THE PROTONATION OF THE ETHYLENEDIPHOSPHINETETRAACETATE ANION AND THE CRYSTAL STRUCTURE OF THE BIS (HYDROGEN BROMIDE) OF ETHYLENEDIPHOSPHINETETRAACETIC ACID*

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Dedicated to Professor Dr S. Škramovský on the occasion of his 80th birthday.

The equilibria and mechanism of addition of protons to the ethylenediphosphinetetraacetate anion (L^{4-}) were studied in solution by the UV, IR, ^1H and ^{31}P-NMR spectroscopic methods. A total of six protons can be bonded to the anion. They are added stepwise, first with partial formation of zwitterions containing P–H bonds, which then dissociate with formation of the free acid, H_4L, where all four protons are bonded in carboxyl groups. The formation of zwitterions is strongly dependent on the concentration. In the final stage, the acid bonds two additional protons to form the bis-phosphonium cation, H_6L^{2+}. A number of isostructural salts containing this cation, $H_4L.2\,HX$ ($X = Cl, Br, I$), have been prepared. The X-ray crystal structure determination of the bromide confirmed the expected arrangement. The bromide crystals are monoclinic, $a = 578{\cdot}2$, $b = 1\,425{\cdot}0$, $c = 1\,046{\cdot}7$ pm, $\beta = 103{\cdot}07°$ with a space group of $P2_1/c$, $Z = 2$. The final R factor was 0·059 based on 1 109 observed reflections. The structure consists of H_6L^{2+} cations containing protons bonded to phosphorus atoms (P–H distance 134 pm) and of bromide anions, located in gaps which are also sufficiently large for I^- anions in the isostructural iodide. The interbonding of phosphonium cations proceeds through hydrogen bonds, C—OH···O=C, in which the O···O distance is 275·3 pm.

Ethylenediphosphinetetraacetic acid is an exact structural analogue of EDTA, containing a potentially interesting combination of soft and hard donor atoms. The synthesis of this substance, isolation of the tetrasodium salt and its brief characteristics were described in the previous paper in this series[1]. In contrast to EDTA, the infrared spectra of concentrated aqueous solutions[1] originally did not suggest the formation of zwitterions. The values of the proton association constants and the behaviour in the presence of metal ions, however, unambiguously indicate that at least partial formation of zwitterions must be considered in dilute solutions,

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[*] Part XVIII in the series Compounds Structurally Related to Complexones; Part XVII: This Journal *46*, 1222 (1981).

especially in order to enable interpretation of equilibria in solutions containing the ligand, protons and metal ions[2]. Consequently, a more detailed study of protonation of the ligand in solution and in the solid state was carried out.

EXPERIMENTAL

The synthesis of the tetrasodium salt of ethylenediphosphinetetraacetic acid was described in a previous work[1]. D_2O, 25% DCl in D_2O and 25% $DClO_4$ in D_2O (isotopic purity all $> 99\%$) were the products of Alfa Inorganics. The solution of NaOD in D_2O (carbonate free) was prepared according to the literature[3]. Anhydrous sodium perchlorate was obtained from the doubly recrystallized monohydrate by drying at 140°C. The other chemicals were of *p.a.* purity.

All the physical measurements except for X-ray structural analysis were carried out in the absence of oxygen. The pD value was measured using the method recommended by Bates[4]. A combined Radiometer GK 2301 C electrode and a Radiometer PHM 64 instrument were calibrated[5] by titration of $DClO_4$ with a NaOD solution in D_2O to directly yield the $-\log [D^+]$ values, and then controlled[4] using buffers in H_2O. The appropriate correction for the pH-meter data between pH 2 and 9 was $+0{\cdot}33 \pm 0{\cdot}01$, which apparently includes terms for the pH/pD conversion ($+0{\cdot}41$, see[4]) and for pD/$-\log [D^+]$ ($-0{\cdot}08$, see ref.[6]). The method of obtaining data and their treatment were then identical to those described in an earlier work[7].

The UV spectra were measured on Unicam SP 800 and VSU-2 (Zeiss, Jena) instruments at 25°C in Suprasil cells. The solutions were freed of dissolved gases prior to the measurement.

