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Infrared Spectra of Organophosphorus Compounds. III.*

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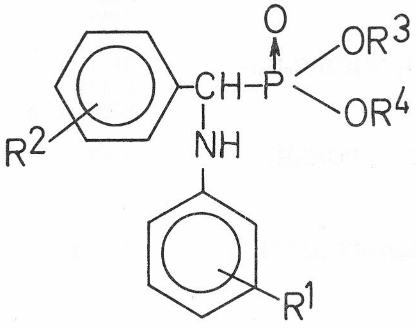
Infrared spectra of α-anilinobenzylphosphonic acid derivatives, $R^1C_6H_4NHCH(C_6H_4R^2)PO(OR^3)(OR^4)$, ($R^1$, R^2 = Br, OH, COOH, NO_2, NH_2; R^3, R^4 = H, Na, Et, Oct) have been studied. Assignments for the N—H, P=O, PO_2^-, P—O—H and P—O—R bonds are proposed. The complexity of the P—O—(C) absorptions in diesters is discussed in terms of the two nonequivalent ethoxy ester groups. Of the monoesters studied, only 2-bromobenzyl (**11, 12**) and 4-carboxyanilino derivatives (**17, 18**) show the N—H stretching bands at about 3300 cm^{-1} and absorption bands in the 1600—2800 cm^{-1} region, characteristic of the hydrogen bonded P(O)OH group. Such bands exhibit neither hydroxy-substituted monoesters (**13—16**) nor the free acid (**19**), because of their zwitterion structure. The bands found with all these compounds in the 900—1000 cm^{-1} region are believed to represent various modes of the P—O stretching.

INTRODUCTION

In this paper the infrared spectra of a number of new derivatives of α-anilinobenzylphosphonic acid (I) have been studied. The assignments of frequencies associated with N—H, P=O, PO_2^-, P—O—H and P—O—C groupings in neutral esters, monoesters, sodium salts of monoesters, a free acid and its disodium salt are proposed and discussed.



I

R^1, R^2 = Br, OH, COOH, NO_2, NH_2; R^3, R^4 = H, Na, Et, Oct. (For details see Tables I—III).

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* For part I and II see the references 1 and 2, respectively.

EXPERIMENTAL

The preparation of phosphorus compounds has been described in a previous paper[3]. Their infrared spectra were recorded on a Model 257 and Model 137 Perkin-Elmer Infrared Spectrometer, in Nujol mulls and KBr discs. The absorption bands are given using the following abbreviations: (w) weak, (m) medium, (s) strong, (sh) shoulder, (b) broad, (sym.) symmetric, (asym.) asymmetric.

TABLE I

Infrared Frequencies (in cm^{-1}) and Assignments for Diesters of α-Anilinobenzylphosphonic Acid

Compd.	Formula	ν OH, ν NH	ν P=O	ν P—O—C
1	$C_6H_5NHCH(2\text{-}BrC_6H_4)PO(OC_2H_5)_2$	3300 m	1230 s	1060 m 1025 s, b 980 s 965 s
2	$C_6H_5NHCH(2\text{-}HOC_6H_4)PO(OC_2H_5)_2$	3200 s, b 2400— 2800 w, b	1220 s, b	1060 s 1025 s 975 s, b
3	$C_6H_5NHCH(3\text{-}HOC_6H_4)PO(OC_2H_5)_2$	3500 w 3250 s 2400— 2800 w, b	1230 s 1200 m	1060 m 1020 s 980 m 960 m
4	$C_6H_5NHCH(4\text{-}HOC_6H_4)PO(OC_2H_5)_2$	3450 s 3300 s 2400— 3000 m, b	1250 m, sh 1230 s, b 1210 m, sh	1060 s 1025 s 980 s 970 s
5	$(2\text{-}HOC_6H_4)NHCH(C_6H_5)PO(OC_2H_5)_2$	3500 m 3200 s 2400— 2800 w, b	1220 s 1205 s 1180 m	1060 s 1025 s 980 s 970 s
6	$(3\text{-}HO, 4\text{-}HOOCC_6H_3)NHCH(C_6H_5)\cdot$ $\cdot PO(OC_2H_5)_2$	3450 m 2400— 3300 m, b	1245 s 1215 s, b 1165 s	1040 s 1020 s 980 s 975 s, sh
7	$C_6H_5NHCH(4\text{-}O_2NC_6H_4)PO(C_2H_5)_2$	3350 s	1250 m 1235 s	1060 s 1030 s 980 m 960 m
8	$C_6H_5NHCH(4\text{-}O_2NC_6H_4)PO(OC_8H_{17})_2$	3300 m	1250 s	1010— 1080 s, b 980 s 930 w
9	$C_6H_5NHCH(4\text{-}H_2NC_6H_4)PO(OC_2H_5)_2$	3500 m 3300 m	1220 s	1060 s 1025 s 990 m 970 m
10	$C_6H_5NHCH(4\text{-}H_2NC_6H_4)PO(OC_8H_{17})_2$	3300 s	1245 s, b	950— 1080 s, b

