (C^4), 21.46 d (C^5, $^3J_{CP}$ 12.68 Hz), 23.41 d (C^3, $^3J_{CP}$ 11.93 Hz), 26.19 d (C^6, $^2J_{CP}$ 20.74 Hz), 134.10 d (C^1, $^1J_{CP}$ 135.63 Hz), 146.81 d (C^2, $^2J_{CP}$ 9.06 Hz). ^{31}P NMR spectrum (81 MHz, $CDCl_3$): δ_P 36.08 ppm.

A general procedure for the synthesis of difluorides (IV, V, VI). The corresponding dichlorides (**I**, **II**, **III**) were distilled under the reduced pressure over two-fold amount of the freshly calcined ZnF_2 followed by the repeated fractionating under the reduced pressure.

Cyclohexylphosphonic difluoride (IV). Yield 1.51 g (59.8%), colorless liquid, bp 57–59°C (4 mm Hg). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ_H, ppm: 1.06–1.20 m (3H, H_a^4, $H_a^{3,5}$), 1.26–1.37 m (2H, $H_a^{2,6}$), 1.53–1.56 m (1H, H_e^4), 1.62–1.72 m (2H, $H_e^{2,6}$), 1.85 t (2H, $H_e^{3,5}$, $^2J_{HH}$ 8.80 Hz), 1.95–2.08 m (1H, H_a^1). ^{13}C NMR spectrum (50 MHz, $CDCl_3$), δ_C, ppm: 24.62–25.14 m (C^{2-6}), 32.89 d.t (C^1, $^1J_{CP}$ 139.16, $^2J_{CF}$ 15.10 Hz). ^{31}P NMR spectrum (81 MHz, $CDCl_3$), δ_P, ppm: 25.67 t ($^1J_{PF}$ 1156.01 Hz). ^{19}F NMR spectrum (376 MHz, $CDCl_3$), δ_F, ppm: 99.87 d ($^1J_{FP}$ 1156.01 Hz).

2-Chlorocyclohexylphosphonic difluoride (V). Yield 2.56 g (59%), colorless liquid, bp 65–67°C

(<1 mm Hg). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ_H, ppm: 1.21–1.39 m (2H, $H_a^{5,4}$), 1.55–1.67 m (2H, $H_a^{3,6}$), 1.71–1.84 m (2H, $H_e^{4,5}$), 2.06–2.16 m (1H, H_e^6), 2.20–2.30 m (H_e^3), 2.38–2.49 m (H_a^1), 3.98–4.06 m (H_a^2). ^{13}C NMR spectrum (50 MHz, $CDCl_3$), δ_C, ppm: 23.66 d (C^5, $^3J_{CP}$ 15.75 Hz), 24.66 (C^4), 25.72 d (C^3, $^3J_{CP}$ 4.93 Hz), 36.41 d (C^6, $^2J_{CP}$ 14.19 Hz), 43.16 d.t (C^1, $^1J_{CP}$ 143.54, $^2J_{CF}$ 15.90 Hz), 55.50 d (C^2, $^2J_{CP}$ 6.84 Hz). ^{31}P NMR spectrum (81 MHz, $CDCl_3$), δ_P, ppm: 21.69 t ($^1J_{PF}$ 1146.8 Hz). ^{19}F NMR spectrum (376 MHz, $CDCl_3$), δ_F, ppm: 99.93 d ($^1J_{FP}$ 1146.8 Hz), 104.63 d ($^1J_{FP}$ 1146.8 Hz).

Cyclohex-1-enylphosphonic difluoride (VI). Yield 1.66 g (66%), colorless liquid, bp 62–64°C (4 mm Hg). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ_H, ppm: 1.52–1.64 m (4H, $H^{4,5}$), 2.00–2.25 m (4H, $H^{3,6}$), 7.02 d (1H, H^2, $^2J_{HP}$ 26.41 Hz). ^{13}C NMR spectrum (50 MHz, $CDCl_3$), δ_C, ppm: 20.60 (C^4), 21.23 d (C^5, $^3J_{CP}$ 11.93 Hz), 23.44 d (C^3, $^3J_{CP}$ 10.32 Hz), 26.36 d (C^6, $^2J_{CP}$ 21.14 Hz), 121.11 d.t (C^2, $^2J_{CP}$ 193.71, $^3J_{CF}$ 25.16 Hz), 151.90 d (C^1, $^1J_{CP}$ 9.51 Hz). ^{31}P NMR spectrum (81 MHz, $CDCl_3$): δ_P 11.71 t ($^1J_{PF}$ 1101.09 Hz). ^{19}F NMR spectrum (376 MHz, $CDCl_3$), δ_F, ppm: 100.92 d ($^1J_{FP}$ 1101.09 Hz).

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