

Stable phosphinous acids

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Abstract

The electronic properties of organyl element compounds are strongly influenced by the electronic characteristics of the organic substituents. The bonding of two CF_3 groups to a phosphorus atom effects a drastically decreased basicity. That is the phosphorus atom is the least basic centre in the compound $(\text{CF}_3)_2\text{POH}$. This compound, synthesized in 1960 by Burg and Griffiths, is the only known example of a phosphinous acid, although there should be a general interest in this class of compounds. However, only a few investigations have been reported which may be explained by the tedious and risky synthesis. In this paper a safe one step and high yield synthesis of $(\text{CF}_3)_2\text{POH}$ is described. The compound $(\text{C}_6\text{F}_5)_2\text{POH}$, originally claimed as a phosphinous acid, is proved to exist at room temperature exclusively in the tautomeric oxide form. $(\text{C}_6\text{F}_5)_2\text{P(O)H}$ crystallizes in the triclinic space group $P\bar{1}$ (no. 2) with a 992.9(1) pm; b 1501.9(2) pm; c 1539.4(2) pm; α 117.48(1)°; β 100.39(1)°; γ 96.02(1)° and Z 6.

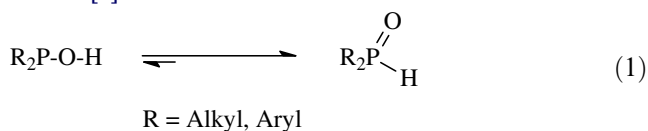
Quantum chemical investigations prove the electron withdrawing effect of s-triazinyl groups (1,3,5-triazin-4-yl derivatives) to be much stronger than that of pentafluorophenyl groups. Quantum chemical calculations at the B3PW91/6-311G(3d,p) level of theory predict for the bis(s-triazinyl) derivative $(\text{C}_3\text{N}_3\text{H}_2)_2\text{POH}$ the phosphinous acid isomer to be favored by $\Delta E_{\text{ZP}} = 22$ kJ/mol in relation to the corresponding phosphane oxide isomer. The phosphinous acid $(\text{CF}_3)_2\text{POH}$ (C_s symmetry) is favored at the same level of theory by about $\Delta E_{\text{ZP}} = 14$ kJ/mol compared with the phosphane oxide structure (C_s symmetry).

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1. Introduction

Phosphinous acids R_2POH ($\text{R} = \text{Alkyl}$ and Aryl) with a trivalent central phosphorus atom are unstable in relation to the tautomeric pentavalent phosphorus oxides [1]:



However, it is possible to stabilize phosphinous acid derivatives by coordination to transition metal complexes [2].

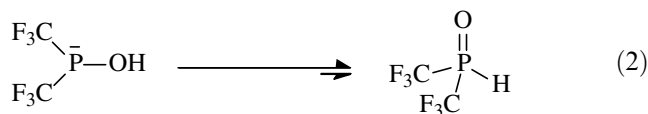
The electronic properties of perfluoroorganyl element compounds are strongly influenced by the electronic characteristics of the perfluoroorganyl groups. The high group electronegativities of perfluoroorganyl groups effect a strong electron withdrawing effect. The group electronegativity of a trifluoromethyl group for example exceeds the electronegativity of a chlorine atom [3]. Therefore perfluoroorganylphosphanes exhibit higher ionisation energies [4] and reduced Lewis basicities [5] in comparison with their non-fluorinated counterparts. The high Lewis acidities [6] of perfluoroorganylphosphane derivatives are depicted by the readily addition of nucleophilic groups forming phosphoranides, PR_4^- [7].

The bonding of two CF_3 groups to a phosphorus atom effects a drastically decreased basicity. That is the phosphorus atom is the least basic centre in the compound $(\text{CF}_3)_2\text{POH}$. This compound is, to our knowl-

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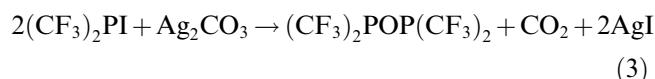
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edge [8], the only well characterized example of a phosphinous acid, which is even stable at ambient temperature

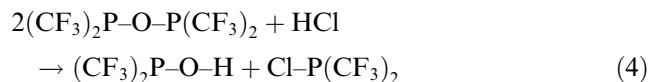


Although this extraordinary compound, which was synthesized already in 1960 by Burg and Griffiths, should exhibit an outstanding chemistry, due to the tedious and risky synthesis [9,10], only a few investigations have been reported.

