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Infrared Spectra of Aminophosphonic Acids. II.*

V. Jagodić and Lj. Tušek

Institute »Ruđer Bošković«, 41000 Zagreb, Croatia, Yugoslavia

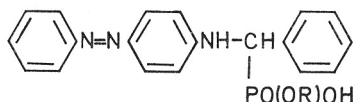
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Infrared spectra of diesters, monoesters and sodium salts of the monoesters of several new aminophosphonic acids containing benzeneazo group, *e. g.* derivatives of [α -(4-benzeneazoanilino)-*N*-benzyl]phosphonic acid, and [4-benzeneazo- α -(anilino)-benzyl]phosphonic acid, have been studied. Assignments for vibrations of the N—H, P=O, PO₂⁻, P—O—H and P—O—R (R = Et, Bu) groups in these compounds were made. On the basis of the infrared spectra and determination of molecular weights of the monoesters, the molecular structure of the compounds is proposed. It was found that the site of the benzeneazo group in the molecule influences the properties of the monoesters. Thus, monoesters of [α -(4-benzeneazoanilino)-*N*-benzyl]phosphonic acid are dimers in chloroform solution, and are also associated, presumably dimeric, in the solid state, owing to strong hydrogen bonds between phosphoryl and acidic hydroxyl groups. Monoesters of [4-benzeneazo- α -(anilino)benzyl]phosphonic acid exist in the solid state as zwitterions.

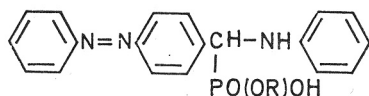
INTRODUCTION

Assignments of the infrared frequencies of various phosphorus compounds have been investigated by a number of researchers and many a correlation between the characteristic frequencies and functional groups in the molecule has been made. Some organophosphorus compounds have found an application as extractants and complex-forming agents for metals. Infrared spectral studies have been often utilized to study the nature of such compounds and their metal complexes. Since many of the compounds contain P=O and P—O links, the absorption of these groups has been extensively studied. It has been found that infrared absorptions of these groups are highly influenced by the type, number and position of substituents. The P=O group is particularly reactive and it possesses strong donor properties. It easily forms hydrogen bonds, which result in a considerable shift of the frequencies.

In this paper the infrared spectra of the following compounds are investigated:



compound I, R = Et
compound II, R = n-Bu



compound III, R = Et
compound IV, R = n-Bu

* For part I see the reference 13.

In addition to the monoesters, the sodium salts of the monoesters, as well as the corresponding neutral esters have also been studied. Assignments for the absorption bands of the N—H, P=O, PO_2^- , P—O—H and P—O—R groups are proposed.

EXPERIMENTAL

Syntheses of the phosphorus compounds were described earlier.¹ Sodium salts of the monoesters III and IV were prepared by neutralization of the alcoholic solution of III and IV, respectively, with an aqueous sodium hydroxide solution. The solvents were evaporated and the residue was recrystallized from ethanol. Sodium salts of III (m. p. 239—240° C) crystallizes with *ca.* 1.5 molecules of water, and the sodium salt of IV (m. p. 223—224° C) contains 1 molecule of water. The content of water was determined by thermogravimetric analysis.

Infrared spectra were recorded on a Perkin-Elmer Infrared Spectrophotometer, Model 257 in Nujol mulls and checked on KBr disks.

Molecular weights were determined by Clark's modification of Signer method² and with a Mechrolab Vapour Pressure Osmometer.³ As a standard solute for these determinations, penta-acetylglucose (B. D. H. micro-analytical reagent) was used.

RESULTS

Molecular Weights of the Monoesters

Molecular weights of the monoesters were determined in chloroform solution. For I and II they were obtained by both methods^{2,3} whereas the molecular weight of IV was determined only with the osmometer. It was impossible to determine the molecular weight of III due to its insufficient solubility in chloroform. The results obtained are given in Table I. Compounds I and II exist in chloroform solution as dimers. Compound IV is only partially dimerized in the concentration range studied.

