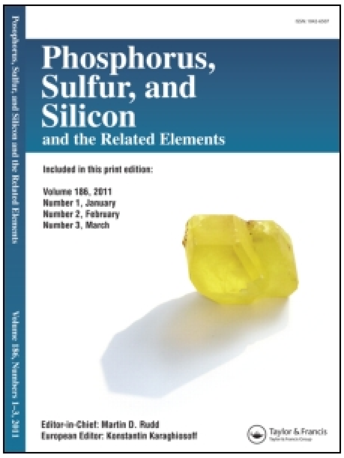

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SYNTHESIS AND ^{31}P AND ^{13}C NMR STUDIES OF PYROPHOSPHONIC ACIDS

G. Ohms[a]; G. Großmann[a]; B. Schwab[a]; H. Schiefer[b]
[a] Institut für Analytische Chemie, Technische Universität Dresden, Dresden, Mommsenstraße 13 [b] Forschungsinstitut fur Aufbereitung, Freiberg, Straβe 40

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SYNTHESIS AND ^{31}P AND ^{13}C NMR STUDIES OF PYROPHOSPHONIC ACIDS

G. OHMS, G. GROẞMANN AND B. SCHWAB
Technische Universität Dresden, Institut für Analytische Chemie, D-O-8027 Dresden, Mommsenstraße 13

and

H. SCHIEFER
Forschungsinstitut für Aufbereitung, D-O-9200 Freiberg, Chemnitzer Straße 40

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Pyrophosphonic acids were prepared by partial hydrolysis of phosphonic acid dichlorides and by dehydration of phosphonic acids, respectively. The pyrophosphonic acids as well as their ammonium salts were characterized by NMR spectroscopy. The geminal coupling constant $^2J_{POP}$ was obtained from spectral analysis and its sign was determined by spin tickling experiments. Furthermore, semiempirical quantum chemical calculations of $^2J_{POP}$ were carried out.

Key words: Pyrophosphonic acids; ^{13}C and ^{31}P NMR spectroscopy; P-P coupling constants.

INTRODUCTION

During hydrolysis of phosphonic acid dichlorides 1 phosphonic acid anhydrides $(RPO_2)_n$, pyrophosphonic acids 2 and phosphonic acids 3 are formed.[1–4] The yield of the different reaction products depends on the conditions of the reaction (e.g. molar ratio of the reactants, temperature). Andreev and Grishina[4] investigated the reaction of cyclohexylphosphonic acid dichloride and water in a molar ratio of 1:1. They proposed a mechanism after which pyrophosphonic acids and their acid chlorides are instable intermediates forming oligomeric phosphonic acid anhydrides during heating.

In this paper we have studied formation and stability of pyrophosphonic acids. The aim of our investigations consisted in finding optimal conditions for the preparation of pyrophosphonic acids and characterizing pyrophosphonic acids and their corresponding diammonium salts by NMR spectroscopy. Applying two different preparative methods we have synthesized pyrophosphonic acids 2 and diammonium pyrophosphonates 4 where:

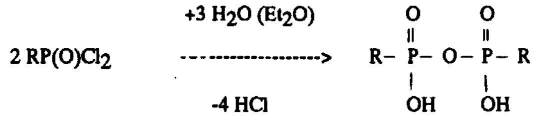
R	Ph	p-CH_3Ph	PhCH_2	PhCH_2CH_2	PhCH=CH	PhC(=CH_2)	Indenyl	c-Hex	i-Bu
	a	b	c	d	e	f	g	h	i

RESULTS AND DISCUSSION

Preparation of 2 and 4

First investigations of the hydrolysis of $RP(O)Cl_2$ at ambient temperature using a large excess of water showed that the stability of pyrophosphonic acids against water differs considerably. Even after 5 days 2e and 2h are detectable in the reaction solution, whereas 2a, d and g can be observed only during the first few hours in the ^{31}P NMR spectra.