The reaction of $(\text{CF}_3)_2\text{PI}$ with silver carbonate results in a 80% yield of the diphosphoxane $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$. Before the product can be isolated via fractional condensation, the part of $(\text{CF}_3)_2\text{PI}$ which has not reacted has to be converted by AgCl to the removable $(\text{CF}_3)_2\text{PCI}$



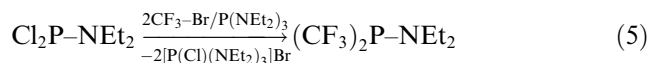
The diphosphoxane $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ represents a unique compound showing no rearrangement to a phosphane oxide. It can be cleaved by gaseous HCl yielding $(\text{CF}_3)_2\text{PCI}$ and $(\text{CF}_3)_2\text{POH}$ (86 h, 100 °C). The phosphinous acid is separated in a 90% yield via a trap to trap condensation of the gaseous mixture, which reacts very violently on contact with air



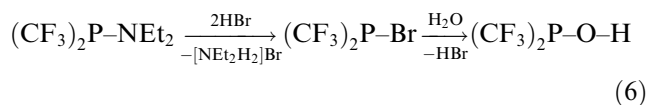
The presumed $(\text{CF}_3)_2\text{POH}$ structure was supported by the infrared spectrum showing the O–H stretching frequency at 3620 cm^{-1} and the very strong P–O stretching at 854 cm^{-1} . The tautomeric oxide form $(\text{CF}_3)_2\text{P}(\text{O})\text{H}$ can be excluded by the absence of a P=O stretching band, which should be expected near 1285 cm^{-1} by comparison with 1328 cm^{-1} for $(\text{CF}_3)_3\text{P}=\text{O}$ and 1415 cm^{-1} for $\text{F}_3\text{P}=\text{O}$ [9]. A deeper inspection of the infrared spectrum of $(\text{CF}_3)_2\text{POH}$ reveals two O–H stretching frequencies, which were attributed to rotational isomers [10].

2. Improved synthesis of the bis(trifluoromethyl) phosphinous acid

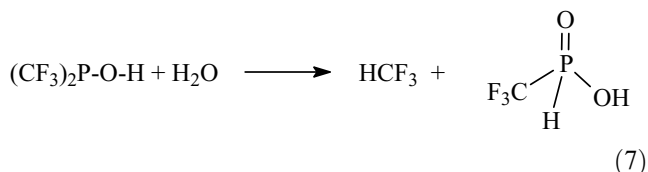
To explore the chemistry of the extraordinary bis(trifluoromethyl)phosphinous acid a safer and easier access would be desirable. An easily and safely manageable bis(trifluoromethyl)phosphane derivative is $(\text{CF}_3)_2\text{P-NEt}_2$ which is synthesized in a 200 g scale via the Ruppert procedure – reacting Cl_2PNEt_2 with CF_3Br in the presence of $\text{P}(\text{NEt}_2)_3$ [11]:



Bis(trifluoromethyl)halogenophosphanes like $(\text{CF}_3)_2\text{PBr}$ are accessible by reacting $(\text{CF}_3)_2\text{PNEt}_2$ with gaseous HBr . Bis(trifluoromethyl)bromophosphane reacts easily with H_2O to yield $(\text{CF}_3)_2\text{POH}$ and HBr

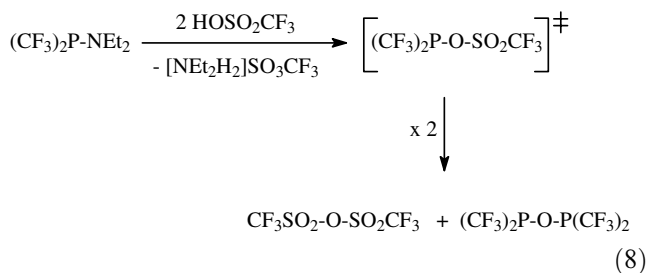


Attempts to separate $(\text{CF}_3)_2\text{POH}$ from the reaction mixture were less successful, and yielded a mixture of $(\text{CF}_3)_2\text{POH}$ and its product of continued hydrolysis compound $\text{CF}_3\text{PH}(\text{O})\text{OH}$ [12]. Under strong acidic conditions $(\text{CF}_3)_2\text{POH}$ is stable towards hydrolysis. In neutral or even basic conditions $(\text{CF}_3)_2\text{POH}$ is very sensitive towards hydrolysis. During the work up of the reaction mixture of $(\text{CF}_3)_2\text{PBr}$ and H_2O (cf. Eq. (6)), via fractional condensation, we obtained a mixture of $(\text{CF}_3)_2\text{POH}$ (b.p. 61 °C [9]) and H_2O . In the absence of HBr , this mixture, upon warming to room temperature, immediately reacts according to



