

89. (*o*-Hydroxyphenyl)methylphosphonic Acids: Spectrophotometric Determination of Their pK_a Values and of the Deprotonation Sequence

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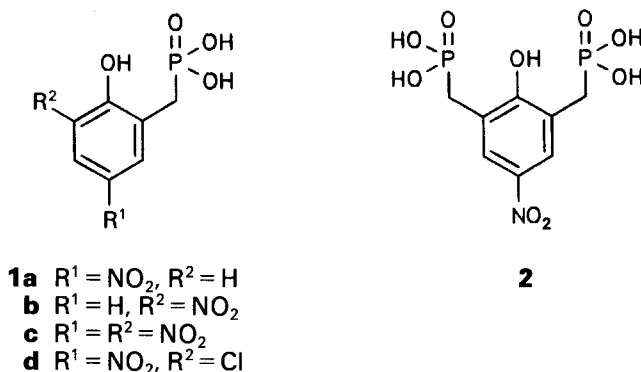
UV/VIS Absorption spectra of nitrosubstituted (*o*-hydroxyphenyl)methylphosphonic acids (*o*-(phosphonomethyl)phenols) were measured as a function of pH at 25° in 0.1M NaClO₄ solutions. Computational treatment of the whole set of optical density data between 200 and 500 nm resulted in the determination of the dissociation constants of these polyacids and also of the individual electronic spectra of all the species involved in the deprotonation sequence. The spectral behavior gives information on the structure of the anions formed and consequently the order of the subsequent deprotonation steps could be deduced. For the (2-hydroxy-3-nitro(or 5-nitro)phenyl)methylphosphonic acid and the 2-hydroxy-5-nitro-1,3-phenylenebis(methylphosphonic acid), the phenolic proton dissociates in the last step, while, in the case of (2-hydroxy-3,5-dinitrophenyl)methylphosphonic acid, the last dissociating proton comes from a P–OH group. An intermediate situation is found for (3-chloro-2-hydroxy-5-nitrophenyl)methylphosphonic acid. Generally, the deprotonation sequence is governed by intramolecular H-bonds involving the phenolic OH group.

Introduction. – In the preceding paper [1], we have described the synthesis of new mono- and bisphosphonic acids derived from phenols. Their pK_a values were determined by potentiometric titration, a method which, however, gives no information on the structure of the anions formed or, in other words, on the order of the subsequent deprotonation steps. This information can be obtained, at least in part, by UV/VIS spectrophotometry, especially for those compounds where chromophoric groups like the NO₂ group are present in the aromatic moiety.

Especially for the *p*-nitrophenol system it is known, that the $\pi \rightarrow \pi^*$ absorption band undergoes an increasingly stronger bathochromic shift (accompanied usually also by an increase in the absorption intensity) the more the strength of the O–H bond in the phenolic OH group decreases [2]. The absorption maximum for *p*-nitrophenol itself for instance shifts from 285 nm in isoctane [3] to 302 nm in dioxane [4], where the solvent acts as a H-bond acceptor. In the interaction with Et₃N, the following species with increasing λ_{\max} have been distinguished [3]: H-bonded complexes [PH ··· A] ($\lambda_{\max} = 305$ nm in isoctane and $\lambda_{\max} = 332$ nm in the more polar 1,2-dichloroethane), H-bonded ion pairs [P⁽⁻⁾ ··· HA⁽⁺⁾] (e.g. in 1,2-dichloroethane with $\lambda_{\max} = 390$ nm) and solvent-separated ion pairs [P⁽⁻⁾ ··· S ··· AH⁽⁺⁾] (e.g. in MeCN with $\lambda_{\max} = 426$ nm). The free *p*-nitrophenolate anion which is formed only in protic solvents then shows again an absorption maximum

at lower wavelength ($\lambda_{\max} = 400$ nm), due to its solvation *via* H-bonds to the phenolate oxygen. In principle, this behavior is observed also for alkylated *p*-nitrophenols (with slightly bathochromically shifted maxima), and the variation in λ_{\max} and ϵ_{\max} was also indicative of the different strength of intramolecular H-bonds in the monoanions of oligonuclear phenolic compounds containing a *p*-nitrophenol unit [5].

Here, we describe a detailed UV-spectroscopic study of the dissociation of the monophosphonic acids **1a–d** and the bis-phosphonic acid **2**, derived from *o*-, *p*-, and dinitrophenol. Computational treatment of the set of spectra, obtained for different pH values, results in the dissociation constants ($\text{p}K_a$ values) and in the individual electronic spectra for all species involved in the deprotonation sequence. These $\text{p}K_a$ values are compared with the potentiometric results reported in [1]. The absorption spectra of the various anions (deprotonated species) formed during the dissociation allow also a structural characterization, especially with respect to the situation of the phenolic OH group. Consequently, the order of deprotonation steps can be deduced.