To avoid further hydrolysis the preparation of 2 was carried out by treating an ether solution of $RP(O)Cl_2$ with water-saturated ether containing the stoichiometric quantity of water (method A)[3]:

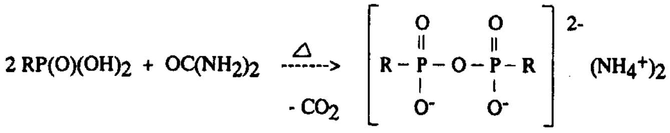


$$2\,RP(O)Cl_2 \xrightarrow[-4\,HCl]{+3\,H_2O\,(Et_2O)} R-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-R$$

1 2

The hydrolysis products 2a, d, e, g and h crystallize from ether solution. According to paperchromatographic investigations they are pure or contain only small quantities of 3 (for analytical data see Table I). Except of compound 2h the stability of the products 2 is in general low. Without visual changes they transform into phosphonic acids. Therefore, it is advisable to convert 2 into the corresponding diammonium salts 4 (see Table II), which are more stable.

Furthermore, pyrophosphonic acids 2 were prepared from pyrophosphonates 4 by reaction with NH_4HSO_4. 4 was synthesized by dehydration of phosphonic acids in a melt of urea as described in[8] (method B):



$$2\,RP(O)(OH)_2 + OC(NH_2)_2 \xrightarrow[-\,CO_2]{\Delta} \left[R-\underset{\underset{O^-}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{O^-}{|}}{\overset{\overset{O}{\|}}{P}}-R\right]^{2-} (NH_4^+)_2$$

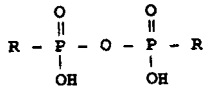
3 4

Pyrophosphonates with R = aryl, cyclohexyl and isobutyl were obtained in high yield (Table II), but in case of *n*-pentyl, *n*-hexyl and 4-methylpenten-2-yl-1-phosphonic acid it was not possible to isolate ammonium- or cyclohexylammonium pyrophosphonates of a definite composition.

In order to separate 4 from the ammonium phosphonates the higher solubility of 4 in ethanol or methanol/water (10:1) can be utilized. A disadvantage of method B is the application of an excess of water. The compounds 2a–h crystallize from water, however some of them contain hydrate water. This effects the stability of the P—O—P -bond and the preparation of compounds with constant melting points. Differing melting points were measured for 2a (Table I). The compounds 2a e, f and i are very sensitive against hydrolysis.

TABLE I

Analytical data of pyrophosphonic acids 2



$$R-P(=O)(OH)-O-P(=O)(OH)-R$$

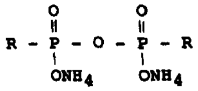
Compound No.	R	Yield (%) Method A	Yield (%) Method B	M.p.(°C) (Lit.)	Formula (Mol.weight)	% calc./found C	% calc./found H	% calc./found P	δ_P (ppm) [RP(O)(OH)$_2$]	2/3 (%)[b)]
2a	Ph	69	96	110-114	$C_{12}H_{12}O_5P_2$	48.33	4.06	20.78	7.1	67/33
				(79.5-80.0)[3]	(298.2)	48.11	4.17	20.67	[16.3]	
				(82.5-83.0)[5]						
				(115-118)[6]						
2b	p-CH$_3$Ph	-	86	151-157	$C_{14}H_{16}O_5P_2$	51.55	4.94	18.99	7.2	100/0
				(acetone/hexane)	(326.2)	50.66	4.96	19.65		
2c	PhCH$_2$	-	87	175-178	$C_{14}H_{16}O_5P_2$	51.55	4.94	18.99	17.1	85/15
					(326.2)	51.34	5.10	19.07	[25.5]	
2d	PhCH$_2$CH$_2$	65	73	118-122	$C_{16}H_{20}O_5P_2$	54.23	5.69	17.48	20.7	72/28
				(EtOAc)	(354.4)	54.19	5.86	16.92	[29.3]	
2e	PhCH=CH	86	62	153-157	$C_{16}H_{16}O_5P_2$	54.87	4.61	17.69	7.1	70/30
					(350.3)	53.61	5.11	17.05	[16.3]	
2f	PhC(=CH$_2$)	-	57	125-140[a)]	$C_{16}H_{20}O_5P_2$	49.78	5.22	16.04	5.4	50/47
				(113-118)[7]	(386.3)	50.07	5.44		[14.2]	
2g	Inden-2-yl	74	67	150-155	$C_{18}H_{16}O_5P_2$	57.76	4.31	16.55	2.3	100/0
					(374.3)	56.61	4.28	16.14		
2h	Cyclohexyl	73	83	145-147	$C_{12}H_{24}O_5P_2$	46.45	7.80	19.97	24.7	97/3
				(EtOAc)	(310.3)	46.14	7.75	19.73	[32.7]	
2i	i-Bu	-	72		$C_6H_{16}O_5P_2$	31.30	7.02	26.93	21.7	18/82
					(230.2)				[30.3]	