The acidic cleavage of the P–N bond in $(\text{CF}_3)_2\text{P-NEt}_2$ and the following hydrolysis (cf. Eq. (6)) can be performed in one step in a two phase system, treating a CH_2Cl_2 solution of $(\text{CF}_3)_2\text{PNEt}_2$ with concentrated aqueous HCl . Nevertheless, after the work up of the CH_2Cl_2 solution of $(\text{CF}_3)_2\text{POH}$ via fractional condensation we end up with a mixture of $(\text{CF}_3)_2\text{POH}$ and $\text{CF}_3\text{PH}(\text{O})\text{OH}$. In fact it is possible to separate these two compounds, but the yields are low.

In 1982 Dahl postulated the existence of reactive phosphonium derivatives $\text{R}_2\text{P}^+\text{CF}_3\text{SO}_3^-$, cleaving a P–N bond of R_2PNMe_2 derivatives with $\text{R} = \text{Ph}$, NMe_2 on treatment with trifluoromethylsulfonic acid [13]. On treatment of $(\text{CF}_3)_2\text{PNEt}_2$ with $\text{CF}_3\text{SO}_3\text{H}$ we postulate the formation of a comparable compound $(\text{CF}_3)_2\text{P-O-SO}_2\text{CF}_3$ though with a covalent rather than an ionic bonding situation. Indeed, the mixed anhydride $(\text{CF}_3)_2\text{P-O-SO}_2\text{CF}_3$ could not be observed, but its products of rearrangement, the symmetric anhydrides $(\text{CF}_3)_2\text{P-O-P}(\text{CF}_3)_2$ and $\text{CF}_3\text{SO}_2\text{-O-SO}_2\text{CF}_3$



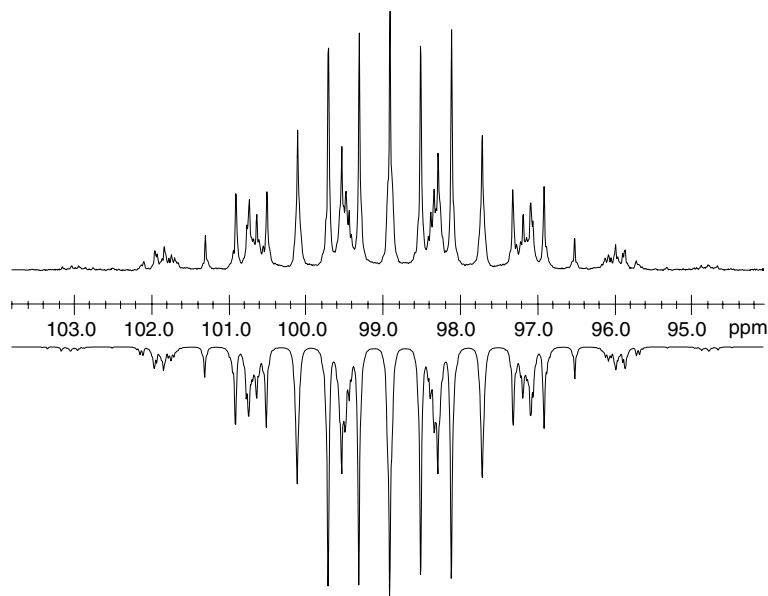
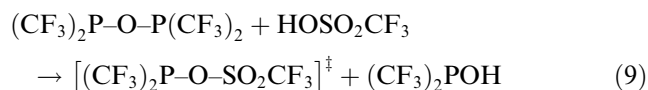


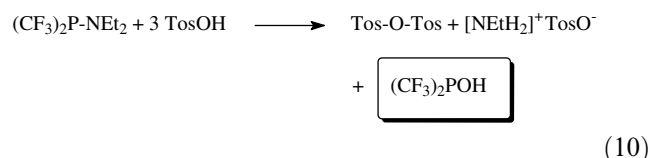
Fig. 1. Experimental (top) and calculated (bottom) ^{31}P NMR spectrum (81.01 MHz) of $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ (compare text).