The UR-20 instrument (Zeiss, Jena) was used to measure IR spectra. CaF_2 cells with 50 μm thick polyethylene spacers were used for D_2O solutions between 1 500 and 1 800 cm^{-1}. The reference cell contained the solvent. The samples were transferred to the cells in a glove box in a nitrogen atmosphere. Both the absorbance and transmittance were measured and the agreement of the scales was previously controlled using rotating segments. The solid sample spectra were measured in the range 400—4 000 cm^{-1} in nujol and hexachlorobutadiene suspensions.

The ^1H-NMR spectra were measured in D_2O at 29°C on a Tesla BS 483A instrument at 80 MHz using tert-butanol as an internal standard. The solution concentration was 0·05—0·8M. The chemical shifts were read with a precision of 0·01 ppm from a calibrated graphical recording and related to tetramethylsilane ($\delta_{tert\text{-}BuOH} = 1{\cdot}25$ ppm). A Fourier-transform Varian XL-200 instrument was used at 80·8941 MHz for 31 $P\{^1H\}$-NMR measurements. The spectra of D_2O solutions (external deuterium lock) were related to 85% H_3PO_4 as an external standard; the downfield chemical shifts are defined as positive in agreement with the IUPAC convention[8]. The chemical shifts were read with a precision of 0·02 ppm from a digital spectrum recording.

Preparation of solid phosphonium salts: An 18% aqueous solution of HCl (40% HBr, 50% HI) was saturated with solid $Na_4L.H_2O$ in an argon atmosphere with heating. After filtering and leaving to stand overnight at 5°C, the separated crystals were filtered off and recrystallized from the appropriate acid. The pure crystals were washed with acetic acid and ether and dried in vacuum. Yields were 50—80%. $H_4L.2$ HCl: m.p. 125°C; for $C_{10}H_{18}Cl_2O_8P_2$ (399·1) calculated: 1·52% H^+, 17·77% Cl, 15·52% P; found: 1·52% H^+, 15·16% P(III), 17·92% Cl, 15·47% P (total); IR spectrum: 1 695 vs, 1 740 s ν(C=O), 2 480 w ν(PH), 2 660 m, vb, 3 140 vs, b ν(OH).

$H_4L.2$ HBr: m.p. 164—167°C (decomp.); for $C_{10}H_{18}Br_2O_8P_2$ (488·0) calculated: 1·24% H^+, 32·75% Br, 12·69% P; found: 1·22% H^+, 33·47% Br, 12·57% P(III), 12·88% P (total); IR spectrum: 1 708 vs, 1 740 vs, 1 740 s ν(C=O), 2 468 w ν(PH), 2 710 s, vb, 3 185 s, b ν(OH).

$H_4L.2$ HI: m.p. 157—158°C; IR spectrum: 1 712 vs, 1 740 s ν(C=O), 2 462 m ν(PH), 2 890 vs, vb, 3 240 s, b ν(OH); for $C_{10}H_{18}I_2O_8P_2$ (582·0) calculated: 1·04% H^+, 43·61% I, 10·64% P; found: 1·04% H^+, 43·45% I, 10·54% P(III), 10·67% P (total).

$H_4L.2\,HBr$ single crystals were obtained by slow cooling of a hot 2% solution in 35% HBr. A crystal with dimensions $0{\cdot}05 \times 0{\cdot}05 \times 0{\cdot}12\ \text{mm}^3$ was monoclinic with the following parameters: $a = 578{\cdot}2\ (2)$, $b = 1\,425{\cdot}0\ (7)$, $c = 1\,046{\cdot}7\ (4)$ pm, $\beta = 103{\cdot}07\ (3)°$, $V = 840{\cdot}1\ (6) . 10^6\ \text{pm}^3$ $Z = 2$, $F_{000} = 484$. The unit cell dimensions were obtained from 13 reflections, measured on an automatic four circle Syntex $P2_1$ diffractometer at room temperature using MoK_α radiation ($\lambda = 71{\cdot}069$ pm, $\mu = 49{\cdot}2\ \text{cm}^{-1}$) with a graphite monochromator; these 13 reflections were treated by the least squares method. Systematic absences (for $h0l$: $l = 2n + 1$, for $0k0$: $k = 2n + 1$) yielded the space group $P2_1/c$ with $Z = 2$ and a calculated density of $1\,920\ \text{kg m}^{-3}$ ($D_m = 1\,900\ \text{kg m}^{-3}$ was measured by flotation in a mixture of bromoform and benzene).