Results. – a) *UV/VIS Measurements.* The absorption spectra of **1a–d** and **2** were measured between 200 and 500 nm from solutions where the pH is gradually increased from 1 to 12 keeping the ionic strength constant at 0.1M and for **2** also at 1.0M.

Fig. 1 shows as an example a selection of spectra for the bis-phosphonic acid **2**, which is the most complicated case in this study. In going from pH 1 to pH 12, the main absorption band shifts from 322 to 448 nm. Up to pH 9, this shift is only small without any significant variations of the intensities, but occurs in two well distinguished steps. Between pH 2 and 5, the main maxima are found around 331 nm and between pH 7.5 and 9.5 around 351 nm. Over this whole region, the extinction coefficient varies only between about 7500 and 7800 $\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. Above pH 9, the main absorption band around 350 nm decreases regularly, and two other absorption maxima appear, one with a small intensity at 280 nm, the other with a very strong intensity increase at 448 nm. This last pronounced new band has an ϵ_{\max} of 20000 $\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ and corresponds to the pentaanion.

Two other absorption bands around 215 and 250 nm are observed: they correspond to the usual E bands of aromatic systems and are weakly pH dependent [2].

Careful inspection at enlarged scale shows at least three isosbestic points at 338 nm ($7500 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), at 290 nm ($2000 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), and 386 nm ($4800 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$). The last two correspond to the two species which are involved in the equilibrium of the last deprotonation step.

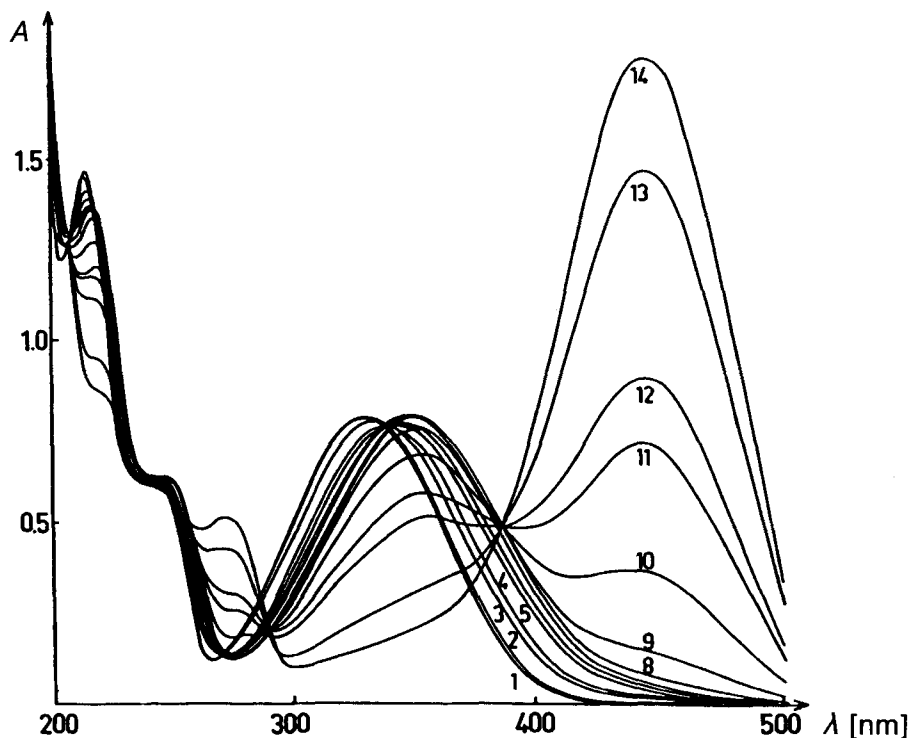


Fig. 1. Experimental absorption spectra of the 2-hydroxy-5-nitro-1,3-phenylenebis(methylphosphonic acid) (2). $[\text{H}_5\text{L}]_0 = 10^{-3} \text{ mol} \cdot \text{l}^{-1}$; $l = 0.1 \text{ cm}$; $\mu = 0.1 \text{ M}$ (NaClO_4); spectra/pH range: 1 to 14/3 to 12.