TABLE I
Determination of Molecular Weights of Aminophosphonic Acid Monoesters

Compound	M. W. calcd. for dimer	Signer's method		With osmometer	
		Concn. at equilibrium mol dm ⁻³	M. W. found	Concn. range used mol dm ⁻³	M. W. found
I	780.7	0.1903	799.5	0.1 — 0.013	783
II	846.9	0.1529	873.2	0.1 — 0.013	818
IV	846.9			0.03—0.003	600

Infrared Spectra

Characteristic absorption bands of the compounds and the proposed assignments are summarized in Tables II—V. The abbreviations used in Tables are: (w) weak, (m) medium, (s) strong, (sh) shoulder, (b) broad, (sym.) symmetric, (asym.) antisymmetric. The frequencies of Nujol are omitted in the Tables. Infrared spectra of monoesters II and IV are shown in Fig. 1.

a) *The N—H Absorptions.* — In the neutral esters of I, II, III and IV the N—H stretching bands occur at 3280 cm⁻¹, 3270 cm⁻¹, 3300 cm⁻¹ and 3395 cm⁻¹, respectively.

In sodium salts of the monoesters the N—H absorptions are obscured by the strong absorptions due to the water of crystallization.

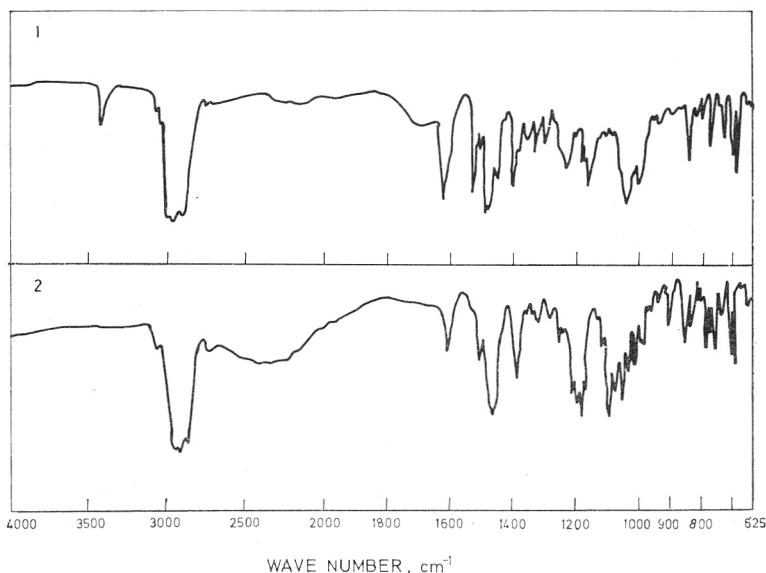


Fig. 1. Infrared spectra of (1) monoethyl ester [α -(4-benzeneazoanilino)-*N*-benzyl]phosphonic acid, and (2) of monobutyl ester [4-benzeneazo- α -(anilino)benzyl]phosphonic acid in Nujol mulls.

In the free monoesters only I and II show the N—H stretching, at 3370 cm^{-1} and 3400 cm^{-1} , respectively. Monoesters III and IV do not show any absorption in the 3400 cm^{-1} region, but give instead a very broad band between $2000\text{—}2700\text{ cm}^{-1}$, which indicates the presence of the NH_3^+ ion.

The N—H deformation modes are expected to occur at about 1600 cm^{-1} . In the same region come also the benzene ring vibrations. Our compounds give very strong bands at 1605 cm^{-1} as a combination of the N—H bending and the aromatic ring vibrations. In the monoesters III and IV the disappearance of the N—H stretching is accompanied by a noticeable decrease in the intensity of the 1605 cm^{-1} band. A similar decrease in absorption in this region was observed on conversion of monoethyl anilinobenzylphosphonate (MOABP) to its hydrochloride. Here also, the band at about 3300 cm^{-1} vanished, and was replaced by new strong bands between $2200\text{—}2800\text{ cm}^{-1}$.