The formed diphosphoxane $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ is characterized by its very characteristic ^{19}F and ^{31}P NMR resonances. The experimental higher order ^{31}P NMR resonance is shown in the upper trace of Fig. 1. The $^2J(\text{PF})$ and the long range $^4J(\text{PF})$ couplings with values of 92 and 5 Hz, respectively, give rise to magnetic non-equivalence of the two $\text{P}(\text{CF}_3)_2$ moieties, resulting in a high order $[\text{AX}_6]_2$ spin system with $\text{A} = \text{P}$ and $\text{X} = \text{F}$. The experimental high order ^{31}P NMR spectrum (Fig. 1) is in excellent agreement with the calculated spectrum displayed in the bottom trace. Because $^2J(\text{PF})$ couplings are, in contrast to the always negative $^1J(\text{PF})$ couplings, positive [14], the analysis of the ^{31}P NMR spectrum as an $\text{A}_6\text{A}'_6\text{XX}'$ spin system favours a positive sign for the $^4J(\text{PF})$ coupling. For spin systems which are based on a $\text{AA}'\text{XX}'$ system only the relative signs of the AX - and AX' couplings are assignable [15].

The phosphinous acid $(\text{CF}_3)_2\text{POH}$ is always observed as a side product of the reaction of $(\text{CF}_3)_2\text{PNEt}_2$ with two equivalents of $\text{CF}_3\text{SO}_3\text{H}$, caused by the reaction of $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ with $\text{CF}_3\text{SO}_3\text{H}$



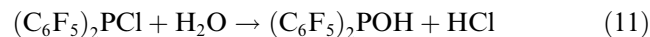
Finally, the treatment of $(\text{CF}_3)_2\text{PNEt}_2$ with at least three equivalents of carefully dried *p*-toluenesulfonic acid (TsOH) results in a complete transformation of $(\text{CF}_3)_2\text{PNEt}_2$ into $(\text{CF}_3)_2\text{POH}$. If the less volatile solvent 1,6-dibromohexane is used, the product is removed in vacuo as the only volatile compound in a 90% yield



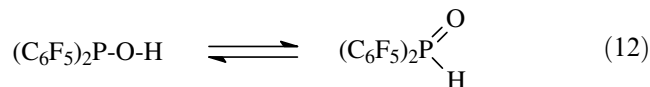
The reaction pathway of the one step and high yield synthesis of $(\text{CF}_3)_2\text{POH}$ is described in Scheme 1.

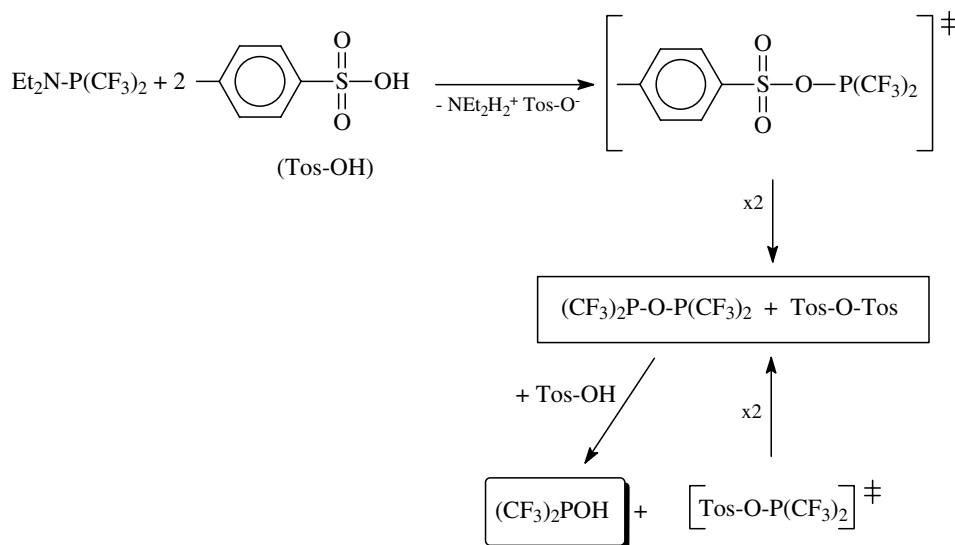
3. Diarylphosphinous acids and outlook

In 1966 Magnelli et al. [16] postulated the phosphinous acid $(\text{C}_6\text{F}_5)_2\text{POH}$ to be formed in the hydrolysis of $(\text{C}_6\text{F}_5)_2\text{PCl}$