From the chemical structure and also as a result of the potentiometric measurements, the number of individual species involved in these absorption spectra is known for all compounds; this number can also be proved independently by the optical-density matrix rank analysis [6] which calculates the minimum number of absorbing species and confirms the presence of the six species going from H_5L to L^{5-} . A more precise identification of the peaks can only be achieved with the calculation of the dissociation constants reported next which will characterize rigorously the successive deprotonation equilibria and allow the understanding of the spectroscopic behavior of these molecules.

b) *pH Scale*. The pH calibration for all spectrophotometric determinations was done with HClO_4 solutions of known concentrations and with the ionic strength adjusted to

0.1M (or 1.0M) with NaClO_4 . Consequently, the $\text{p}K_a$ values are based on the 'concentration scale' according to *Sigel et al.* [7] like the potentiometric data obtained by the Method 2 reported in [1]. Due to the small difference to the 'practical pH-scale', a comparison with values obtained by Method 1 in [1] is also justified.

c) $\text{p}K_a$ Values. Simultaneous determination of the dissociation constants and the specific extinction coefficients, $\epsilon_x(\lambda)$ of each species (where x is the number of protons remaining in the ligand) was performed by computation with the program LETAGROP-SPEFO for (N, L) sets of data, where N is the number of solutions differing in pH and L the wavelengths [8]. In general, (N, L) is (25, 30). In *Table 1*, the $\text{p}K_a$ values thus obtained from spectrophotometric data are presented and compared with the corresponding potentiometric results [1]. In general, there is a good agreement between both series of results.

Table 1. $\text{p}K_a$ Values of NO_2 -Substituted Mono-methylphosphono, H_3L (1), and Di-methylphosphono Derivatives of Phenols, H_5L (2), Calculated from UV/VIS Absorption Data. The given $\text{p}K_a$ deviations correspond to 3σ (99%), σ is the standard deviation.

1	μ	$\text{p}K_{a1}$	$\text{p}K_{a2}$	$\text{p}K_{a3}$
1a	0.1	1.91 ± 0.25	6.24 ± 0.15	9.22 ± 0.06
	0.1 ^{a)} b)	1.68 ± 0.15	6.00 ± 0.09	9.10 ± 0.03
1b	0.1	1.91 ± 0.23	6.62 ± 0.14	9.93 ± 0.08
	0.1 ^{a)} c)	1.92	6.67	9.78
1c	0.1	1.29 ± 0.42	4.29 ± 0.09	7.95 ± 0.09
	0.1 ^{a)} b)	1.10 ± 0.27	4.22 ± 0.09	7.96 ± 0.09
1d	0.1	1.56 ± 0.36	5.17 ± 0.18	8.50 ± 0.15
	0.1 ^{a)} c)	1.56	5.17	8.52

2	μ	$\text{p}K_{a1}$	$\text{p}K_{a2}$	$\text{p}K_{a3}$	$\text{p}K_{a4}$	$\text{p}K_{a5}$
	0.1	1.63 ± 0.15	2.03 ± 0.18	5.78 ± 0.06	7.80 ± 0.09	10.43 ± 0.12
	0.1 ^{a)} b)	1.65 ± 0.12	2.00 ± 0.15	5.78 ± 0.06	7.75 ± 0.08	10.30 ± 0.09
	0.1 ^{a)} c)	1.01	2.20	5.88	7.90	10.54
	1.0	0.98 ± 0.05	1.52 ± 0.25	5.03 ± 0.20	7.05 ± 0.15	9.57 ± 0.12
	1.0 ^{a)} b)	–	–	5.24 ± 0.15	7.07 ± 0.12	9.57 ± 0.09

a) $\text{p}K_a$ Values from potentiometric data reported in [1].
b) Concentration pH scale.
c) Practical pH scale.

For compound 2, results obtained at $\mu = 1\text{M}$ are included in *Table 1*. As expected, higher ionic strength of the solutions leads to higher 'apparent' dissociation constants (*i.e.* lower stability constants), which means lower $\text{p}K_a$ values [9]. Thus, reliable $\text{p}K_{a1}$ and $\text{p}K_{a2}$ were not available from potentiometric measurements by calculations using *Miniquad* [10] due to the increasing uncertainty of the potentiometric method in the corresponding pH range. This difficulty is avoided in spectrophotometric measurements where the concentration ratio $[\text{H}_4\text{L}^-]/[\text{H}_5\text{L}]$ can be determined with principally the same accuracy for any given pH. Consequently, the first $\text{p}K_a$ values (especially those at 1M ionic strength) might be obtained more confidently from spectrophotometric data than from potentiometric data.