The intensity measurement was carried out on the same diffractometer for one quadrant of the reciprocal space (h, k, $\pm l$) to $2\Theta = 57°$ using the scanning technique, $\omega - 2\Theta$. The scan rate varied from 1·5 to 29·3° min^{-1} in 2Θ. After each 47 reflections, the intensity of 3 standard reflections was controlled; no significant fluctuation was observed during the measurement. Of the total number of 2 145 reflections, 1 109, for which $I > 1{\cdot}96\sigma\,(I)$, were used for the calculation ($\sigma(I)$ was calculated from the counting statistics) and the remaining reflections were considered as "unobserved". The intensity values were corrected using the Lorentz polarization factor. No correction was made for absorption ($\mu = 49{\cdot}2\ \text{cm}^{-1}$).

The structure was solved by the heavy atom method using the TLS program system[9]. The position of the bromine atom was found from the three-dimensional Patterson synthesis. The remaining non-hydrogen atoms were found by Fourier synthesis. Their positions were refined by the full-matrix least squares method to $R = \sum||F_0| - |F_c||/\sum|F_0| = 0{\cdot}094$ with isotropic and to $R = 0{\cdot}065$ with anisotropic temperature factors. The refinement was continued until the changes in the parameters were less than 0·25 of their standard deviation. The positions of all the hydrogen atoms were found from the difference map. They were assigned the isotropic temperature factors of their bonding partners. After one cycle of refinement of the positions of all atoms, final values of $R = 0{\cdot}059$ and $R_w = [\sum w(|F_0| - |F_c|)^2/\sum w|F_0|^2]^{1/2} = 0{\cdot}076$ were obtained with individual weights $w = 1/\sigma^2(F_0)$, where $\sigma(F_0) = F_0\sigma(I)/2I$. The final difference map exhibited the largest maximum value $0{\cdot}4e/(100\ \text{pm})^3$. The atomic scattering factors were taken from the literature[10]. All the calculations were carried out on a ICL 4—72 computer.

RESULTS AND DISCUSSION

The ^{1}H and ^{31}P-NMR spectra of a 0·1 M ligand solution in D_2O at various acidities are depicted in Fig. 1. The ^{1}H-NMR spectra[1] exhibit no or only slight similarity to that of EDTA (ref.[11]) due to P-H coupling which, under certain conditions[12], leads to a deceptively simple spectra. While the resonances of the nonlabile protons are affected only indirectly by various protonation sites[13], the ^{31}P spectra clearly reflect changes in the shielding of phosphorus as a result of protonation[14]. Typical ^{31}P chemical shift values are -20 ppm for $P(CH_2COOR)_n$ (R = H, Na, Et)[15] and $+10$ ppm for the quaternary phosphonium salt[14] with one P-H bond.

In general, both the ^{1}H and ^{31}P-NMR spectra convincingly indicate partial protonation of the phosphorus atoms in the range $2{\cdot}5 < \text{pD} < 7{\cdot}5$ and also at $[D^+] > 0{\cdot}05\ \text{mol . dm}^{-3}$. The protonation is incomplete unless the concentration of strong acid is less than at least $10\ \text{mol . dm}^{-3}$.The marked broadening of the ^{31}P signal at $\text{pD} = 2{\cdot}5 - 7{\cdot}5$ indicates slow exchange (in the NMR time scale) between two nonequivalent phosphorus atoms, i.e. one in phosphine and one in phosphonium.

Addition of further protons to the region of predominant existence of H_4L causes the frequency and width of the NMR signal to return to the original values, corresponding to the acid in which all 4 protons are bonded to carboxyl groups. Further protonation in strongly acid medium leads to a marked signal shift, but does not change its width. This effect is in agreement with the rapid proton exchange between phosphorus atoms, apparently favoured by the high concentration of the strong acid.

This behaviour is markedly dependent on the ligand concentration. The formation of zwitterions is suppressed and eventually completely eliminated at higher concentrations, as is apparent from Fig. 2 depicting the dependence of the parameters of the ^{31}P signal on the concentration. As only a limited amount of the substance was available, this effect was not studied further and detailed measurements were limited to the concentration range $c_L \leqq 0{\cdot}1 \text{ mol . dm}^{-3}$, which is most important for the study of the coordination behaviour of the ligand.