The composition of the crystalline white solid was proved by elemental analysis. Unfortunately, the authors were not able to assign any vibrational mode in the observed infrared spectrum to identify the compound as the phosphinous acid or phosphane oxide. Therefore they measured a proton magnetic resonance spectrum in CDCl_3 . The two signals observed at 4.0 and 13.3 ppm were assigned to the phosphane oxide and phosphinous acid, respectively. Following these assignments they described the compound $(\text{C}_6\text{F}_5)_2\text{POH}$ as an equilibrium mixture of the two tautomeric forms:



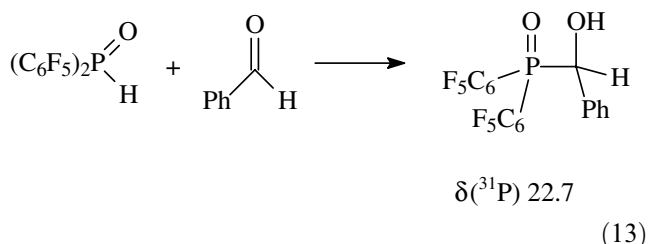
Scheme 1. Reaction pathway of the improved synthesis of $(\text{CF}_3)_2\text{POH}$.

Because the compound $(\text{C}_6\text{F}_5)_2\text{POH}$ is sensitive towards hydrolysis in basic conditions we treated a CH_2Cl_2 solution of $(\text{C}_6\text{F}_5)_2\text{PBr}$ with concentrated aqueous HCl at 0°C . Evaporation of the organic phase yields the product in a 80% yield as a white solid. The proton magnetic resonance spectrum of the product dissolved in CDCl_3 exhibits, in contrast to Magnelli's observations, two signals at 7.3 and 10.1 ppm – a doublet centered at 8.7 ppm with a splitting of 560 Hz. The ^{31}P NMR spectrum exhibits a doublet at -18.5 ppm with a $^1J(\text{PH})$ coupling of 560 Hz. Therefore the equilibrium (12) is shifted to the right side.

The two ^1H NMR signals, observed by Magnelli et al., exhibit a difference of 9.3 ppm. Assuming, that these authors used a 60 MHz NMR spectrometer, this difference is calculated to 558 Hz. Therefore Magnelli et al. collected the right data, a doublet at 8.6 ppm with a $^1J(\text{PH})$ coupling of 558 Hz, which are comparable with our data, but the interpretation of these data by Magnelli et al. is wrong. The multinuclear NMR spectra of the compound $(\text{C}_6\text{F}_5)_2\text{POH}$ dissolved in CDCl_3 exhibit only signals for the phosphane oxide.

The vibrational spectra of the solid compound support the formulation of a phosphane oxide, interpreting the signals at 1209 and 2472 cm^{-1} as the $\text{P}=\text{O}$ and $\text{P}-\text{H}$ valence modes, respectively. Further evidence is obtained by a single crystal X-ray structure analysis. The phosphane oxide $(\text{C}_6\text{F}_5)_2\text{P}(\text{O})\text{H}$ crystallizes in the triclinic space group $P\bar{1}$. The averaged $\text{P}-\text{O}$ distance of the three crystallographically independent molecules of 146.9 pm describes a typical $\text{P}=\text{O}$ double bond. The collected X-ray data allowed an isotropic refinement of the hydrogen atoms bonded to the phosphorus atoms (cf. Fig. 2).

