Phosphonic Acid Anhydrides $[\text{RPO}_2]_n$: Oligomerization and Structure

Stefan Fuchs, Hubert Schmidbaur*

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstraße 4,
D-85747 Garching, Germany

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The phosphonic acid anhydrides of the general formula $[\text{RPO}_2]_n$ have been prepared with $\text{R} = \text{Me}$, Et , $i\text{-Pr}$, $t\text{-Bu}$, and Ph from the corresponding phosphonic acids and their chlorides and esters. Mass spectrometric data indicate that the trimers are the dominant oligomers for all five systems. According to their NMR spectra, the methyl and t -butyl compounds have a symmetrical (C_{3v}) structure with equivalent RP groups, while the ethyl, i -propyl and phenyl homologues have the C_s structure with non-equivalent PR groups in the ratio 1:2.

Introduction

Phosphonic acid anhydrides have been known for at least a century. In 1892 A. Michaelis reported the synthesis of "Phosphenylsäure", which we now classify as phenylphosphonic acid PhPO_2H , as the hydrolysis product of "Phosphenylchlorid" (dichlorophenylphosphine and/or dichlorophenylphosphine oxide $\text{PhP}(\text{O})\text{Cl}_2$). Condensation of these two components gave "Phosphinobenzol", most probably phenylphosphonic acid anhydride [1]. This product remained poorly characterized even up to the present time, and neither the degree of oligomerisation nor the structure have been determined. Most surprisingly this is also true for the alkyl homologues, in spite of their wide-spread usage as condensation and dehydration reagents [2]. We have therefore initiated a study of the title compounds in order to elucidate further their structure and properties.

Contrary to expectations, this proved to be an extremely difficult task. None of the members of a series of five compounds could be obtained in satisfactory purity, none of them could be crystallized, and analytical and spectroscopic data gave ambiguous results in more than one case. Our results are summarized in this Note, because even the new limited data are meaning a small progress leading out of the complete lack of information, as one would describe the present situation in all

reference treatises on Organophosphorus Chemistry [3–5].

Preparation and Properties of the Compounds

Conventional methods for anhydride preparation were used for the synthesis of the title compounds. These included the condensation of phosphonic acid dichloride and phosphonic acid dimethyl ester ($\text{R} = \text{Me}$), hydrolysis of phosphonic acid dichlorides ($\text{R} = \text{Et}$), and reaction of a phosphonic acid with its dichloride ($\text{R} = i\text{-Pr}$, $t\text{-Bu}$ and Ph). The yields were generally quite acceptable, and elemental analyses gave satisfactory data. However, according to spectroscopic data the purity of the products is poor in most cases (for details see the Exp. Part below and references [6–8]).

$(\text{MePO}_2)_n$ is a colourless solid, m.p. 168–175 °C, which is insoluble in most standard organic solvents, with the exception of dimethylformamide and dimethylsulfoxide. All attempts to purify the compound by crystallization or distillation were unsuccessful.

$(\text{EtPO}_2)_n$ is obtained as a yellowish, resinous material after distillation (with decomposition) at 210 °C/0.1 Torr, which is soluble in chloroform and dichloromethane, but could not be crystallized. The purity is unsatisfactory as checked by NMR spectroscopy (below).

$(i\text{-PrPO}_2)_n$ is a colourless, resinous solid, b.p. 205 °C/0.1 Torr, readily soluble in benzene and chloromethane solvents.

* Reprint requests to Prof. Dr. H. Schmidbaur.

(*t*-BuPO₂)_{*n*} is a white powder (from toluene/pentane), m.p. 194–195 °C, soluble in benzene and chloromethane solvents.

(PhPO₂)_{*n*} is a white powder with a broad melting range (120–180 °C), soluble in dimethylsulfoxide. The literature melting point (209–212 °C) could not be reproduced.

Mass Spectrometric Data

Mass spectra with chemical ionization were obtained for all five compounds. In each case the mono-ions of the *trimers* have been detected as the parent peaks in high relative intensity. These experiments thus confirm assumptions made in most previous papers considering phosphonic acid anhydrides. Surprisingly, the mass of the *hexamers* also showed up in low relative intensity (*ca.* 1%) in the spectra of the compounds. It is not clear if this result indicates some “secondary” association of the compound in the condensed phase, or if the conditions prevailing in the mass spectrometer induce and favour short-lived associations. Minor amounts of a *tetramer* have been observed only in the mass spectra of the ethyl and isopropyl compound. There was no evidence for these higher oligomers in the NMR spectra of solutions of these compounds, however, and it therefore appears that only small non-equilibrium amounts are present in the solid materials obtained directly from the reaction mixtures, which are difficult to purify.

With the *trimers* as the dominant species, the mass spectral data suggest six-membered ring structures, which can appear in two different configurations, for each of which two different chair conformations are possible (**A**, **B**). The first structure has threefold symmetry in both conformations (point group C_{3v}), while the other has a mirror plane for both conformations (point group C_s). Boat or twist conformations are not considered here, because they are likely to be high energy components of the ring inversion equilibria in solution.