a) probably dihydrate; purification with EtOAc

b) Mol-% P in ^{31}P NMR-sample

TABLE II

Analytical data of pyrophosphonates 4



$$R-\overset{\overset{O}{\parallel}}{\underset{\underset{ONH_4}{|}}{P}}-O-\overset{\overset{O}{\parallel}}{\underset{\underset{ONH_4}{|}}{P}}-R$$

Compound No.	R	Yield (%)	M.p. (°C)	Formula (Mol.weight)	Elem.anal. calc./found. N	P	δ_P (ppm) (ref.[8])
4a	Ph	93	195-206 (EtOH)	$C_{12}H_{18}N_2O_5P_2$ (332.2)	8.43 8.42	18.65 17.89	5.1 (4.7)
4b	p-CH_3Ph	95	190-196 (EtOH)	$C_{14}H_{22}N_2O_5P_2$ (360.3)	7.78 7.59	17.19 17.20	5.4 (4.9)
4c	PhCH_2	78	170-175 (EtOH)	$C_{14}H_{22}N_2O_5P_2$ (360.3)	7.78 8.13	17.19 17.16	13.9 (14.0)
4d	PhCH_2CH_2	81	175-180 (EtOH)	$C_{16}H_{26}N_2O_5P_2$ (388.4)	7.21 7.38	15.95 15.67	17.6 (17.3)
4e	PhCH=CH	90	208-218 (EtOH)	$C_{16}H_{22}N_2O_5P_2$ (384.3)	7.29 7.21	16.12 16.04	5.2 (4.8)
4f	PhC(=CH_2)	88	164-172 (EtOH/acetone)	$C_{16}H_{22}N_2O_5P_2$ (384.3)	7.29 7.34	16.12 15.96	3.5 (3.4)
4g	Inden-2-yl	40	230-235 (H_2O/acetone)	$C_{18}H_{22}N_2O_5P_2$ (408.3)	6.86 6.79	15.17 15.60	1.8
4h	Cyclohexyl	88	193-200 (H_2O/acetone)	$C_{12}H_{30}N_2O_5P_2$ (344.3)	8.14 8.10	17.99 18.03	21.7 (21.5)
4i	i-Bu	90	165-175 (EtOH)	$C_8H_{26}N_2O_5P_2$ (292.3)	9.59 9.60	21.19 21.26	18.5

NMR Investigation

The identity of the prepared pyrophosphonic acids 2 and ammonium pyrophosphonates 4 was confirmed by ^{31}P and ^{13}C NMR spectroscopy. Due to the low solubility of 2 and 4 in organic solvents we had to investigate aqueous solutions. ^{31}P spectra of 2 and 4 were recorded immediately after dissolving the compounds in water. In the ^{31}P spectra of the salts 4 only one signal was observed whereas in the spectra of 2 ^{31}P signals of pyrophosphonic acid and its hydrolysis product (phosphonic acid) were observed simultaneously (see Tables I and II). Resonance signals upfield to the signal of 2 were only detected in the ^{31}P spectrum of 2f, which points to the presence of higher condensed products.

The ^{31}P chemical shift of 2 is about 9 ppm highfield shifted in comparison to that of $RP(O)(OH)_2$. This is caused by the substitution of an H-atom by the bulkier RP(O)(OH)-group. A similar highfield shift is known from phosphoric acid (δ_P = 0 ppm) and pyrophosphoric acid (δ_P = −11 ppm).[9]

A comparison of the spectra of 2 and 4 shows that the ^{31}P chemical shift of the anions is always smaller than that of the acid. The difference between the shifts amounts to about 3 ppm for aliphatic and about 2 ppm for aromatic and olefinic compounds. These differences are considerably smaller than in the case of monophosphonic acids (about 8 ppm and 5 ppm, respectively).[10] Reasons consist in the greater number of negative charges per phosphonic acid group in the monomer and in the protolysis reaction of the ammonium ion. The measured chemical shifts are only average values depending on chemical shift and portion of acid and anion.