The agreement of the mathematical treatment of potentiometric and spectrophotometric data was already found for other equilibrium studies implying successive mononuclear complexes formation [9] and using nonlinear least-squares methods based on the *Marquardt* algorithm [11] for multiwavelength data analysis [12]. More recently, newer developments in this field demonstrate clearly for various multicomponent equilibria that the spectrophotometric methods are as precise as the potentiometric one [16].

Nevertheless, the calculated deviations of the pK_a values are, in general, slightly larger for the spectrophotometric results than for the potentiometric results. These differences can be related to the nonlinear least-squares method for the interpretation of spectrophotometric data: the dissociation constants and the specific extinction coefficients are both the parameters to be optimized, but they are not linearly independent. This situation is completely mastered in the search of the best values of the acidity constants (pK_a) corresponding to the minimum of the least-squares function which is the most important criterium to improve the goodness of the fit. But, one of the consequences of the multiwavelength calculation performed with LETAGROP-SPEFO is slightly larger deviations for the acidity constants compared to those estimated from potentiometric data calculations.

d) *Calculated Electronic Spectra of the Deprotonated Ligands.* With the pK_a values obtained, the $\epsilon_x(\lambda)$ data were calculated over the whole wavelengths range and the individual electronic spectra of all possible species could be constructed.

The coordinates of the main absorption maxima for the acids **1a–d** and **2** are reported in *Table 2*. Comparison of the calculated absorption spectra of H_xL and L^{x-} with

Table 2. Main Absorption Maxima, λ_{max} [nm], ($\epsilon_{x,max}$ [$l \cdot mol^{-1} \cdot cm^{-1}$]), Calculated for **2** and **1a–d**, and for Their Anions

H_5L	H_4L^-	H_3L^{2-}	H_2L^{3-}	HL^{4-}	L^{5-}
322 (8200)	331 (7600)	332 (7700)	350 (7800)	352 (7800)	448 (20000)
	H_3L	H_2L^-	HL^{2-}	L^{3-}	
1a	324 (9400)	326 (8700)	344 (8000)	424 (22500)	
(<i>p</i> -) ^{a)}	315 (9000)			400 (18200)	
1b	377 (3100)	380 (2800)	374 (2300)	454 (5000)	
(<i>o</i> -) ^{a)}	350 (3080)			418 (4700)	
1c	266 (14300)	273 (13500)	372 (18200)	380 (19200)	
	325 (5500) sh	330 (6000) sh	410 (8900) sh	425 (10800) sh	
(<i>di</i> -) ^{a)}	260 (12800)			360 (15300)	
	295 (9700) sh			395 (12000) sh	
1d	315 (8400)	321 (8300)	390 (9400)	422 (17700)	

^{a)} Absorption maxima for *p*-, *o*-, and dinitrophenols, (HL) in acidic medium and (L^-) in alkaline medium.

experimental absorption spectra of *p*-, *o*-, and dinitrophenol in acidic and alkaline media was made (the corresponding absorption maxima are also reported in *Table 2*): the analogous spectral features enable a qualitative identification of the species under investigation. The spectra for the acids **1a**, **1c**, **1d**, and **2** and their various anions are shown in *Fig. 2*. These data and figures are the basis of the following discussion.