Absorption in the region of 1300 cm^{-1} has been attributed to the C—N stretching from the NH—Ph group.^{4,5} We have investigated this region in the infrared spectra and have found that not a single band but rather a series of peaks appeared, whose intensities differed in the compounds examined. In all neutral esters, sodium salts of the monoesters, and in monoesters I and II a band of medium intensity appears at $1305\text{—}1327\text{ cm}^{-1}$. This band is, however, very weak in monoesters III and IV. In addition to this band, another occurs between $1270\text{—}1290\text{ cm}^{-1}$. It is of medium intensity in all neutral esters, but weak or absent in the sodium salts of the monoesters. The latter absorption is shown also by monoesters I and II in which the band is of medium intensity, but in monoesters III and IV it is very weak or absent. As it has been shown that monoesters III and IV contain a NH_3^+ ion, it could be expected that the absorption due to the NH—C_{arom.} bond in III and IV must be different from

TABLE II
Infrared Frequencies (in cm^{-1}) and Assignments for Monoester I and Its Derivatives

Diethyl ester		Sodium salt of monoethyl ester		Monoethyl ester	
Observed frequencies	Proposed assignments	Observed frequencies	Proposed assignments	Observed frequencies	Proposed assignments
3280 m	$\nu\text{N}-\text{H}$	3620 m, b	H_2O	3370 w	$\nu\text{N}-\text{H}$
1605 s	$\delta\text{N}-\text{H}, \nu\text{C}=\text{C}$	3550 m, b	H_2O	2800-2600 w, b	$\nu(\text{P})-\text{O}-\text{H}$
1530 w		3340 m, b	$\text{H}_2\text{O}, \nu\text{N}-\text{H}$	2400-2200 w, b	$\delta(\text{P})-\text{O}-\text{H} + \nu\text{P}-\text{O}-(\text{H})$
1500 w	$\nu\text{C}=\text{C}$	1605 vs	$\delta\text{N}-\text{H}, \nu\text{C}=\text{C}$	1750-1650 w, b	$\nu\text{P}=\text{O} + ?$
1412 w		1515 m	$\nu\text{C}=\text{C}$	1605 s	$\delta\text{N}-\text{H}, \nu\text{C}=\text{C}$
1340 vw		1494 m		1518 s	$\nu\text{C}=\text{C}$
1312 w		1412 m		1493 w	
1280 w	$\nu\text{C}_{\text{arom.}}-\text{N}$	1350 m		1416 vw	
1235 vs	$\nu\text{P}=\text{O}$	1332 m		1340 w	
1185 vw		1314 m		1327 w	
1154 m	$\delta(\text{O})-\text{Et}$	1289 w	$\nu\text{C}_{\text{arom.}}-\text{N}$	1316 w	$\nu\text{C}_{\text{arom.}}-\text{N}$
1140 s		1262 w		1290 w	
1125 w		1218 s		1254 vw	
1098 w		1194 m	$\nu_{\text{asym.}}\text{PO}_2$	1237 m, b	$\nu\text{P}=\text{O}$
1072 vw		1182 m		1192 m	
1047 s		1156 m		1172 w	
1020 s	$\nu\text{P}-\text{O}-\text{C}$	1144 s	$\delta(\text{O})-\text{Et}$	1162 w	
970 w, b		1078 s	$\nu_{\text{sym.}}\text{PO}_2$	1153 m	
940 w	$\nu_{\text{aliph.}}\text{C}-\text{C}$	1055 s	$\nu\text{P}-\text{O}-\text{C}$	1144 m	
835 w		952 w	$\nu_{\text{aliph.}}\text{C}-\text{C}$	1100 w	$\delta(\text{O})-\text{Et}$
800 w		924 w		1072 vw	
770 w		875 vw		1036 s	$\nu\text{P}-\text{O}-\text{C}$
700 w		830 w		1010 s	$\nu\text{P}-\text{O}-(\text{H})$
690 m		795 w		960 w	$\nu_{\text{aliph.}}\text{C}-\text{C}$
		770 m		920 vw	
		700 m		840 w	
		690 m		812 w	
				794 w	
				697 m	