The dimeric structure of 2 and 4 is confirmed by the presence of P—P couplings which can be observed in the $^{31}P\{^1H\}$-^{13}C satellite spectrum or the ^{13}C spectrum (see Table III). Any ^{13}C-atom of the organyl group in α-, β- or γ-position couples with both ^{31}P-atoms and gives an AA'X-spin system resulting in a splitting of the ^{13}C signals into 5 lines (X-part). In dependence on the ratio $J_{AA'}/(J_{AX}\text{-}J_{A'X})$ different line intensities are observed. Figure 1 shows the ^{13}C NMR spectrum of 4h. From the distances and intensities of the 5 lines in a) $J_{PP'}$, J_{PC} and $J_{P'C}$ can be calculated.[9,11-13] Deviations are obtained mainly due to inaccuracies in the measured line intensities.

Provided, the ^{31}P NMR spectrum is highly resolved, $J_{PP'}$ can also be obtained directly from the ^{31}P NMR spectrum (AA'-part). Here it appears several times as

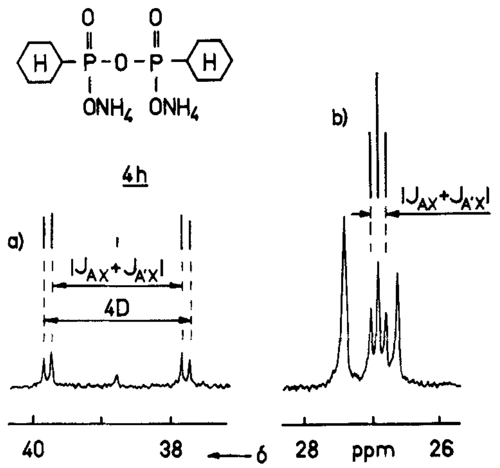


FIGURE 1 ^{13}C NMR spectrum of 4h; a) $|J_{AA'}/(J_{AX}\text{-}J_{A'X})| \approx 0.26$, b) $|J_{AA'}/(J_{AX}\text{-}J_{A'X})| \approx 2.3$.

distance between the low intensive ^{13}C satellite lines. The rather broadness of the signals of the acids 2 caused by exchange and a strong temperature dependence of the resonance signal always decrease the accuracy of the measured values. For all compounds 2 and 4 under investigation we obtained geminal P—O—P coupling constants between 25.5 Hz (styrylphosphonate) and 37.5 Hz (cyclohexylphosphonate).

The P—P coupling constant of pyrophosphonic acids and pyrophosphonates has about the same order of magnitude as $^{2}J_{POP}$ of monothiopyrophosphates (20 Hz),[14] ATP at pH = 10 (20.6 Hz; 21.3 Hz)[15] and pyrophosphite (−10.7 Hz).[16] Since in pyrophosphite J_{POP} has a negative sign[16] we were interested in the sign of $^{2}J_{POP}$ of pyrophosphonates. For this purpose $^{13}C\{^{1}H,^{31}P\}$ triple resonance experiments were carried out. Through irradiation of a ^{31}P resonance frequency, which corresponds to a line in the $^{31}P\{^{1}H\}$-^{13}C satellite spectrum, and observation of a spin tickling phenomenon in the ^{13}C spectrum it is possible to determine the relative sign of $J_{PP'}$ in relation to $N = J_{PC} + J_{P'C}$. Since for all compounds under investigation $|J_{P'C}| < |J_{PC}|$ is valid N has the same sign as J_{PC}.

The spin tickling experiment was carried out with phenylpyrophosphonate. The P—P coupling constant was obtained from the $^{31}P\{^{1}H\}$-^{13}C satellite spectrum of the α-carbon atom. We chose the meta-C-signal ($^{5}J_{P'C} \sim 0$) for our investigation since it is of a higher intensity than the ipso-C-signal and it is well separated from ortho- and para-C-signals. Due to the high intensity of the ^{31}P main signal the ^{13}C satellites of the meta-C-atoms are not observable. Therefore, the position of these satellites was calculated using the measured values of $^{2}J_{PP}$ and $^{3}J_{PC}$ and considering the positive sign of $^{3}J_{PCCC}$ which has been determined by Lequan et al.[17] for several propinephosphonic acid derivatives. We were able to confirm this sign. With a series of $\{^{31}P\}$ off-resonance decoupling experiments according to the method of Fritz and Sauter[18] we could show that in phenylene-1,3-diphosphonic acid tetraethylester $^{1}J_{PC}$ and $^{3}J_{P'C}$ are of the same sign and within positive.