In order to obtain quantitative data on the various mentioned equilibria, "macroscopic" constants[16] were determined, corresponding to the overall addition of protons, and "microscopic" constants[16], describing the equilibria among tautomeric forms. In an earlier work[1], the protonation constants $\beta_1^H - \beta_4^H$ ($\beta_i^H = [H_iL]/[H]^i\,[L]$, charges are omitted) were found potentiometrically. Because the part of the present

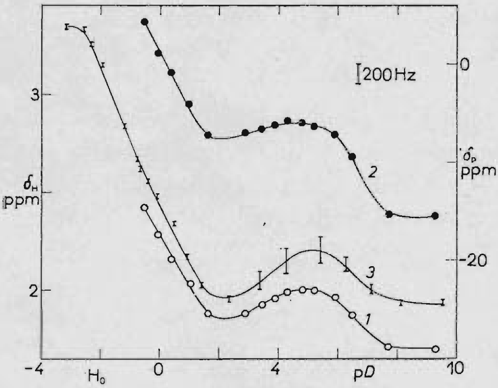


FIG. 1

The dependence of the chemical shift and half-width of the NMR signal on the acidity. Curve *1* PCH_2CH_2P, curve *2* CH_2COO curve *3* P

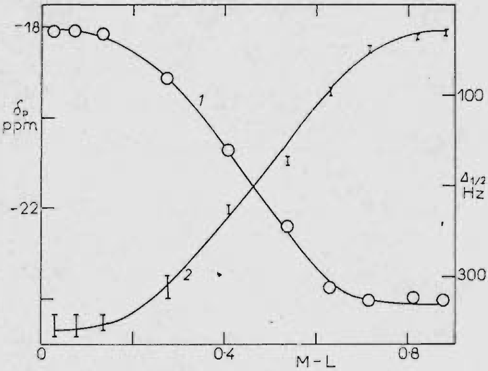


FIG. 2

The dependence of the chemical shift (curve *1*) and half-width (curve *2*) of the ^{31}P signal on the ligand concentration at pD 5·2 work was carried out in D_2O, these constants were determined by an analogous method in D_2O (25°C, $I = 0{\cdot}1$ $NaClO_4$):

Value	Constant β_1	β_2	β_3	β_4
$\log \beta^H(3\sigma)$	5·97 (2)	10·50 (4)	14·17 (4)	16·79 (5)
$\log \beta^D(3\sigma)$	6·40 (1)	11·52 (2)	15·73 (2)	19·13 (3)

The remaining constants K_5 and K_6, describing formation of the phosphonium salts, were found from the UV spectra in strongly acid media. The far-UV spectra of the ligand in HCl solutions of various concentrations at $I = 4$ (H, Na) Cl and 25°C change systematically in the region 250–200 nm. The spectra were treated using the SQUAD program[17] and the following constants were obtained: $K_5 = [H_5L]/([H_4L]\,[H]) = 1{\cdot}0 \pm 0{\cdot}3$, $K_6 = [H_6L]/([H_5L]\,[H]) = 3{\cdot}6 \pm 0{\cdot}2$. These values demonstrate that the solutions can contain only a small amount of H_5L species, in agreement with the sharpness of the ^{31}P resonance during acidification.

The microconstants were determined using the diagnostic behaviour of the $\nu(C{=}O)$ infrared vibration on changes in the surroundings of the carboxyl group. Similarly as for the nitrogen analogues[18], it was assumed that three types of carboxyl group absorb differently: $R_2PCH_2COO^-$ at ca. 1 570 cm^{-1}, $R_2\overset{+}{P}(H)CH_2COO^-$ at ca. 1 610 cm^{-1} and R_2PCH_2COOH at ca. 1 690 cm^{-1}. This assignment is supported by trends in the spectra of L^{4-} in D_2O on a change in the acidity and also by analogy with the simpler phosphineacetates studied earlier[19–22]. The infrared spectra of

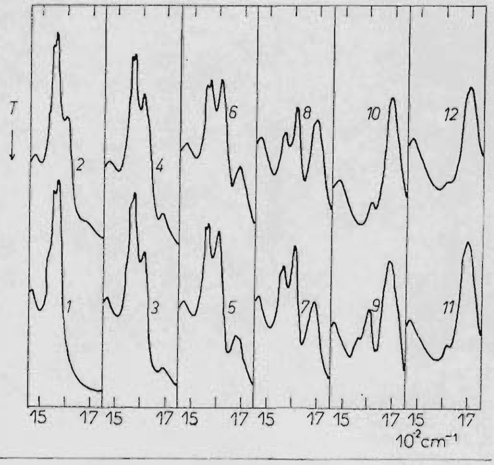


FIG. 3

The infrared spectra of 0·1M ligand in D_2O in dependence on the acidity. pD: *1* 7·87; *2* 6·35; *3* 6·00; *4* 5·69; *5* 5·17; *6* 4·83; *7* 4·37; *8* 3·93; *9* 3·41; *10* 2·20; *11* 1·79; *12* 0·92