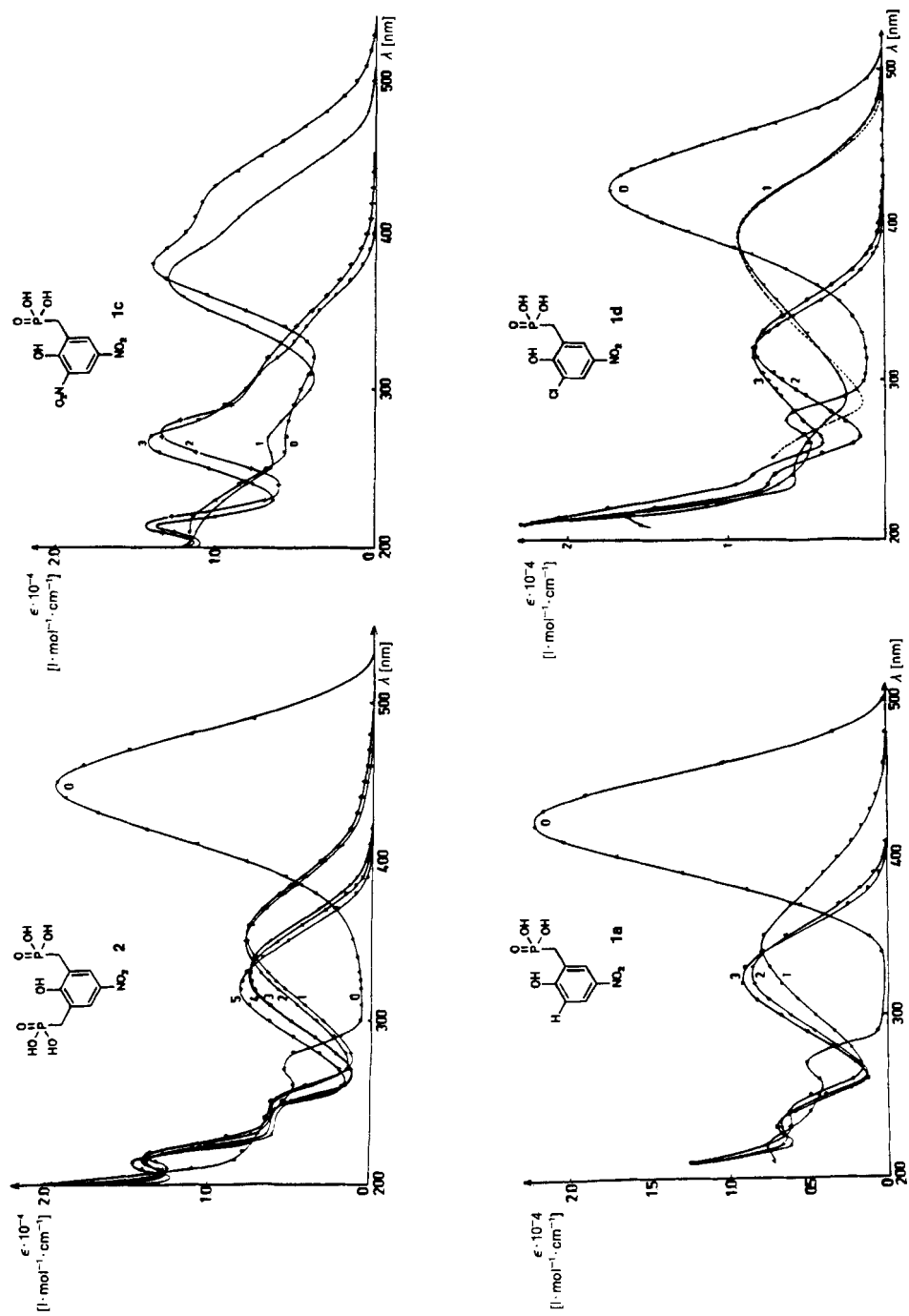


Fig. 2. Calculated electronic spectra of the NO_2 -substituted penta- (H_2L) and triacids (H_3L) and of the corresponding anions. pK_a values used: 1.63, 2.03, 5.78, 7.80, 10.43 for 2; 1.91, 6.24, 9.22 for 1a; 1.29, 4.29, 7.95 for 1c; 1.56, 5.17, 8.52 for 1d (dashed line); simulated values for the absorption of HL^{2-} were calculated by $\epsilon = 0.52\epsilon_A + 0.48\epsilon_B$, where ϵ_A was obtained by shifting the H_2L^- spectrum by (+22 nm) and ϵ_B by shifting the L^{3-} spectrum by (-23 nm).

Discussion. – For the mono-methylphosphonic acid **1a** derived from *p*-nitrophenol, four absorbing species have to be expected (H_3L , H_2L^- , HL^{2-} , L^{3-}). As shown in *Fig. 2* (**1a**), the absorption maximum originally found at 324 nm is only slightly shifted in the monoanion ($\lambda_{\max} = 326$ nm) and somewhat more in the dianion ($\lambda_{\max} = 344$ nm). These bathochromic shifts are accompanied by a slight decrease in the extinction coefficient. A strong increase in ϵ_{\max} and a bathochromic shift to 424 nm is found, however, for the completely deprotonated trianion. Comparison of these data with the spectra of *p*-nitrophenol and *p*-nitrophenolate unambiguously shows that the proton from the phenolic OH group is split off as the last one. Its O–H bond is nearly unchanged in the mono-anion H_2L^- and only ‘stretched’ by an intramolecular H-bond in the dianion HL^{2-} . This result is not completely unexpected, since the second pK_a of the diphosphonic acid is in the same range as the pK_a of *p*-nitrophenol.