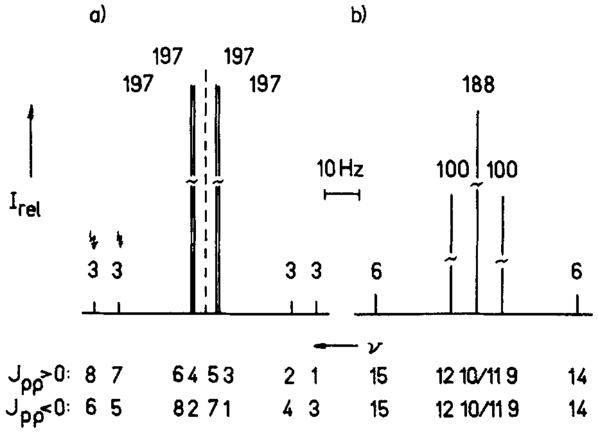


FIGURE 2 Calculated AA′X spectrum of phenylpyrophosphonate 4a with one meta-^{13}C-atom. The transitions are numbered according to Reference 19 under consideration that $N > 0$. a) $^{31}P\{^{1}H\}$-^{13}C satellite spectrum (AA′ part), b) $^{13}C\{^{1}H\}$ spectrum (X part).

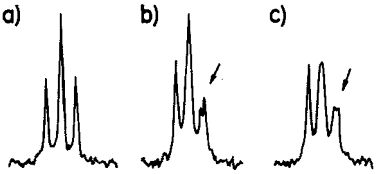


FIGURE 3 Results of spin tickling experiments of phenylpyrophosphonate 4a. a) $^{13}C\{^1H\}$ spectrum of the meta-^{13}C-atom. b) like a) but irradiation of the ^{31}P transission of the highest frequency (ν_P + 33.9 Hz). c) like a) but irradiation of the ^{31}P transission of the second highest frequency (ν_P + 26.7 Hz).

The calculated transitions are numbered like given in[19] for the ABX-system. Thus, the two possible assignments for the AA′-part (depending upon the sign of J_{PP}) are given in Figure 2. The assignment of the X-part follows straightforward from $N > 0$.

Irradiation at the ^{31}P signal of highest frequency causes splitting of line 9 in the X-part. The same observation is made if the second highest ^{31}P frequency is irradiated (compare Figure 3). Since the transitions 5 and 6 are connected with transition 9 due to common spin states a negative sign of $^2J_{PP}$ results. Thus, for pyrophosphonates the same sign of $^2J_{POP}$ is obtained as for pyrophosphites.[16]

Since there was no correlation between the magnitude of $^2J_{POP}$ and the substituents of the two P-atoms (e.g. hybridization of the α-C-atom, bulkiness of group R, presence of acid or anion) (see Table III) we have carried out some semiempirical quantum chemical calculations on LCAO MO level. INDO calculations employing a simple approximation method according to Pople and Santry[20] (sum over states method) were carried out for three model compounds of the type R(R′O)(O)P—O—P(O)(OR′)R. Although such calculations are not very precise their results should allow some conclusions concerning parameters which influence the magnitude of $^2J_{POP}$. Starting point was an ab initio structure of a pyrophosphorous acid[21] with $\sphericalangle POP = 128°$. In the same publication[21] compounds of the type $H_4P_2O_{2n-1}$ ($n = 1 \ldots 4$) are described and it is mentioned that these compounds are characterized by relatively large bond angles POP (about 130°) and small energy barriers with regard to a linear arrangement of P—O—P.

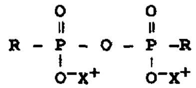
Our calculations yielded in the following results: 1) $^2J_{POP}$ depends on the bond angle POP. Stepwise increase of $\sphericalangle$POP from 100° to 180° causes a decrease of $^2J_{POP}$. A change of the sign of $^2J_{POP}$ from plus to minus is observed (see Table IV). 2) On the condition that conformation and $\sphericalangle$POP remain unchanged a small dependence of $^2J_{POP}$ on the substituents of P is observed. 3) $^2J_{POP}$ slightly depends on the conformation.