TABLE I

Relative intensity of infrared bands (cm^{-1}) at various acidities

$-\log [D^+]$	Relative intensity, %			Calculated constants
	1 570	1 610	1 690	
7·87	100·0	0	0	—
6·35	77·6	15·3	7·1	K_1
6·00	65·6	19·1	15·3	K_1, K_2
5·69	56·0	24·0	20·0	K_1, K_2
5·17	45·3	29·5	25·2	K_1, K_2, K_3
4·83	40·0	28·4	31·6	K_1, K_2, K_3
4·37	30·5	24·7	44·8	K_1, K_2, K_3, K_4
3·93	25·7	18·9	55·4	K_2, K_3, K_4
3·41	20·4	10·0	69·6	K_2, K_3, K_4
2·20	0	7·8	92·2	K_3, K_4
1·79	0	0	100·0	—

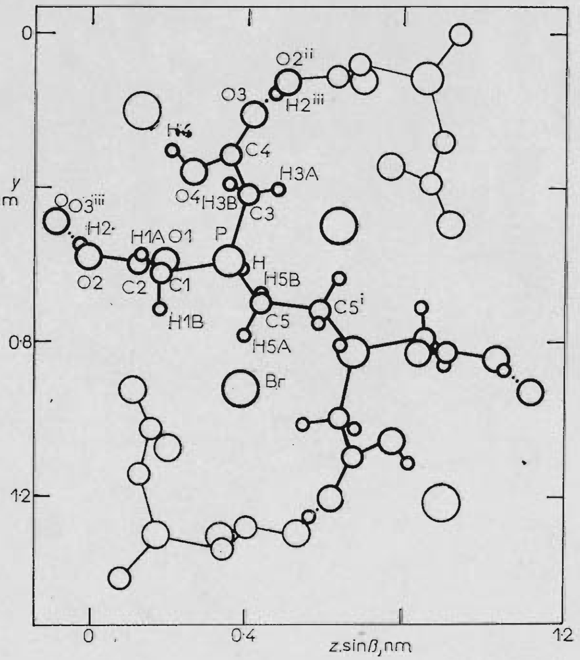


FIG. 4

Projection of the structure of $H_4L.2\ HBr$ onto the $yz \sin \beta$ plane (see also Table III)

D_2O solutions at various pH values exhibit systematic intensity changes for the given 3 bands (Fig. 3). The following observations and assumptions were used in interpretation of these spectra: *1*) the molar absorptivities of various forms of the carboxyl groups are the same within experimental error, as follows from the fact that the overall area under the three maxima is independent of pD. *2*) The relative intensity can be interpreted assuming that only a single phosphorus atom is protonated in the interval pD = 2·5−7·5, *i.e.* no "double" zwitterions are formed: this is in agreement with the ^{31}P-NMR spectra but is very different from EDTA. *3*) The structures of the phosphonium salts $R_2P(H)CH_2COOH$ can exist only in strongly acid media. *4*) Both carboxyl groups $RP(H)(CH_2COO^-)_2$ absorb at the same wavenumber, *5*) There is a rapid proton exchange between carboxyl groups bonded to unprotonated phosphorus atoms.