A completely analogous result is obtained for the diphosphonic acid **2** derived from *p*-nitrophenol. The spectra for its six different absorbing species (H_3L to L^{5-}) are shown in *Fig. 2* (**2**). Their interpretation is straightforward: the spectra for H_4L^- and H_3L^{2-} are nearly identical and slightly bathochromically (331, 332 nm) shifted with respect to H_3L (322 nm). Hence, the first two protons split from each of the two $PO(OH)_2$ groups. The spectra for H_2L^{3-} and HL^{4-} again are very similar with a maximum which is somewhat more bathochromically shifted (350, 352 nm). These bathochromic shifts are accompanied by a slight decrease in the extinction coefficients which are practically the same for all four species (7600–7800 $l \cdot mol^{-1} \cdot cm^{-1}$). Thus, it can be concluded that the next two protons again dissociate from each of the two PO_2OH^- groups present in H_3L^{2-} . A strong bathochromic shift to $\lambda_{\max} = 448$ nm for L^{5-} together with an increase in the absorption intensity shows, that only at this step the nitrophenolate system is formed. This means, the last proton dissociates from the phenolic OH group. In other words, the tetraanion HL^{4-} contains a *p*-nitrophenol system, in which the aromatic O–H bond is only slightly weakened by intramolecular H-bonds to (one of) the adjacent PO_3^- -groups, and not a nitrophenolate system stabilized by an intramolecular H-bond from the adjacent PO_2OH group. Obviously, the situation of the proton between the competing phenolate and phosphonate O-atom is not determined by the higher acidity of *p*-nitrophenol ($pK_a = 7.0$) or 2,6-dimethyl-4-nitrophenol ($pK_a = 7.2$) in comparison to the second acidity constant of benzylphosphonic acid ($pK_{a2} = 7.5$).

This result means, that the pK_a corresponding to the *p*-nitrophenol structure is increased by more than three units. Although surprising, it is quite in line with the similarity of pK_{a1} to pK_{a4} found for all dimethylphosphonic acids of type **2** with different substituents in *para*-position. Since all these phenols are basically weaker acids than *p*-nitrophenol, it is sure that the phenolic proton in all these cases dissociates in the last step, which is also reflected in pK_{a5} values varying by *ca.* 1.5 units due to the influence of the different substituents in *para*-position [1].

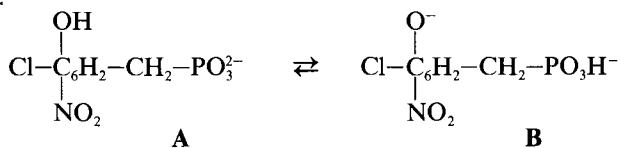
For the monophosphonic acids, a behavior analogous to **1a** may be expected for all compounds derived from phenols which are of the same or of lower acidity than the *p*-nitrophenol. This was further confirmed by **1b** where again the strongest spectral change is connected with the last dissociation step (*Table 2*).

The situation may change, however, if the phenol is getting more acidic. *Fig. 2* (**1c**) shows the spectra for the different species (H_3L to L^{3-}) in the case of **1c**. A slight spectral change in going from H_3L ($\lambda_{\max} = 267$ nm) to H_2L^- ($\lambda_{\max} = 272$ nm) shows again that the first proton dissociates from the phosphonic acid group. In contrast to **1a** and **1b**, a strong

bathochromic shift ($\Delta\lambda \approx 100$ nm) is now found already for the dianion, while the formation of the trianion causes only a small further shift ($\Delta\lambda \approx 10$ nm) to longer wavelengths. This clearly indicates, that in this case the second proton dissociates from the phenolic OH group, and that the dianion is a phenolate, stabilized by an intramolecular H-bond from the remaining PO_3H^- group (*cf. Table 2*). This spectroscopic conclusion holds also with regards to the $\text{p}K_{\text{a}2}$ values calculated spectrophotometrically (4.29) and potentiometrically (4.22) as reported in *Table 1* and the very close $\text{p}K_{\text{a}}$ value of 4.14 of the dinitrophenol [2].

Interesting is the case of the compound **1d** derived from 2-chloro-4-nitrophenol ($\text{p}K_{\text{a}} = 5.2$), the acidity of which is in-between *p*-nitrophenol ($\text{p}K_{\text{a}} = 7.0$) and 2,4-dinitrophenol ($\text{p}K_{\text{a}} = 4.1$) [13]. Compound **1d** shows also a spectral behavior intermediate to **1a**, **1b**, and **1c** (*Fig. 2 (1d)*). As for all other compounds, the spectra of the fully protonated H_3L acid and the monoanion H_2L^- are very similar. As for **1c**, the main bathochromic shift occurs in going from the monoanion to the dianion ($\Delta\lambda = 69$ nm), but in contrast to **1c** an appreciable further bathochromic shift ($\Delta\lambda = 32$ nm) as well as a strong increase in ε_{max} occurs when the trianion is formed.