For methylpyrophosphonic acid geometry optimizations with respect to the torsion angles were carried out. We obtained for the racemic compound three conformers with staggered conformation and one conformer with eclipsed conformation, and for the meso isomer two with staggered conformation and one with eclipsed conformation. The eclipsed conformers are characterized by intramolecular H-bonds (O—H . . . O distance 2.42 Å) and therefore energetically favoured. For all these conformers the geminal coupling constant $^2J_{POP}$ ranges from −2.5 Hz to 4.7 Hz.

If one considers that with the applied semiempirical quantum chemical method

TABLE III

Chemical shifts in ppm and coupling constants in Hz of pyrophosphonic acids and pyrophosphonates



$$R-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-X^+}{|}}{P}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-X^+}{|}}{P}}-R$$

Comp. No.	R	X	$^2J_{PP}$	$\delta(C_1)$ ($^1J_{PC}$; $^3J_{P'C}$)	$\delta(C_2)$ ($^2J_{PC}+^4J_{P'C}$)	$\delta(C_3)$ ($^3J_{PC}+^5J_{P'C}$)	$\delta(C_4)$	$\delta(C_5)$	$\delta(C_6)$	$\delta(C_2^*)$ ($^2J_{PC}+^4J_{P'C}$)
2a	Ph	H			131.6	129.1 (+15.3)	132.7			
4a	Ph	NH_4	-28.6[a)]	133.9 (+182.1;-1.0)	130.5 (10.0)	127.7 (+14.5)	130.4			
2b	p-CH_3Ph	H	-29.9[a)]	128.4 (+183.7;+0.7)	131.8 (11.0)	129.6 (+15.3)	143.5 (2.6)	21.5		
4b	p-CH_3Ph	NH_4	-29.7[c)]	131.6 (+188.0;+0.3)	131.8 (10.2)	129.1 (+14.5)	141.9	21.3		
2c	PhCH_2	H	-30.3[b)]	36.0 (+136.2;-0.4)	133.8 (8.8)	130.5 (<5,broad)	129.4	127.4		
4c	PhCH_2	NH_4	-28.7[b)]	36.9 (+134.5;+0.3)	135.9 (8.7)	130.6 (+5.8)	129.1	126.8		
2d	PhCH_2CH_2	H	-29.7[c)] -30.3[a)]	30.3 (+138.5;-0.5)	29.3 broad	142.4 (+13.8)	129.4	128.9	127.0	
4d	PhCH_2CH_2	NH_4	-31.2[a)]	31.5 (+136.3;+1.0)	30.1 (4.2)	143.6 (+19.6)	129.4	129.0	126.9	
2e	PhCH=CH	H		118.5 (Σ 190)	146.9 broad	135.9 (+23.7)	128.3	129.6	130.7	

TABLE III (*continued*)

Comp. No.	R	X	$^2J_{PP}$	$\delta(C_1)$ $(^1J_{PC};^3J_{P'C})$	$\delta(C_2)$ $(^2J_{PC}+^4J_{P'C})$	$\delta(C_3)$ $(^3J_{PC}+^5J_{P'C})$	$\delta(C_4)$	$\delta(C_5)$	$\delta(C_6)$	$\delta(C_2^*)$ $(^2J_{PC}+^4J_{P'C})$
4e	PhCH=CH	NH_4	-25.5[c)]	121.8 (+184.5;+0.4)	144.2 (5.5)	136.7 (+22.7)	128.0	129.5	130.0	
2f	PhC(=C*H$_2$)	H	-33.2[c)]	142.9 (Σ 180.6)	138.1 (13.6)	128.3 (+5.2)	129.2	128.8		130.2 (8.4)
4f	PhC(=C*H$_2$)	NH_4	-31.7[a)]	145.3 (+175.9;+1.3)	139.5 (11.9)	128.5 (<5,broad)	129.0	128.4		128.0 (7.6)
2h	Cyclohexyl	H	-33.9[b)]	37.8 (+143.1;-0.9)	26.6 (4.3)	26.4 (+17.2)	26.2			
4h	Cyclohexyl	NH_4	-37.5[a)]	38.7 (+142.0;+0.7)	27.4 (3.9)	26.9 (+16.2)	26.2			
2i	i-Bu	H			24.4	24.2				
4i	i-Bu	NH_4	-30.1[b)]	38.6 (+137.4;-0.3)	24.6 (4.5)	24.5 (+11.5)				