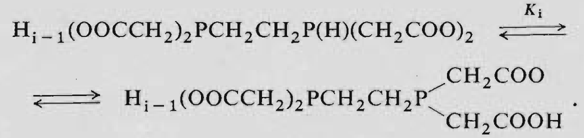
The relative intensities, *i.e.* the areas under the bands in the spectra (Table I) were found by computer band separation[23]. Using the given assumptions, the intensities

TABLE II

Final fractional coordinates (. 10^4, for H-atoms, . 10^3) with standard deviations in parentheses and isotropic temperature factors (. 10^{-4} pm^2), related to β_{ij} used in refinement using the relationship $B = 4[V^2 \det(\beta_{ij})]^{1/3}$

Atom	*x*	*y*	*z*	*B*
Br	1 213(1)	1 454·1(6)	1 203·5(8)	2·85
P	5 890(3)	4 157(1)	3 413(2)	1·58
O1	1 050(8)	4 137(4)	1 786(4)	2·97
O2	2 027(8)	4 084(4)	—0 162(5)	2·76
O3	7 405(8)	1 514(4)	3 997(4)	2·64
O4	7 816(10)	2 563(4)	2 486(5)	3·08
C1	5 093(12)	4 388(5)	1 682(6)	1·67
C2	2 462(12)	4 191(5)	1 129(6)	2·34
C3	5 232(13)	2 959(5)	3 798(7)	1·70
C4	6 955(12)	2 256(5)	3 461(7)	2·35
C5	4 343(12)	4 954(5)	4 263(7)	1·81
H	823(11)	430(4)	375(6)	1·58
H1A	624(12)	410(4)	117(6)	1·67
H1B	568(11)	508(5)	168(6)	1·67
H3A	527(12)	288(4)	468(7)	1·70
H3B	355(13)	279(4)	342(6)	1·70
H5A	435(11)	554(5)	381(7)	1·81
H5B	279(12)	473(5)	424(6)	1·81
H2	050(12)	386(5)	— 040(7)	2·76
H4	862(13)	217(5)	200(7)	3·08

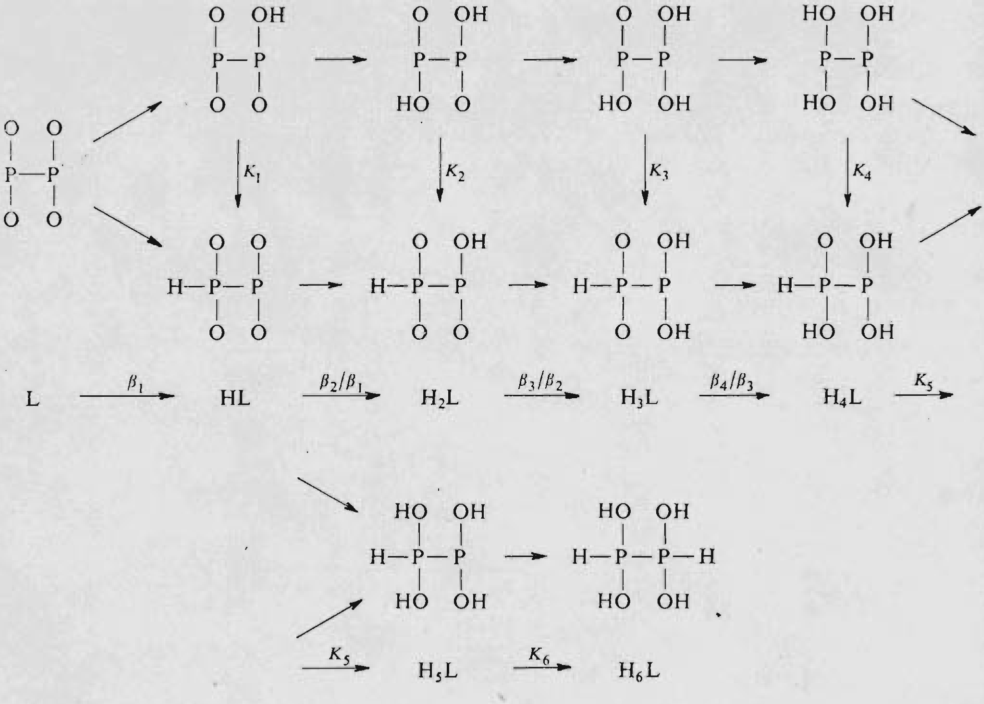
were treated by a simple least squares program to obtain the tautomerization microconstants $K_1 = 0{\cdot}94\,(5)$, $K_2 = 1{\cdot}9\,(2)$, $K_3 = 0{\cdot}6\,(1)$, $K_4 < 0{\cdot}05$. Microconstants $K_1 - K_4$ are defined by the general equilibrium



$$H_{i-1}(OOCCH_2)_2PCH_2CH_2P(H)(CH_2COO)_2 \overset{K_i}{\rightleftharpoons} H_{i-1}(OOCCH_2)_2PCH_2CH_2P\begin{matrix}CH_2COO\\CH_2COOH\end{matrix}.$$

In data treatment, a possible model of simultaneous protonation of both phosphorus atoms was considered, but acceptable agreement with the experimental values was not obtained.