TABLE III
Infrared Frequencies (in cm^{-1}) and Assignments for Monoester II and Its Derivatives

Dibutyl ester		Sodium salt of monobutyl ester		Monobutyl ester	
Observed frequencies	Proposed assignments	Observed frequencies	Proposed assignments	Observed frequencies	Proposed assignments
3270 s	$\nu\text{N}-\text{H}$	3620 w, b	H_2O	3400 w	$\nu\text{N}-\text{H}$
1605 s	$\delta\text{N}-\text{H}, \nu\text{C}=\text{C}$	3350 m, b	$\text{H}_2\text{O}, \nu\text{N}-\text{H}$	2700—2500 w, b	$\nu(\text{P})-\text{O}-\text{H}$
1527 m	$\nu\text{C}=\text{C}$	1608 vs	$\delta\text{N}-\text{H}, \nu\text{C}=\text{C}$	2300—2100 w, b	$\delta(\text{P})-\text{O}-\text{H} + \nu\text{P}-\text{O}-(\text{H})$
1500 m		1519 s	$\nu\text{C}=\text{C}$	1750—1650 w, b	$\nu\text{P}=\text{O} + ?$
1414 m		1494 w		1604 s	$\delta\text{N}-\text{H}, \nu\text{C}=\text{C}$
1342 w		1414 m		1510 s	$\nu\text{C}=\text{C}$
1324 m		1342 m, b		1492 w	
1312 m	$\nu\text{C}_{\text{arom.}}-\text{N}$	1316 m		1337 w	
1284 w		1290 w	$\nu\text{C}_{\text{arom.}}-\text{N}$	1311 w	$\nu\text{C}_{\text{arom.}}-\text{N}$
1240 vs	$\nu\text{P}=\text{O}$	1260 w		1281 w	$\nu\text{P}=\text{O}$
1140 s	$\delta(\text{O})-\text{Bu}$	1220 s		1217 m, b	
1100 w		1200 m	$\nu_{\text{asym.}}\text{PO}_2$	1183 vw	
1072 m		1183 m		1164 w	
1023 s	$\nu\text{P}-\text{O}-\text{C}$	1155 m		1142 m	$\delta(\text{O})-\text{Bu}$
990 s, b		1142 s		1017 s, b	$\nu\text{P}-\text{O}-(\text{H})$
960 m, sh	$\nu_{\text{aliph.}}\text{C}-\text{C}$	1086 s			$\nu\text{P}-\text{O}-\text{C}$
920 vw		1070 s, sh	$\nu_{\text{sym.}}\text{PO}_2$		$\nu_{\text{aliph.}}\text{C}-\text{C}$
904 vw		1030 m	$\nu\text{P}-\text{O}-\text{C}$	980 s	
838 m		980 w	$\nu_{\text{aliph.}}\text{C}-\text{C}$	938 vw	
810 vw		923 w		920 vw	
790 w		890 w		830 m	
770 m		845 w, b		810 w	
692 m		820 w		790 w	
		775 w		762 m	
		700 w		700 m	
				690 m	

TABLE IV
Infrared Frequencies (in cm⁻¹) and Assignments for Monoester III and Its Derivatives