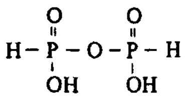
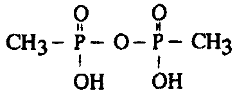
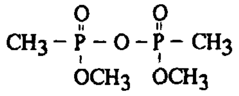
a) from $^{31}P\{^1H\}$-^{13}C satellite spectrum

b) from ^{13}C spectrum using line intensities

c) from ^{13}C spectrum using 4D and neglecting $J_{A'X}$

TABLE IV

Calculated P—P coupling constants in dependence on the bond angle POP[a])

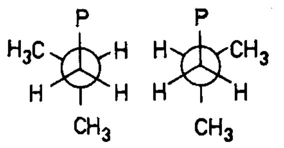
Compound			$^2J_{POP}$ (Hz)				
No.		∢POP	120°	128°	140°	160°	180°
5	 $H-\underset{OH}{\overset{O}{\overset{\|}{P}}}-O-\underset{OH}{\overset{O}{\overset{\|}{P}}}-H$		6.41	3.51	1.38	-5.03	-14.73
6	 $CH_3-\underset{OH}{\overset{O}{\overset{\|}{P}}}-O-\underset{OH}{\overset{O}{\overset{\|}{P}}}-CH_3$		2.27	0.53	-2.51	-3.95	-12.01
7	 $CH_3-\underset{OCH_3}{\overset{O}{\overset{\|}{P}}}-O-\underset{OCH_3}{\overset{O}{\overset{\|}{P}}}-CH_3$		4.04	5.66	-0.57	-6.67	-8.77

[a]) The calculations are based on:
an ab initio structure of 5 given in ref.[21],
geometry optimized structures of 6 and 7 for a bonding angle ∢POP of 128°.
The energetically favoured conformation of 5, 6 and 7 is the racemic form of the diastereomer where the substituents of one phosphorus atom are staggered to the other phosphorus (dihedral angle POP(=O) 307° (5), 314° (6) and 313° (7), respectively) and the substituent R (H or CH_3) is trans with respect to the phosphorus.

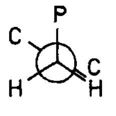
in general coupling constants of a too small absolute value, but shifted in direction of positive values, are calculated compared with the experimental values our results can be summarized as follows: 1) The sign of $^2J_{POP}$ is negative for all pyrophosphonic acids and pyrophosphonates. 2) A rather similar and large POP bond angle can be assumed for all compounds under investigation. 3) Effects from conformation and substituents *R* play a minor role only.

The ^{13}C spectra of 2 and 4 confirm the structure of the organyl substituent. A comparison of the NMR data of 2 and 4 shows that the chemical shift of the α-C-atom of the salt is greater than that of the acid. This result is in agreement with observations concerning phosphonic acids[10] and can be explained with the greater dipole moment of the $(PO_3)^-$-group and the resulting stronger polarization of the C—P bond.

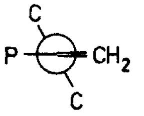
The direct P—C coupling constant of the investigated pyrophosphonic acids and pyrophosphonates shows the known dependence on the hybridization of the α-C-atom. In our examples $^1J_{PC}$ of the unsaturated compounds is about 40–50 Hz greater than $^1J_{PC}$ of the saturated compounds.