The equilibria in solution can be summarized as follows:



(P-P represents the core $(OCCH_2)_2PCH_2CH_2P(CH_2CO)_2$.)

Bis(phosphine) salts with composition $H_4L.2\,HX$ (X = Cl, Br, I) crystallize from Na_4L solutions in strong hydrogen halide acids. These compounds are stable in the air and highly soluble in water but of limited solubility in HX solutions. Their powder patterns indicate that they are isostructural and the infrared spectra suggest a phosphonium salt structure with non-equivalent carboxyl groups, bonded by hydrogen bonds. The proposed structure was confirmed by X-ray structural analysis of the bromide. The parameters for the structure are listed in Tables II and III. Projection of the structure onto the *yz* sin *β* plane is depicted in Fig. 4, from which the atomic numbering is also apparent.

The formula unit consists of two crystallographically independent halves, related through a centre of symmetry in the middle of the C5-C5^{i} bond. Only one half of the formula unit will therefore be discussed below.

Coordination around the phosphorus atom is close to tetrahedral and the angles are from 104·7 to 112·2°. This interval is typical for phosphonium salts, but is very diffe-

TABLE III

The bond distances (pm) and angles (°) with standard deviations in parentheses

Atoms	Distance	Atoms	Angle
P—C1	179·6(6)	C1—P—C3	112·2(3)
P—C3	181·4(7)	C1—P—C5	109·9(3)
P—C5	180·0(7)	C3—P—C5	109·4(3)
P—H	134(6)	C1—P—H	105(3)
C5—C5^{i}	156(1)	C3—P—H	110(3)
C5—H5A	96(7)	C5—P—H	111(3)
C5—H5B	95(7)	P—C5—C5^{i}	110·8(4)
C1—C2	153(1)	P—C1—C2	110·8(4)
C1—H1A	103(7)	P—C3—C4	112·9(5)
C1—H1B	104(7)	C1—C2—O1	123·4(5)
C3—C4	151(1)	C1—C2—O2	110·5(5)
C3—H3A	93(7)	C3—C4—O3	124·1(6)
C3—H3B	99(7)	C3—C4—O4	110·4(5)
C2—O1	118·3(8)	O1—C2—O2	126·0(6)
C2—O2	132·6(8)	O3—C4—O4	125·5(6)
O2—H2	92(7)	O2—H2—O3^{ii}	175(5)
C4—O3	119·7(9)		
C4—O4	130·8(9)		
O4—H4	95(7)		
O2—O3^{ii}	275·3(7)		
H2—O3^{ii}	184(7)		

Symmetry code used

^{i} $1-x, 1-y, 1-z$; ^{ii} $x-1, 1/2-y, z-1/2$; ^{iii} $x+1, 1/2-y, 1/2+z$.

rent from that for tertiary phosphines[24]. For comparison, the angles around tetracoordinated phosphorus in the complexes of phosphineacetates with metals[25,26] are distorted more from ideal tetrahedral geometry than in the phosphonium salts, obviously because of the steric requirements of the metal ion. The P—H distance of 134 pm is quite normal for phosphonium salts[24].

The carbonyl and hydroxyl oxygen atoms can be clearly differentiated in both the carboxyl groups: the C=O distances are 118 – 120 pm and the C–OH distances are 131 – 133 pm. In considering further interactions, the two carboxyl groups are not equivalent, as one is a proton donor and the other is a proton acceptor in the hydrogen bond system, leading to a three-dimensional arrangement. The remaining oxygen atoms O1 and O4-H4 do not take part in any further interactions at distances of less than 310 pm, of course with the exception of bonds to the carbon atoms. The existence of two different C=O groups and of two different C—OH groups is apparent from the infrared spectra, where both the ν(C=O) and ν(OH) bands are split. The degree of splitting and absolute positions of these bands exhibit the expected systematic trends in the Cl – Br – I series.

The bromide anion is located in the large gap in the structure and this gap can accomodate larger anions, such as *e.g.* iodide. The closest vicinity of the bromide anion is formed by 10 oxygen atoms in an irregular arrangement, with distances from the bromine atom varying in the interval 306 – 427 pm.

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