NMR Spectroscopic Data

The methyl and the *t*-butyl compound have been found to show only a single set of resonances in their {¹H}³¹P, ¹H and {¹H}¹³C NMR spectra indicative of equivalent RPO₂ units in the rings of a C_{3v}

structure. The resonances of the proton-coupled spectra show the usual second order splittings owing to coupling between magnetically non-equivalent nuclei in (A_{*n*}X)_{*x*} spin systems. Representative examples are shown in Figures 1 and 2.

The ethyl, *i*-propyl, and phenyl compounds exhibit NMR spectra readily assigned to structures with non-equivalent PRO₂ units in the relative abundance of 2:1, as expected for a C_s-configuration. The {¹H}³¹P NMR spectra show AB₂ spin systems with similar ²J(P–P) coupling constants for all three examples. The proton and carbon spectra have the corresponding multiplet features, details of which are given in the Experimental section.

A few experimental observations are noteworthy. The primary product of the phenylphosphonic acid anhydride initially showed a singlet phosphorus resonance, which slowly transformed into the A₂B doublet/triplet pattern upon storage of the samples or their solutions at ambient tem-

Fig. 1. {¹H}¹³C NMR spectrum of (MePO₂)₃ in DMSO-d₆ at 25 °C.

Fig. 2. $\{^1\text{H}\}^{31}\text{P}$ NMR spectrum of $(\text{PhPO}_2)_3$ in CDCl_3 at 25 °C.

perature. This result may indicate that the more symmetrical structure may be kinetically controlled and may not represent the ground state structure. Such phenomena may also explain the difficulties experienced in attempts to purify the materials by standard techniques. The presence of small amounts of other oligomers (above) is another source of ambiguities regarding the physical properties of the systems.

Conclusions

Although the present results have delineated the basic configurations of a few phosphonic acid anhydrides, they do not allow any assignments of the analytical and spectral data to specific conformations (chair/boat/twist rings; axial/equatorial groups R). Based on steric arguments we propose, however, that the *t-butyl* compound should have a symmetrical structure **A** with three equatorial *t*-butyl groups. For the *i-propyl*, *ethyl* and *phenyl* compound mirror symmetry structures **B** appear to be valid, with rapidly interconverting chair conformations. For the *methyl* compound, finally, again a structure type **A** is to be assumed, which may have all-axial methyl groups in the preferred conformation, as suggested by the structures of other $(\text{PO}_2\text{X})_3$ compounds with small substituents X.

Experimental Part

All reactions were carried out under dry and purified nitrogen. The solvents were dried using standard techniques (Na , Na/K -alloy, P_4O_{10} ,

LiAlH_4 , molecular sieves), distilled, and stored under nitrogen. All glassware was heated to 150 °C, evacuated and filled with nitrogen. – NMR: JEOL GX 400. References: Tetramethylsilane for ^1H and ^{13}C spectra, external H_3PO_4 (85% in H_2O) for ^{31}P . The spectra were recorded at 25 °C. – MS: Varian MAT 90 (CI, Isobutane), Varian MAT 311 A (EI, 70 eV). – Elemental analysis: Microanalytical laboratory of this Institute (M. Barth). – Melting points: Electrothermal IA 9200 (not corrected). Reagents were commercially available or prepared according to the cited literature.

Preparation of the compounds

$(\text{MePO}_2)_n$ [6]: Dimethyl methylphosphonate was slowly added to equivalent quantities of methylphosphonic dichloride (up to 5% excess) at 70 °C. Stirring was continued for 4 h and excess phosphonic chloride removed under reduced pressure. A colourless, microcrystalline solid was obtained after crystallization from dichloromethane/hexane. – Yield 68%, m.p. 168–175 °C. ^1H NMR (d_6 -DMSO): δ = 1.49 (m, $\text{A}_3\text{XX}'_2\text{A}'_6$ or $(\text{A}_3\text{X})_3$). ^{13}C NMR (d_6 -DMSO): δ = 13.95 (m, AXX'_2 , $^1J(\text{PC})$ = 147.5, $^3J(\text{PC})$ = 3.2 Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (d_6 -DMSO): δ = 18.8 (s). ^{31}P NMR (d_6 -DMSO): δ = 18.8 (m, X-part of $(\text{A}_3\text{X})_3$). CI-MS: m/z (%): 234.9 (100) $[\text{M}+\text{H}^+]$, 219.9 (1.5) $[\text{M}+\text{H}^+-\text{CH}_3]$.

$\text{C}_3\text{H}_9\text{O}_6\text{P}_3$ (234.02)

Calcd	C 15.40	H 3.88	P 39.71%
Found	C 15.53	H 4.07	P 39.21%

$(\text{EtPO}_2)_n$: Water was carefully added to ethylphosphonic dichloride (molar ratio 1:1) with vigorous stirring in such a way that the internal temperature did not exceed 50 °C. Stirring at ambient temp. was continued for 1 h and excess phosphonic chloride removed under reduced pressure. – Yield 100%, yellowish resin, b.p. 210 °C/0.1 Torr (with dec.). ^1H NMR (CDCl_3): δ = 1.05–1.35 (m, A_3 of $\text{A}_3\text{B}_2\text{XY}_2$, 9H), 1.75–2.35 (m, B_2 of $\text{A}_3\text{B}_2\text{XY}_2$, 6H). ^{13}C NMR (CDCl_3): δ = 5.23–5.98 (AXY_2 -multiplets, CH_3), 18.81–22.26 (AXY_2 -multiplets, CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ = 16.92 (AB_2 , d, $^2J(\text{PP})$ = 35.6 Hz, 2P), 19.21 (t, 1P). CI-MS: m/z (%): 277.2 (100) $[\text{M}+\text{H}^+]$, 248.2 (3.4) $[\text{M}+\text{H}^+-\text{C}_2\text{H}_5]$.