4i



4c



2f

The vicinal P—C coupling constant is a sensitive probe to the PCCC dihedral angle. Karplus type functions are known[13,22–24] and can be used for the discussion of the measured $^3J_{PC}$ values. For the two cyclohexyl compounds 2h and 4h the magnitude of $^3J_{PC}$ (17.2 Hz; 16.2 Hz) indicates the predominance of conformers with equatorial phosphorus.[25] Isobutylpyrophosphonate 4i is without any doubt a mixture of conformers, but the vicinal coupling of 11.5 Hz suggests the only presence of the two trans/gauche conformers. In benzylphosphonate 4c the vicinal coupling constant amounts only to 5.8 Hz. But this value is considerably greater than in the case of 90° dihedral angles. It indicates that the phenyl group is twisted about the CH_2—C bond. One PCCC dihedral angle is increased to about 120° while the second is reduced to about 60°. From the magnitude of $^3J_{PC}$ (5.2 Hz) of the phenylvinyl compound 2f it can be concluded, that the phenyl ring is turned out off the P—C$=$$CH_2$ plane and consequently the conjugation between aromatic and olefinic π-electronic system is cancelled. Vicinal coupling constants of 23.7 Hz and 22.7 Hz of the styryl compounds 2e and 4e give evidence for the trans configuration of both compounds. The $^3J_{PC}$ values of the phenylethyl compounds 2d and 4d differ considerably, acid (13.8 Hz) and salt (19.6 Hz). This suggests the only presence of the trans conformer of 4d whereas in the case of the acid gauche conformers are of some importance in the mixture of conformers.

Comparing the vicinal coupling constants $^3J_{P'C}$ it becomes obvious that all values obtained from the spectra are very low. If one assumes a Karplus-like dependence of $^3J_{POPC}$ on the dihedral angle vicinal couplings <1.5 Hz would suggest that dihedral angles of 180° are of low probability, only.

EXPERIMENTAL

Preparation of pyrophosphonic acids.

a) Through restricted hydrolysis of phosphonic acid dichlorides, (method A). To a stirred solution of 5 mmol $RP(O)Cl_2$ in 15 ml of abs. ether, 12.9 ml of water saturated ether containing 7.5 mmol water (water content 1.45 wt-% at 20°C[26]) were added slowly at room temperature. 2a, d, e and g precipitate after a short time, 2h after several days (some products first forming oils crystallize after a few days). The isolated products are washed with ether and dried over KOH under vacuum to remove HCl. Purification is reached by recrystallization (2a, d, h) or heating with ethyl acetate (for yields and analytical data see Table I).

For the preparation of the diammonium salts 4 solutions of 2 in ethanol (10–20 ml ethanol/g 2a, d, h; 40 ml/g 2e; 100 ml/g 2g) are neutralized by NH_3. For crystallization of the better soluble salts 4 acetone is added (Table II).

b) From pyrophosphonates *4* (method B). 20 mmol of $RP(O)(OH)_2$ and 30 mmol of urea are heated for 60–90 minutes at 170°C (R = indenyl: 10 mmol and 30 mmol of urea at 200°C).[8] The products are purified by extraction (1–3 times) with acetone/water (20 ml/1 ml) till negative biuret reaction. The products of 3g are additionally extracted using hot ethanol. The diammonium salts 4a–i were recrystallized from ethanol or water/acetone (Table II).

To a solution of 2 mmol of 4 in ice water 0.46 g (4 mmol) NH_4HSO_4 in 5 ml of ice water are added. 2a–h crystallize. After isolation the products are washed with ice water and dried over P_4O_{10}. For recrystallization dry solvents are used (Table I). 2i was only obtained in a mixture with 3i by extracting the aqueous phase using chloroform.

Paper chromatography. For qualitative screening the chromatograms were developed upwards (mobile phase II according to Biberacher[27], developing time 8 hours); visualization with ammoniummolybdate solution in UV light[28]; 2 and 4 violet till blue violet spots (R_F-values 0.80–0.90); 3 light blue or blue spots (R_F-values 0.45–0.55).

NMR spectroscopy. For hydrolysis investigations and the determination of ^{31}P chemical shifts the samples were dissolved in water, an external C_6D_6-lock was added and the spectra were taken with a Bruker WH 90DS at 36.44 MHz. For ^{13}C NMR the samples were dissolved in water and CD_3OD was added. ^{13}C spectra were taken with a Bruker MSL 300 at 75.475 MHz.

The digital resolution was 0.8 Hz for ^{31}P spectra and 0.4 Hz for ^{13}C spectra. The coupling constant $^2J_{POP}$ was obtained with an accuracy of ± 1.5 Hz from $^{31}P\{^1H\}$-^{13}C satellite spectra, ± 3 Hz from ^{13}C spectra using signal intensities for the calculation and ± 1 Hz from ^{13}C spectra using the line distances (4D, N) and neglecting the magnitude of $J_{A'X}$.

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