Diethyl ester		Sodium salt of monoethyl ester		Monoethyl ester	
Observed frequencies	Proposed assignments	Observed frequencies	Proposed assignments	Observed frequencies	Proposed assignments
3300 s	$\nu\text{N}-\text{H}$	3640 w, b	H_2O	2720 m, b	νNH^+
1605 s	$\delta\text{N}-\text{H}, \nu\text{C}=\text{C}$	3380 m, b	$\text{H}_2\text{O}, \nu\text{N}-\text{H}$	2570 m, b	
1523 w	$\nu\text{C}=\text{C}$	1660 w, b	$\delta\text{O}-\text{H}$	1605 m	$\delta\text{N}-\text{H}, \nu\text{C}=\text{C}$
1500 s	$\nu\text{C}=\text{C}$	1604 s	$\delta\text{N}-\text{H}, \nu\text{C}=\text{C}$	1498 m	$\nu\text{C}=\text{C}$
1305 w	$\nu\text{C}_{\text{arom.}}-\text{N}$	1500 s	$\nu\text{C}=\text{C}$	1308 vw	$\nu\text{C}_{\text{arom.}}-\text{N}$
1270 m		1340 w		1260 vw	
1235 vs	$\nu\text{P}=\text{O}$	1315 m		1217 w	
1180 vw	$\delta(\text{O})-\text{Et}$	1265 m	$\nu\text{C}_{\text{arom.}}-\text{N}$	1200 s, b	$\nu_{\text{asym.}}\text{PO}_2$
1160 m		1220 vs	$\nu_{\text{asym.}}\text{PO}_2$	1165 s, b	
1120 vw		1190 m		1104 m	
1100 w		1180 w		1084 s	
1072 m		1160 w	$\delta(\text{O})-\text{Et}$	1070 s	$\nu_{\text{sym.}}\text{PO}_2$
1045 s	$\nu\text{P}-\text{O}-\text{C}$	1110 w		1050 s	$\nu\text{P}-\text{O}-\text{C}$
1017 s		1095 m		1020 m, sh	
975 s, b	$\nu_{\text{aliph.}}\text{C}-\text{C}$	1074 vs	$\nu_{\text{sym.}}\text{PO}_2$	954 m, b	$\nu_{\text{aliph.}}\text{C}-\text{C}$
882 w		1045 vs	$\nu\text{P}-\text{O}-\text{C}$	876 w	
847 m		1014 w		850 w	
774 s		954 m	$\nu_{\text{aliph.}}\text{C}-\text{C}$	800 w	
757 s		885 w		782 w	
690 m		860 w		770 w	
		845 w		755 m	
		767 s		690 s	
		755 s			
		690 m			

that in I and II. Since the absorptions at about 1280 cm^{-1} and 1310 cm^{-1} are actually very weak only in monoesters III and IV, it might be concluded that these two bands probably represent various modes of the $\text{NH}-\text{C}_{\text{arom.}}$ stretching vibrations. The $\text{NH}-\text{C}_{\text{aliph.}}$ bond stretching should appear at lower frequencies, and in these compounds it could not be detected with certainty.

b) *The P=O Frequencies.* — Stretching bands of the phosphoryl group in these neutral esters lie between $1235\text{--}1240\text{ cm}^{-1}$. They are strong and sharp.

In the monoesters the $\text{P}=\text{O}$ stretching absorptions appear to be more complex. Thus I and II give broad and complex bands at about 1237 cm^{-1} and 1217 cm^{-1} , respectively.

It is well known that in acidic phosphorus compounds the phosphoryl group forms very strong intermolecular hydrogen bonds.⁶⁻⁸ Thus, monoesters I and II are dimers in chloroform solution, and are also associated, presumably dimeric, in the solid state, owing to strong hydrogen bonds between phosphoryl and acidic hydroxyl groups.