The phosphane oxide $(\text{C}_6\text{F}_5)_2\text{P}(\text{O})\text{H}$ adds at room temperature to the carbon oxygen double bond of benzaldehyde. The product, a white crystalline solid, exhibits one ^{31}P NMR resonance at 22.7 ppm, while the ^{19}F NMR spectrum shows six resonances, three for each diastereomeric C_6F_5 ring



The reaction mixture of $(\text{C}_6\text{F}_5)_2\text{P}(\text{O})\text{H}$ and acetone exhibits, surprisingly, three resonances: one doublet

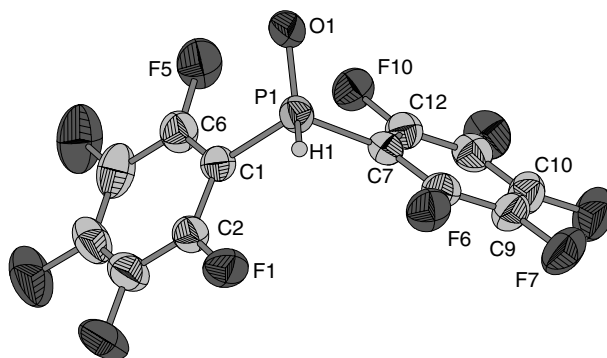


Fig. 2. Molecular structure of one of three crystallographically independent $(\text{C}_6\text{F}_5)_2\text{P}(\text{O})\text{H}$ molecules showing the atom numbering scheme and thermal ellipsoids (50%). Selected bond lengths (pm) and angles ($^\circ$): $\text{P}(1)-\text{O}(1)$ 147.6(3); $\text{P}(1)-\text{H}(1)$ 133(3); $\text{P}(1)-\text{C}(1)$ 181.6(3); $\text{P}(1)-\text{C}(7)$ 181.8(3); $\text{C}(1)-\text{P}(1)-\text{C}(7)$ 105.9(1); $\text{C}(1)-\text{P}(1)-\text{O}(1)$ 111.6(1); $\text{C}(7)-\text{P}(1)-\text{O}(1)$ 113.7(1).

for unchanged $(\text{C}_6\text{F}_5)_2\text{P}(\text{O})\text{H}$ at -19.1 ppm, a singlet at 29.2 ppm for the addition product $(\text{C}_6\text{F}_5)_2\text{P}(\text{O})\text{-C}(\text{OH})\text{Me}_2$ and a quintet at 74.5 ppm ($^3J(\text{PF}) = 34$ Hz). On evaporation of the reaction mixture to dryness, the remaining white solid exhibits the same weight as the starting material of $(\text{C}_6\text{F}_5)_2\text{P}(\text{O})\text{H}$. Dissolving this residue in CDCl_3 and examining its multinuclear NMR spectra reveals exclusively the NMR resonances for the phosphane oxide $(\text{C}_6\text{F}_5)_2\text{P}(\text{O})\text{H}$. Evaporation to dryness and redissolving of the residue in acetone again results in the described three resonances in the ^{31}P NMR spectrum.

To assign the ^{31}P NMR resonance at 74.5 ppm the ^1H , ^{19}F and ^{31}P NMR spectra of $(\text{C}_6\text{F}_5)_2\text{P}(\text{O})\text{H}$ are collected using different solvents. Solutions of $(\text{C}_6\text{F}_5)_2\text{P}(\text{O})\text{H}$ in toluene, dichloromethane, chloroform and acetonitrile exhibit only one resonance in the ^{31}P NMR spectrum – a doublet at around -19 ppm with a $^1J(\text{PH})$ coupling in the range of $560\text{--}600$ Hz for the phosphane oxide (cf. Table 1.). Solutions of $(\text{C}_6\text{F}_5)_2\text{P}(\text{O})\text{H}$ in methanol, DME, THF, Ether, DMF and DMSO exhibit an additional resonance with an increasing relative intensity at around 74 ppm: a quintet with a $^3J(\text{PF})$ coupling of around 34 Hz. This resonance, which is comparable to the resonance of $(\text{CF}_3)_2\text{POH}$ ($\delta(^{31}\text{P})$ 79.0 (sept); $^2J(\text{PF})$ 83 Hz), is assigned to the phosphinous acid. The ^1H NMR resonance of $(\text{C}_6\text{F}_5)_2\text{POH}$ in THF-d_8 , a singlet at 7.0 ppm at room temperature exhibits a temperature depending shift from 5.5 to 8.1 ppm between $+50$ and -70 °C. The ratio of the two tautomeric forms, the phosphane oxide and the phosphinous acid reveals no temperature dependency. The relative intensities of ^1H , ^{19}F and ^{31}P NMR resonances of the tautomeric forms exhibit no significant temperature dependency within the investigated temperature range.