The asymmetric shape of the absorption band of the dianion HL^{2-} already suggests the presence of at least two absorbing species in comparable amounts [14]. In the light of the above discussion, this must be the two tautomeric forms, **A** with an undissociated phenolic OH group and a diphosphonate structure, **B** with a phenolate and a monophosphonate group:



The determination of the corresponding prototropic equilibrium constant K_{pro} requires additional assumptions [15]. Replacing the $\text{CH}_2\text{PO}_3\text{H}_2$ group by the CH_3 group, 2-chloro-4-nitro-6-methylphenol (**3**) could be used for instance as a spectroscopic model for **A** and the corresponding phenolate ($\mathbf{3}^-$) as a model for **B**. Another possibility would be the assumption that the spectrum of **A** would be similar to that of the monoanion H_2L^- , while **B** could be imitated by the trianion L^{3-} . In fact, in this case both the possibilities are nearly equivalent, since the spectra of **3** and H_2L^- , the spectra of the anions $\mathbf{3}^-$ and L^{3-} are very similar in the long-wavelength range (*Fig. 2 (1d)*). The coordinates ($\lambda_{\text{max}}[\text{nm}]$, $\varepsilon_{\text{max}}[\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}]$) of the absorption maxima are in a very good fit:

$$\begin{array}{ll}
 \mathbf{3}/\text{H}_2\text{L}^-: & (319, 8290)/(321, 8300) \\
 \mathbf{3}^-/\text{HL}^{2-}: & (414, 17700)/(422, 17800)
 \end{array}$$

A disadvantage of these models is that they do not appropriately take into consideration the intramolecular H-bonding of the phenol/phenolate system in both forms of HL^{2-} which has a strong influence on the absorption behavior as pointed out before. It is reasonable to assume that, in comparison to the models, the spectrum of **A** will be bathochromically shifted by the intramolecular H-bond of the phenolic OH group towards the PO_3^{2-} group (which is not present in **3** and weaker in the monoanion H_2L^- where the singly charged PO_3H^- is a weaker acceptor than PO_3^{2-} in the dianion HL^{2-}), while the spectrum of **B** will show a shift to lower wavelengths, due to the intramolecular H-bond of the PO_3H^- group towards the phenolate O-atom (which is not present in both models).

In fact it is not possible to simulate the spectrum of HL^{2-} just by simple addition of suitable fractions of the absorption spectra of these model compounds. Spectra calculated in this way, always show two absorption maxima.

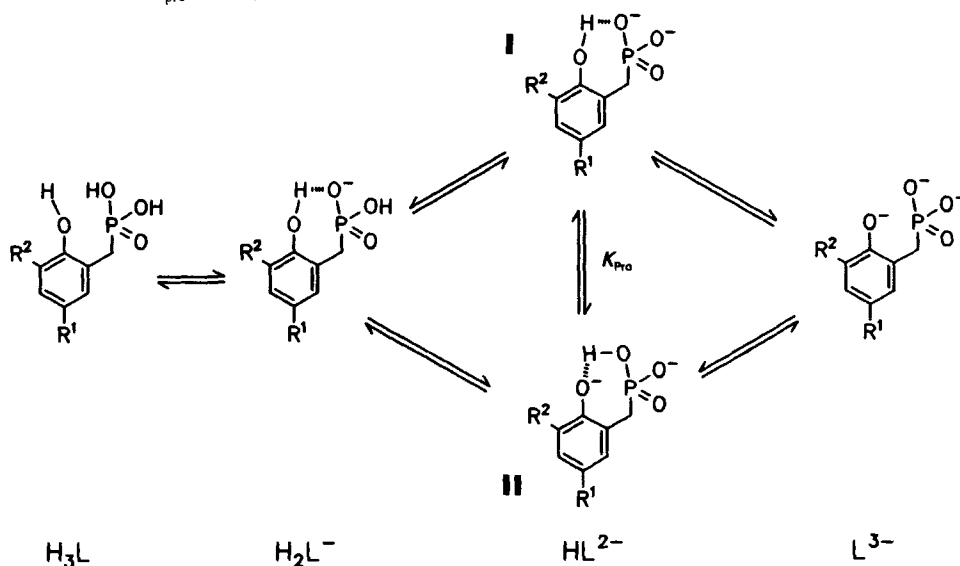
However, the spectroscopic characteristics between the spectrum of HL^{2-} obtained from the general computation of the experimental pH dependent absorption spectra of **1d** and the estimated one (Fig. 2 (**1d**), dashed line) obtained for a calculation with $0.52 \varepsilon(\text{H}_2\text{L}^-)$, bathochromically shifted by 22 nm plus $0.48 \varepsilon(\text{L}^{3-})$ hypsochromically shifted by 23 nm, are very similar. The differences between the values of the extinction coefficients resulting from both methods remain under 5% all over the wavelength range. An even better fit can be obtained taking into account that intramolecular H-bonding in a phenol/phenolate system not only changes λ_{max} but also ε_{max} [5]. We, therefore, believe, that a prototropic equilibrium $\text{A} \rightleftharpoons \text{B}$ exists for the dianion HL^{2-} containing both the tautomeric forms in nearly equal amounts in this special case. This means, K_{pro} is close to 1.

