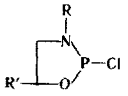
VIBRATIONAL SPECTRA AND STRUCTURES OF A NUMBER OF OXAAZAPHOSPHOLANES

R. R. Shagidullin, I. Kh. Shakirov,
M. A. Pudovik, and S. A. Terent'eva

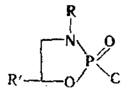
UDC 543.422.4:547.79'546.183

The Raman and IR spectra of six 1,3,2-oxaazaphospholanes with a tri- and tetracoordinated phosphorus atom were obtained. The bands were assigned, and the spectroscopic features of the oxaazaphospholane ring were noted. Assumptions regarding the peculiarities of the three-dimensional structure of the molecules were made on the basis of the change in the characteristic frequencies on passing from trivalent phosphorus compounds to tetracoordinated phosphorus compounds.

The literature contains information regarding the spectroscopic investigations of compounds containing a dioxaphospholane ring [1-4]. The spectra of their close analogs – oxaphospholane compounds – have not been described. We have studied the Raman and IR spectra of I-VI (Figs. 1-3).



I, II, IV



III, V, VI

I $R=CH_3$, $R'=H$; II $R=R'=CH_3$; III $R=R'=CH_3$; IV $R=C_6H_5$, $R'=H$; V $R=C_6H_5$, $R'=H$; VI $R=C_6H_5$, $R'=CH_3$

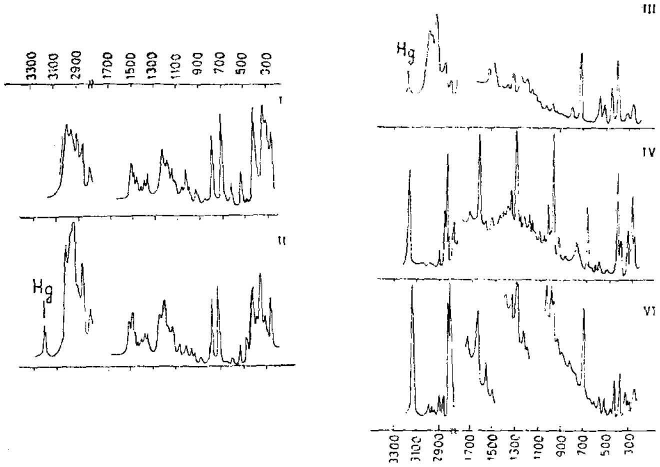


Fig. 1. Raman spectra of liquid I-III and crystalline IV and VI.

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1612-1615, December, 1971. Original article submitted December 17, 1970.

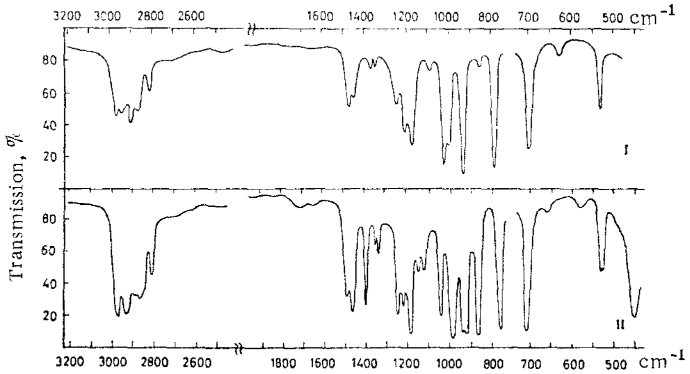


Fig. 2. IR spectra of thin layers of I and II.

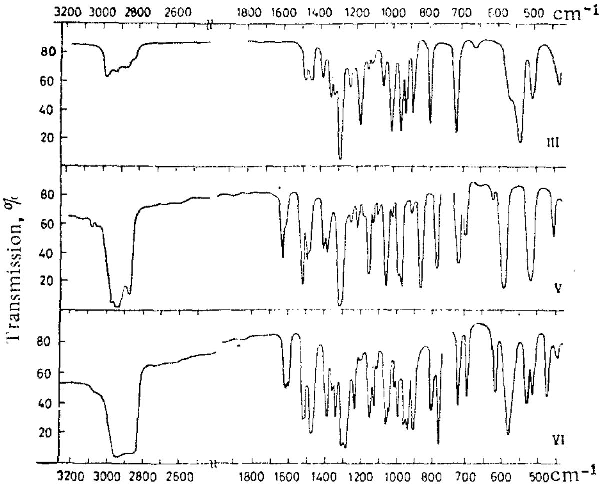


Fig. 3. IR spectra of mineral-oil suspensions of III, V, and VI.