c) *The PO_2^- Frequencies.* — The ionized PO_2^- group is expected to exist in sodium salts of the monoesters and, because of the zwitterion structure, in monoesters III and IV. In fact, sodium salts of I and II give a triplet with maxima between $1180\text{--}1220\text{ cm}^{-1}$. Sodium salt of III gives a broad band at about 1220 cm^{-1} , and sodium salt of IV gives one broad band at about 1220 cm^{-1} and two weaker bands at 1190 cm^{-1} and 1160 cm^{-1} . In addition all sodium salts give a very strong band at about 1075 cm^{-1} . The latter absorption has been assigned to the symmetric stretching vibration of the PO_2^- ion, and the higher absorption to the antisymmetric vibration of this ion.^{9,10} All sodium salts contain strongly bonded water of crystallization. In the infrared spectra, the water appears as broad multiple bands lying between 3640 cm^{-1} and 3330 cm^{-1} . The presence of water, bonded presumably to the PO_2^- group, may change the polarity of the oxygen atoms and bring about the appearance of very broad and multiple bands.¹¹ Sodium salts of monoesters III and IV give broad shallow bands in the region 1650 cm^{-1} , which might be due to the bending vibration of the water of crystallization.¹² This absorption appears neither in the spectra of the sodium salts of I and II nor in those of monoethyl anilinobenzylphosphonate (MOABP) and monoethyl (2-carboxyanilino)benzylphosphonate (MOCABP) though they also crystallize with water.¹³

It was found that compounds which exist in zwitterion form contain PO_2^- anion and give the absorption bands which occur within the limits found for this ion in the numerous phosphorus compounds.¹⁰ Thus monoesters III and IV give strong bands between $1060\text{--}1090\text{ cm}^{-1}$, arising from the symmetric vibration of the PO_2^- anion, in addition to the antisymmetric vibrations appearing at higher frequencies. Monoesters III shows a doublet with peaks at 1200 cm^{-1} and 1165 cm^{-1} , and IV gives four peaks lying at 1202 cm^{-1} , 1190 cm^{-1} , 1175 cm^{-1} and 1160 cm^{-1} .

d) *The P—O—H Frequencies.* — Monoesters I—IV do not show any evidence of the OH stretching in the 3500 cm^{-1} region characteristic for the free OH group. Monoesters I and II give instead three broad and shallow bands

at lower frequencies typical for hydrogen bonded P(O)OH group. Thus I absorbs at 2600—2800, 2200—2400, and 1650—1750 cm^{-1} , and II at 2500—2700, 2100—2300, and 1650—1750 cm^{-1} . Similar bands were found with MOABP and MOCABP¹³ as well as with a number of various acidic phosphorus esters. According to Thomas *et al.*,^{6,7} the highest band represents the stretching of the O—H group bonded to the phosphoryl group, the second one is a combination band of the P—O—(H) stretching and (P)—O—H deformation, and the lowest band is also a combination band involving the P=O vibration.

In monoesters III and IV two higher absorption bands are either masked or substituted by the absorption due to NH_2^+ ion, while the band at 1600—1700 cm^{-1} is missing.

All monoesters absorb in the range of 1000—1050 cm^{-1} . The region 909—1040 cm^{-1} has been assigned to the P—O—(H) stretching vibration.¹⁴ Also the absorption due to P—O—C group is found in this region, which makes precise assignments difficult. Absorption bands of monoesters III and IV are more complex than those of monoesters I and II, probably because of Fermi resonance. In addition, monoesters III and IV absorb at higher frequencies (between 1060—1090 cm^{-1}) in the range normal for the PO_2^- anion.

e) *The P—O—C Frequencies.* — The interval in which the P—O—C_{alk.} group absorbs, lies between 950—1060 cm^{-1} .¹⁴ For P—O—Et group the interval 1008—1042 cm^{-1} and for P—O—Bu ~ 1025 cm^{-1} has been proposed.¹⁵ It is not possible to determine the exact position since strong bands of the P—O—(H) stretching vibration appear in the same region. Yet, by comparison of the spectra of neutral esters with those of monoesters and their sodium salts, we found that in all ethyl esters there is a strong band between 1035—1050 cm^{-1} , and in butyl esters between 1015—1030 cm^{-1} . Therefore the former bands could be assigned to the P—O—Et and the latter to the P—O—Bu link. MOABP and MOCABP also show strong bands at about 1030 cm^{-1} .¹³ The absorption in the interval 1105—1170 cm^{-1} has been associated with the P—O—C group.¹⁵ In monoesters I and II absorptions appear at 1142—1156 cm^{-1} . The band is more complex in monoesters and their sodium salts than in neutral esters. In neutral esters III and IV several weak bands appear at about 1160 cm^{-1} , while in monoesters III and IV and their salts they are superimposed on the antisymmetric vibration of the PO_2^- anion. It is now thought that the absorption in this region arises from a C—H deformation vibration of the alkyl group rather than from the C—O—(P) vibration.^{16,17}