Conclusions. – In phenolic phosphonic acids of type **1** and especially of type **2** a large number of acidic functions are accumulated in immediate vicinity, larger for instance as in analogous carboxylic or sulfonic acids. The acidic properties of these compounds are determined by the mutual interaction of these groups *via* intramolecular H-bonding which may occur in the undissociated acids and in various anions formed during the deprotonation. Nevertheless, structural information on the various species can be obtained from the UV/VIS spectra. Thus, the deprotonation sequence for type **1** can be summarized as shown in the *Scheme*.

The prototropic equilibrium between dianions **I** and **II** is dependent on the acidity of the phenol from which **1** is derived, lying entirely on the side of **I** for **1a** and on the side of **II** for **1c**. A prototropic equilibrium constant of $K_{\text{pro}} \approx 1$ as estimated for **1d** corresponds to a $\text{p}K_{\text{a}}$ of ≈ 5.2 for the underlying phenol. The deprotonation sequence shown is further

Scheme. Deprotonation Process for the NO_2 -Substituted Mono-methylphosphonic Phenol.

K_{pro} is the equilibrium constant between the two possible dianions (prototropy).



confirmed by pH-dependent ^{31}P -NMR spectroscopy which will be reported in detail in a forthcoming paper.

Preliminary studies show, that phosphonic acids of types **1** and **2** form complexes with various divalent cations like alkaline-earth or transition metals. Further studies have to show how the variation of the acidity of the underlying phenol allows a 'fine-tuning' of the corresponding complexation constants (as a function of pH) and consequently of their complexation selectivity.

Experimental. – *Reagents.* All the compounds were synthesized as described in [1]. 0.1M or 1M solns. of NaClO_4 (*Fluka, p.a.*) and 1M NaOH (*Merck*) were prepared with doubly distilled and boiled water. The pH values of the solns. were adjusted by simple addition of acid (HClO_4) or of base under control with a precision pH-meter.

Measurements. The measurements were performed with a *Cary 17D* spectrophotometer connected *via* a *Cary Interface* to a routine printer (*Star LC-10*) for data collection. The concentration of the ligands never exceeded 10^{-3} $\text{mol}\cdot\text{l}^{-1}$ to guarantee accurate and confident optical density values between 0.2 and 2.0. The spectra were run immediately after mixing the reagents, and it took less than 1 min to obtain the absorption curve in the range from 200 to 500 nm. A set of $(N,L) = (25,30)$ data points is sufficient for a reliable numerical analysis. It was ascertained that the solns. were stable for at least 30 min after mixing.

Calculations. The whole set of spectrophotometric data was analyzed using the multiwavelength program LETAGROP-SPEFO [6] which leads simultaneously to two sets of optimized parameters: the dissociation constants (resp. the $\text{p}K_a$ values) and the extinction coefficients of all species involved in the deprotonation sequence. Using these data, the individual electronic spectra for each species could be constructed. The calculated $\text{p}K_a$ values were indicated here with the usual 99% confidence interval ($\pm 3\sigma$); σ is the standard deviation calculated for one (N,L) set of spectrophotometric data. In general, the deviations on the $\text{p}K_a$ (or stability constants) are slightly larger for optical-density data treated by LETAGROP-SPEFO than for potentiometric data treated by *Miniquad* or the $\text{p}K_a$ computation method described in [1]. The quality of the fit is judged, for a given model, from the value of U , sum of the squares of the differences between experimental and calculated absorptions for N solns. at L wavelengths. If U is smaller than 0.02, for $(N,L) = (25, 30)$, a good fit for such rather complicated multi-parameter systems can be stated. The minimum of U leads to the best values of $\text{p}K_a$ which enable the physical chemist to appreciate the understanding of the phenomena and to localize these acids in the $\text{p}K_a$ scale. The constants deviations are secondary factors which do not really improve the goodness of the fit; it is necessary in all programs treating multicomponent systems used up to now to postulate supplementary approximations in the vicinity of the minimum of the least squares function and complementary statistical criteria to obtain satisfactory values of the constants deviations [12].

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