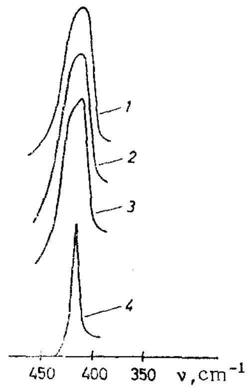


Fig. 4. Temperature dependence of the ν_{P-Cl} band (414 cm^{-1}) in the Raman spectrum of I: 1) +20°C; 2) 0°; 3) −40°; 4) −67°.

An intense narrow line is observed in the Raman spectrum of I at 700 cm^{-1}. The measurements indicated that it is strongly polarized. These results make it possible to assign the line at 700 cm^{-1} to the pulsation vibrations "P" of the oxaazaphospholane ring [5]. The sharp intense band in the IR spectrum corresponds to it. We assign the intense band at 932 cm^{-1} in the IR spectrum of I to the stretching vibration of the ring with predominant participation of the OCCN bonds (ν_{OCCN}). The band at 924-926 cm^{-1} corresponds to it for the dioxaphospholane ring [1-3], while the band at 905 cm^{-1} corresponds to it for the dioxaarsolane ring [4]. The small difference in the position of the band can be explained by the fact that this ring vibration is caused by a grouping of bonds that is not directly associated with the heteroatom. On the other hand, we assign the intense band at 785 cm^{-1} in both the Raman and IR spectra to the vibration of the ring with predominant participation of the NPO bonds (ν_{NPO}). It differs strongly from the corresponding frequency due to the OAsO grouping in the dioxaarsolane ring at 630 cm^{-1} [4]. In analogy with the literature examples [6], it is natural to assign the intense polarized line at 414 cm^{-1} (Raman spectrum), to which the strong absorption in the IR spectrum corresponds, to the ν_{P-Cl} stretching vibrations. The hypothetical interpretation of the vibrational spectrum of I is presented in Table 1. The strongest bands in the IR spectra in the region of the valence vibrations of the phosphorus-containing skeleton can be similarly interpreted for II-VI (Table 2). A sharp increase in the frequency of the P−Cl bond (ν_{P-Cl}) is observed on passing from trivalent to tetracoordinated phosphorus. It is apparent from an analysis of the literature data for compounds of tri- and tetracoordinated phosphorus with similar regular substituents that the transition from the first to the second causes a shift of 50-70 cm^{-1} to higher frequencies [6]. This shift of the characteristic ν_{P-X} vibrations

TABLE 1. Spectral Characteristics of 2-Chloro-3-methyl-1,3,2-oxaazaphospholane (I)*

Frequency, cm^{-1}	Intensity		Approximate assignment	Frequency, cm^{-1}	Intensity		Approximate assignment
	Raman	IR			Raman	IR	
414	s	s	ν_{P-Cl}	1250	m	m	τ_{CH_2}
628	m	w	δ_{ring} (OCC)	1344		w	ω_{CH_2}
700	s	s	ν_{ring} (pulsation "P")	1364	m	w	ω_{CH_2}
785	s	s	ν_{ring} (NPO)	1425	w		$\delta_{CH_3}^{s}$
854	w	w	ρ_{CH_2}	1450	w	m	$\delta_{CH_3}^{E}$
934	w	s	ν_{OCCN}	1470	w	m	δ_{CH_2}
1000	w	m	ν_{C-N}	2810	m	m	$\nu_{CH_3}^{s}$
1030	m	s	ν_{ring} (C—O, C—N)	2900	m	m	$\nu_{CH_2}^{s}$
1090	w	w	ρ_{CH_3}	2940	m	m	$\nu_{CH_2}^{as}$
1211	m	m	τ_{CH_2}	2970	m	m	$\nu_{CH_3}^{E}$ $\nu_{CH_2}^{as}$

*The frequencies were averaged from the Raman and IR spectra; s is strong, m is medium, and w is weak.