DISCUSSION

On the basis of the results presented it appears that the nature of the aminophosphonic acids is quite complex. Molecular weight determination showed that the monoesters I and II are dimers in chloroform solution. From their infrared spectra it may be concluded that they are also associated in the solid state due to bonding between phosphoryl and hydroxyl groups. Molecular weight measurement further revealed that monoester IV is only partially dimerized in chloroform solution. It was impossible to determine the molecular weight of III owing to its insufficient solubility in chloroform. Infrared studies have shown that monoesters III and IV exist in solid state as zwitterions. The

observed association of IV in solution could be due to bonding of the oxygen atom to the NH_2^+ group. This bonding is quite possible since many hydrazine compounds containing NH_3^+ group show also strong hydrogen bonding in the solid state¹⁸ and the hydrogen atom often coordinates with two or even with three acceptor atoms. It should be emphasized that of the compounds examined only monoesters III and IV form zwitterions. Neither monoesters I and II nor monoesters of anilinobenzylphosphonic acid¹³ exhibit such a property. Of the α -aminophosphonic acid monoesters only *N*-alkyl substituted compounds form zwitterions.¹⁹

Absorption bands found with our compounds in the region 900—1000 cm^{-1} still remain to be mentioned. The diesters show two main absorptions lying at about 980 cm^{-1} and 960 cm^{-1} . They are stronger in butyl than in ethyl esters. They are affected on conversion of diesters into monoesters or into sodium salts of the monoesters. Thus, in ethyl monoesters (compounds I and III) and their sodium salts the 980 cm^{-1} band vanishes while the 960 cm^{-1} band remains unaffected. To the contrary, in butyl monoesters (compounds II and IV) the band at 980 cm^{-1} persists while their sodium salts show a medium band at 980 cm^{-1} . It has been found that many alkyl esters with unbranched carbon chain also absorb in this region. The absorption in the region 939—982 cm^{-1} is considered to arise from the C—C vibrations.¹⁵

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IZVOD

Infracrveni spektri aminofosfonskih kiselina. II.

V. Jagodić i Lj. Tušek

Studirani su infracrveni spektri diestera, monoestera i natrijevih soli monoestera nekih novih aminofosfonskih kiselina koje sadrže azobenzensku grupu u molekuli, tj. derivata [α -(4-benzenazoanilino)-*N*-benzil]fosfonske kiseline i [4-benzenazo- α -(anilino)]fosfonske kiseline. Pripisane su frekvencije za N—H, P=O, PO₂⁻, P—O—H i P—O—R (R = Et, Bu) grupe u ovim spojevima. Na osnovu ir. spektara i molekularnih težina monoestera, koje su bile određene, predložena je molekularna struktura ovih spojeva. Nađeno je da položaj azobenzenske grupe u molekuli utječe na svojstva monoestera. Tako su monoesteri [α -(4-benzenazo-anilino)-*N*-benzil]fosfonske kiseline dimeri u otopini kloroforma, a također su asocirani, vjerojatno dimerni, i u krutom stanju, zbog jakih vodikovih veza između fosforilne i kiselinske hidroksilne grupe. Monoesteri [4-benzenazo- α -(anilino)benzil]fosfonske kiseline u krutom su stanju »zwitterioni«.

INSTITUT »RUĐER BOŠKOVIĆ«
41000 ZAGREB

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