$\text{C}_6\text{H}_{15}\text{O}_6\text{P}_3$ (276.10)

Calcd	C 26.10	H 5.48	O 34.77	P 33.65%
Found	C 26.10	H 5.60	O 35.4	P 31.87%

$(i\text{-PrPO}_2)_n$: *i*-propylphosphonic dichloride [7] was added in equimolar amounts to a solution of *i*-propylphosphonic acid [7] in toluene. After re-

fluxing for 4 h solvent and excess phosphonic chloride were driven off under reduced pressure. – Yield 100%, colourless resin, b.p. 205 °C/0.1 Torr (with dec.). ^1H NMR (C_6D_6): δ = 0.97–1.03 (m, A_6BXY_2 , $J(\text{AX})$ = 20.1, $J(\text{AB})$ = 7.33 Hz, CH_3 , 18H), 1.08–1.41 (m, CH, 3H). ^{13}C NMR (C_6D_6): δ = 15.65–15.75 (AXY_2 , $J(\text{AX})$ = 2.2 Hz, CH_3), 25.3 (BXY_2 , $^1J(\text{BX})$ = 147.6 Hz, CH_{ax}), 26.6 (m, $^1J(\text{BX})$ = 158.65 Hz, $^3J(\text{BY})$ = 8.8 Hz, CH_{eq}). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = 18.57 (AB_2 , d, $^2J(\text{PP})$ = 43.4 Hz, 2P), 21.46 (t, 1P). CI-MS: m/z (%): 319.3 (100) [$\text{M} + \text{H}^+$], 276.3 (5.05) [$\text{M} + \text{H}^+ - \text{C}_3\text{H}_7$], 234.2 (3.45) [$\text{M} + \text{H}^+ - 2^*\text{C}_3\text{H}_7$].

$\text{C}_9\text{H}_{21}\text{O}_6\text{P}_3$ (318.18)

Calcd C 33.97 H 6.65 O 30.17 P 29.20%,
Found C 33.65 H 6.58 O 28.49 P 31.14%.

(*t*-BuPO₂)_n: *t*-butylphosphonic dichloride [7] was added in equimolar amounts to a solution of *t*-butylphosphonic acid [7] in toluene. After refluxing for 4 h the solvent was removed under reduced pressure. A white powder was obtained after washing the residue with *n*-pentane. – Yield 54%, m.p. 194–195 °C. ^1H NMR (CDCl_3): δ = 1.22 (d/br, $^3J(\text{PH})$ = 18.07 Hz). ^{13}C NMR (CDCl_3): δ = 24.67 (s/br, CH_3), 31.03 (AXX'_2 , $^1J(\text{PC})$ = 161.68,

$^3J(\text{PC})$ = 11.3 Hz, C). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = 31.16 (s). CI-MS: m/z (%): 361.5 (53.3) [$\text{M} + \text{H}^+$], 304.4 (4.79) [$\text{M} + \text{H}^+ - \text{C}_4\text{H}_9$], 248.3 (2.8) [$\text{M} + \text{H}^+ - 2^*\text{C}_4\text{H}_9$].

$\text{C}_{12}\text{H}_{27}\text{O}_6\text{P}_3$ (360.26)

Calcd P 25.79%,
Found P 26.10%.

(PhPO₂)_n [8]: A mixture of phenylphosphonic dichloride (40% excess) and phenylphosphonic acid was stirred at 200 °C for 2 h. Excess phosphonic chloride was then removed at 150 °C in vacuo. The residue was taken up in benzene, and crystallization induced at 5 °C. After several days the anhydride was filtered off and the filtrate left again at 5 °C for further crystallization. These operations were repeated until the filtrate gave no more crystals (approximately 20 d). – Yield 72%, white powder, m.p. 120–180 °C. ^1H NMR (d_6 -DMSO): δ = 7.37–7.52 (m, Ph), 7.62–7.80 (m, Ph). ^{13}C NMR (d_6 -DMSO): δ = 127.93–134.92 (m, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ = 1.98 (AB_2 , d, $^2J(\text{PP})$ = 40.0 Hz, 2P), 3.68 (t, 1P). CI-MS: m/z (%): 421.0 (100) [$\text{M} + \text{H}^+$].

$\text{C}_{18}\text{H}_{15}\text{O}_6\text{P}_3$ (420.23)

Calcd C 51.45 H 3.60 O 22.84 P 22.11%,
Found C 50.17 H 3.95 O 22.8 P 22.18%.

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