TABLE 2. Vibrational Frequencies of the Oxaazaphospholane Ring*

Compound	ν_{P-Cl}, cm^{-1}	Ring vibrations, cm^{-1}			
		ν_{NPO}	P	ν_{OCCN}	ν_{CO}
I	414	785	700	934	1030
II	405	760	710	950	1050
III	543	790	718	960	1015
IV	420	762	700	941	1036
V	517	760	715	960	1040
VI	575	760	720	985	1055

*The frequencies given are for liquids in the case of I-III and for crystalline states in the case of IV-VI.

is, of course (at least in part), explained by strengthening of the P—X bond in the tetracoordinated state as a result of an increase in its s character. In the case of the compounds that we studied, the corresponding shift is considerably greater and amounts to 100-150 cm^{-1}. A definite portion of the shift on passing from cyclic compounds of trivalent phosphorus to the tetracoordinated state in our case is apparently due to a change in the ring conformation. It can be assumed that the ring has the envelope form with a pseudoaxial chlorine atom in the trivalent compound, while the envelope form with axial orientation of the phosphoryl oxygen (as in phospholenes [7]) and an equatorial chlorine atom is realized on passing to compounds with a tetracoordinated phosphorus atom.

The band of the stretching vibrations of the P—Cl bond at 414 cm^{-1} changes particularly appreciably in the Raman spectrum of I as the temperature changes (Fig. 4). While this band is solitary and quite symmetrical at room temperature, a tendency toward asymmetry is observed as the temperature drops. As the compound freezes (−67°), a single symmetric band is observed instead of a broad asymmetric band. It can be assumed that the band at 414 cm^{-1} of I in the liquid state is not solitary but belongs to different conformational isomers. The latter is possible if the ring is not planar.

EXPERIMENTAL

The methods used to obtain I, II, and IV and their physical constants are described in [8, 9]. The Raman spectra were recorded with a DFS-12 spectrometer. The IR spectra were obtained with a UR-10 spectrometer with slit program 4 and other conditions recommended by the instructions.

2-Chloro-2-oxo-3,5-dimethyl-1,3,2-oxaazaphospholane (III). A mixture of 20.2 g (0.2 mole) of triethylamine and 8.9 g (0.1 mole) of 1-methylamino-2-propanol was added with stirring at 15-20° to 15.3 g (0.1 mole) of phosphorus oxychloride in 150 ml of benzene. The reaction mass was stirred for 2 h, and the triethylamine hydrochloride was removed by filtration. The benzene was removed from the filtrate by distillation, and the residue was vacuum-fractionated to give 5.1 g (30%) of III with bp 90° (0.1 mm), d_4^{20} 1.2853, and n_D^{20} 1.4602. Found: Cl 20.8; P 18.2%; MR_D 36.12. $C_4H_9ClNO_2P$. Calculated: Cl 20.9; P 18.3%; MR_D 36.35.

2-Chloro-2-oxo-3-phenyl-1,3,2-oxaazaphospholane (V). This compound was similarly obtained in 65% yield and had mp 96-97° (from benzene). Found: Cl 16.3; P 14.3%. $C_8H_9ClNO_2P$. Calculated: Cl 16.3; P 14.2%.

2-Chloro-2-oxo-5-methyl-3-phenyl-1,3,2-oxaazaphospholane (VI). This compound was similarly obtained in 63% yield and had mp 114-115°. Found: Cl 15.2; P 13.2%. $C_9H_{11}ClNO_2P$. Calculated: Cl 15.3; P 13.4%.

LITERATURE CITED

1. J. Cason, W. N. Baxter, and W. de Acetis, J. Org. Chem., 24, 247 (1959).
2. T. Madro, Wiadom. Chem., 20, 769 (1966).
3. R. A. Jones and A. K. Katritzky, J. Chem. Soc., 4376 (1960).
4. R. R. Shagidullin and T. E. Pavlova, Izv. Akad. Nauk SSSR, Ser. Khim., 2091 (1966).
5. M. M. Sushchinskii, Raman Spectra of Molecules and Crystals [in Russian], Moscow (1969), p. 244.
6. R. A. Chittenden and L. C. Thomas, Spectrochim. Acta, 20, 1679 (1964).
7. V. A. Naumov, N. M. Zaripov, and V. N. Semashko, Material from Papers Presented at the Scientific Conference of the Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR [in Russian], Kazan (1970), p. 78.
8. I. V. Martynov, Yu. L. Kruglyak, and S. I. Malekin, Zh. Obshch. Khim., 38, 2343 (1968).
9. A. N. Pudovik, M. A. Pudovik, O. S. Shulyndina, and Kh. Kh. Nagaeva, Zh. Obshch. Khim., 40, 1477 (1970).