TABLE II

Infrared Frequencies (in cm^{-1}) and Assignments for Monoesters of α-Anilinobenzylphosphonic Acid

Compd.	Formula	ν OH, ν NH	P(O)OH	ν P=O $\nu_{asym.}$ PO_2^-	$\nu_{sym.}$ PO_2^-	νP—O—(C) ν P—O—(H)
11	$C_6H_5NHCH(2\text{-}BrC_6H_4)PO(OC_2H_5)OH$	3320 m	2000—2800 s, b	1240 s 1190 m	1075 m, sh	1035 s, b 970 s, b
12	$C_6H_5NHCH(2\text{-}BrC_6H_4)PO(OC_8H_{17})OH$	3400 m	2500—2800 w, b 2100—2400 w, b 1650—1750 w, b	1210 m, sh 1175 m, b	1075 w	1025 s, b 980 m, sh
13	$C_6H_5NHCH(2\text{-}HOC_6H_4)PO(OC_2H_5)OH$	2000— 3500 s, b		1250 s 1230 s 1180 s, b	1075 s	1040 s, b 960 s 945 s, sh
14	$C_6H_5NHCH(3\text{-}HOC_6H_4)PO(OC_2H_5)OH \cdot H_2O$	2500— 3500 s, b		1225 s, b 1200 s	1060 s, b	1020 s 980 s 960 s
15	$C_6H_5NHCH(4\text{-}HOC_6H_4)PO(OC_2H_5)OH$	2000— 3500 s, b		1215 s, b 1190 s 1170 s	1080 s 1060 s	1030 s 1020 s 1010 s 925 s
16	$(2\text{-}HOC_6H_4)NHCH(C_6H_5)PO(OC_2H_5)OH \cdot H_2O$	2000— 3630 s, b		1240 s 1230 s 1205 s 1175 s, b	1120 s 1075 s	1040 s, b 950 s, b
17	$(3\text{-}HO, 4\text{-}HOOCC_6H_3)NHCH(C_6H_5)PO \cdot (OC_2H_5)OH$	3350 m	2100—2350 m, b 2550—3200 s, b	1200 m 1165 s	1100 w 1070 w, sh	1030 s, b 1015 s, sh 975 m 965 m
18	$(4\text{-}HOOCC_6H_4)NHCH(C_6H_5)PO(OC_8H_{17})OH$	3300 m	2100—2300 m, b 2500—2700 s, b	1225 m 1180 s 1160 m 1125 m	1075 w 1055 m	1030 s 1015 s, b 980 s, b 960 m, sh
19	$C_6H_5NHCH(2\text{-}HOC_6H_4)PO(OH)_2 \cdot H_2O$	2000— 3600 s, b		1125 s, b	1050 s, b	1020 m, sh 950 s 935 s, b 895 m

TABLE III

Infrared Frequencies (in cm^{-1}) and Assignments for Sodium Salts of Monoesters of α-Anilinobenzyphosphonic Acid

Compd.	Formula	ν OH, νNH	$\nu_{asym.}$ PO_2^-	$\nu_{sym.}$ PO_2^-	ν P—O—(C) ν P—O
20	$C_6H_5NHCH(2\text{-}BrC_6H_4)PO(OC_2H_5)ONa$	3300 m	1240 s 1230 s 1190 m	1080 s	1040 s 945 s
21	$C_6H_5NHCH(2\text{-}BrC_6H_4)PO(OC_8H_{17})ONa \cdot H_2O$	3700 w 3350 m, b	1210 s, b 1185 s, sh 1170 m, sh	1075 s, b	1025 s, b 990 m, sh 970 m, sh 945 w, sh
22	$C_6H_5NHCH(4\text{-}H_2NC_6H_4)PO(OC_8H_{17})ONa \cdot H_2O$	3550 m 3300 s, b 2500— 2700 m, b	1225 s 1190 s 1175 s	1095 m, sh 1075 s, b	1030 m, b 980 m, b 925 m
23	$NaOOCC_6H_4NHCH(C_6H_5)PO(OC_8H_{17})ONa$	3350 m, b	1220 s 1190 m 1175 m	1080 s	1025 m, b 975 m, b 925 m
24	$C_6H_5NHCH(2\text{-}HOC_6H_4)PO(ONa)_2 \cdot H_2O$	2300— 3700 s, b	1120 s, b	1085 m 1055 s, b 1045 m	980 s 935 w

RESULTS AND DISCUSSION

Only the main and characteristic absorption bands are given. The bands that appear to be of a lesser importance for identification of compounds are omitted in the Tables. The frequencies associated with the typical functional groups in neutral esters (**1—10**), monoesters (**11—18**) sodium salts of monoesters (**20—23**), a free acid (**19**) and its disodium salt (**24**), are presented in Tables I—III, respectively.

The N—H Absorptions

In the spectra of diesters the N—H absorption bands are found at about 3300 cm^{-1} and are medium to strong in intensity. Amino-substituted diesters (**9, 10**) show one or two strong and relatively broad bands in the same region. Hydroxy-substituted diesters (**2—6**) give multiple and broad bands because of the overlapping N—H and O—H frequencies. In addition, they show broad bands between 2400—2800 cm^{-1} of the hydrogen bonded O—H group[4].

In monoesters, the N—H band is visible only in the bromo- (**11, 12**) and carboxy-substituted compounds (**17, 18**). The appearance of the N—H band in **17** is not surprising, though this compound has an OH group. The strong intramolecular hydrogen bonding taking place in **17** between the OH and the COOH group shifts the O—H band to lower a frequency, leaving thus visible the N—H absorption. Hydroxy-substituted monoesters (**13—16**) and the free acid (**19**) give a very broad and strong bands between 2000—3600 cm^{-1}, so that neither the N—H nor the NH_2^+ bands are visible.

In the sodium salts of monoesters the N—H group is visible only in **20, 21** and **23** while in other compounds it is masked by the phenolic OH absorption and, in some cases, by the water of crystallization.

The P=O and PO_2^- Absorptions

Since it appears that the differentiation between these groups cannot be always accomplished, their frequencies are discussed together. The P=O group exists presumably in diesters where its frequency occurs between 1220—1250 cm^{-1}, *i. e.* in the range expected for this type of compounds.[5] The bands are relatively sharp in bromo- (**1**), nitro- (**7, 8**) and amino-substituted (**9, 10**) diesters. As anticipated, much broader and multiple bands are observed in hydroxy-substituted diesters (**2—6**), as the result of the intra- and intermolecular hydrogen bonding between the P=O and OH group.

In hydroxy-substituted monoesters (**13—18**) the bands observed between 1170—1250 cm^{-1} are more complex than those in the corresponding diesters. Their position and complexity is arising from the hydrogen bonding and also from the zwitterion structure existing in these compounds. Therefore, these bands should be ascribed to the asymmetric stretching of the PO_2^- group rather than to the P=O frequencies. The existence of the zwitterion form in these monoesters is confirmed by the very strong bands observed between 1060—1080 cm^{-1} that have been assigned to the symmetric PO_2^- stretching. Unfortunately, neither the N—H nor the NH^+ bands are visible. Namely, the 2000—3600 cm^{-1} region is masked by the hydrogen bonded OH groups or even by the water of crystallization found in **14** and **16.** On the other hand, bromo- (**12**) and carboxy-substituted monoesters (**17, 18**) show the N—H bands and give relatively simple bands in the 1175—1240 cm^{-1} region, which can be attributed to the P=O stretching frequency. Consequently, these monoesters give only a weak band in the 1075 cm^{-1} region because of the absence of the PO_2^- ion.

All sodium salts (**20—24**) give a series of complex bands between 1165—1240 cm^{-1} characteristic of the asymmetric stretching and very strong and broad bands near 1075 cm^{-1} of the symmetric stretching of the ionized PO_2^- group.

The P—O—H-Absorptions

On the basis of the foregoing discussion, it can be expected that the frequencies of the P—O—H group should be complex. Monoesters in general do not show the free (P)—O—H group because of the very strong intermolecular hydrogen bonding between the P—O—H and P=O group. They give instead three typical bands in the 1600—1740 cm^{-1}, 2080—2350 cm^{-1} and 2525—2725 cm^{-1} region that are associated with the P(O)OH group[6]. Such bands can be noticed only with monoesters **12**, **17** and **18**. In the latter two compounds, the bands with the frequency above 2500 cm^{-1} are medium in intensity because they are overlapping with the hydrogen bonded (CO)—OH requency, while the bands that should appear between 1600—1740 cm^{-1} are probably masked by the carbonyl absorption. It is interesting that bromosubstituted monoesters (**11**, **12**) behave differently. Although they both show the N—H band, only the octyl monoester (**12**) gives the above mentioned three absorption bands, while ethyl monoester (**11**) gives a strong and broad band in the 2000—2800 cm^{-1} region. Of the two compounds, only the ethyl derivative gives a medium band at 1075 cm^{-1}, characteristic of the PO_2^- ion. It has been discussed that the hydroxy-substituted monoesters exist as zwitter ions. Consequently, they have a PO_2^- group and cannot exhibit the above mentioned three absorption bands characteristic for the P(OH)OH group. The very broad and strong bands that are observed with the hydroxy-substituted monoesters (**13—16**) and the free acid (**19**) in the region 2000—3600 cm^{-1} are due to the hydrogen bonded phenolic OH group and the water of crystallization[3].

The 909—1040 cm^{-1} region has been assigned to the P—O—(H) stretching[7]. This is also the region in which the bands associated with the P—O—C group are found. Monoesters **11—18** give strong bands between 1015—1040 cm^{-1} whose intensity is comparable with the intensities observed with diesters. Also, the free acid (**19**) gives a strong band at 1020 cm^{-1}. Similarly, monoesters and their sodium salts absorb in the 925—980 cm^{-1} range. The free acid (**19**) gives a strong band at 950 cm^{-1} and another one at 935 cm^{-1}, and a medium band at 895 cm^{-1}, while its disodium salt has a strong band at 980 cm^{-1}.

The P—O—C Absorptions

The P—O—C group gives rise to two absorption bands due to the P—O—(C) and C—O—(P) part of the P—O—C bonds. Thus, for ethyl esters there are medium or weak bands in the 1152—1170 cm^{-1} region and strong bands in the 1008—1042 cm^{-1} region. For other alkyl esters the position of these bands somewhat varies[8]. Although opinions still vary as to which absorption frequency is associated with the either bond, the frequencies found in the 905—1060 cm^{-1} region are nevertheless very useful for diagnostic purposes. Diesters (**1—10**) give two strong bands between 1020—1060 cm^{-1} which are usually of comparable strength. The appearance of two frequencies is not surprising since it has been established by NMR spectroscopy that the two ethoxy groups are not equivalent[3]. The X-ray structural analysis of diethyl α-anilinobenzylphosphonate has shown that the P—O distances in the two P—O—C groups differ[9].

The P—O—(C) absorptions of monoesters and their sodium salts also occur in the 1010—1040 cm^{-1} region. These bands are overlapping with the P—O—(H) frequencies already discussed.

The bands in the 900—1000 cm^{-1} region have been assigned by Thomas[10] to the C—C vibrations of the alkyl groups, and to the P—O stretching by some other researchers[11]. Neutral esters give one or two strong bands between 960—980 cm^{-1}. Since monoesters and even the free acid show similar bands, the absorption in the 900—1000 cm^{-1} region should be associated with some mode of the P—O stretching. On the other hand, very strong and complex bands found with dioctyl esters in the 1000—1080 cm^{-1} region could well be the overlapping P—O—C and C—C frequencies.

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SAŽETAK

Infracrveni spektri organofosfornih spojeva. III

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Proučavani su infracrveni spektri derivata α-anilinobenzilfosfonske kiseline, $R^1C_6H_4NHCH(C_6H_4R^2)PO(OR^3(OR^4)$, R^1, R^2 = Br, OH, COOH, NO_2, NH_2; R^3, R^4 = H, Na, Et, Oct). Predložene su asignacije za N—H, P=O, PO_2^-, P—O—H i P—O—C veze. Kompleksnost P—O—(C) apsorpcija diestera objašnjena je postojanjem dviju neekvivalentnih esterskih grupa. Od ispitanih monoestera samo 2-bromobenzil- (**11, 12**) i 4-karboksianilino-derivati (**17, 18**) pokazuju vrpce rastezanja N—H kod oko 3300 cm^{-1} uz vrpce u području 1600—2800 cm^{-1} karakteristične za P(O)OH grupu vezanu vodikovim vezama. Takve vrpce ne daju ni hidroksi-supstituirani monoesteri (**13—16**) niti slobodna kiselina (**19**) zbog njihove strukture »zwitteriona«. Svi proučavani spojevi daju vrpce u području 900—1000 cm^{-1} za koje se vjeruje da predstavljaju razne oblike rastezanja P—O.

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