Table 1

Solvent dependent tautomeric equilibrium between bis(pentafluorophenyl)phosphane oxide and the bis(pentafluorophenyl)phosphinous acid ^a

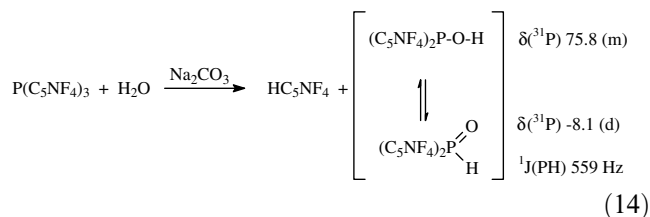
Solvent	$(\text{C}_6\text{F}_5)_2\text{P}(\text{O})\text{H}$	$(\text{C}_6\text{F}_5)_2\text{P-O-H}$
Toluene	100	0
Dichloromethane	100	0
Chloroform	100	0
Acetonitrile	100	0
Methanol	82	18
DME	57	43
THF	45	55
Ether	40	60
DMF	33	67
DMSO	24	76

^a Percentages obtained from the integration of the ^{31}P and ^{19}F NMR spectra.

The solvent dependent tautomeric equilibrium between $(\text{C}_6\text{F}_5)_2\text{P}(\text{O})\text{H}$ and $(\text{C}_6\text{F}_5)_2\text{P-O-H}$ does not surprise, if DFT calculations at the B3LYP/6-311G(2d,p) level are taken into account. The phosphinous acid is favored by only ΔE_{ZPE} 1.7 kJ/mol. The relative energetic difference between the tautomeric forms of the bis(trifluoromethyl) derivatives is calculated at the B3PW91/6-311G(3d,p) level to be ΔE_{ZPE} 14 kJ/mol. This may explain why $(\text{CF}_3)_2\text{POH}$ does not exhibit a solvent dependent tautomeric equilibrium.

In order to synthesize a diarylphosphinous acid which is more stabilized towards the tautomeric diarylphosphane oxide than the C_6F_5 derivative, it is necessary to increase the electron withdrawing effect of the aryl groups.

In a recent paper we demonstrated that the phosphorus-carbon distances in corresponding arylphosphanides, ArPH^- , are a useful indicator for the evaluation of the electron withdrawing effect of aryl groups exerted on a phosphorus atom. Corresponding quantum chemical calculations indicate increasing electron withdrawing capacity of perfluoroaryl groups on successive substitution of fluorine atoms by CF_3 groups or even stronger on successive substitution of CF units by isolobal nitrogen atoms [8]. Following these ideas the tetrafluoropyridin-4-yl substituent should exhibit a stronger electron withdrawing capacity than a C_6F_5 group. This explains why the phosphinous acid $(\text{C}_5\text{NF}_4)_2\text{POH}$ is favored by ΔE_{ZPE} 10.5 kJ/mol over the comparable phosphane oxide at the B3LYP/6-311G(2d,p) level. Both compounds can be observed in an equilibrium within the hydrolysis of $\text{P}(\text{C}_5\text{NF}_4)_3$ under basic conditions:

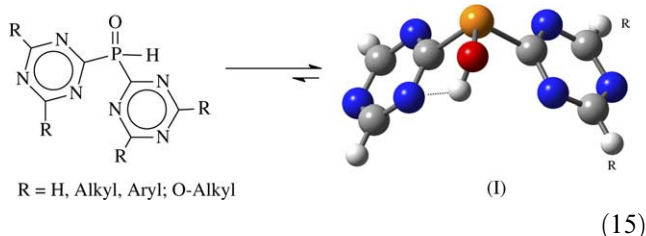


Investigations, to establish whether the compound $(\text{C}_5\text{NF}_4)_2\text{POH}$ favors the tautomeric form of a phosphinous acid or the phosphane oxide form in the solid state, are in progress.

Threefold substitution of CF units in C_6F_5 groups by isolobal nitrogen atoms will create s-triazinyl substituents (1,3,5-triazin-2-yl). Using the method to evaluate the electron withdrawing effect of aryl groups exerted on a phosphorus atom by means of the phosphorus-carbon distances in corresponding arylphosphanides, ArPH^- , leads to the prediction that an s-triazinyl group will show a much stronger electron withdrawing effect than a tetrafluoropyridinyl or a pentafluorophenyl group. It seems to be reasonable that even non fluorinated s-triazinyl groups exhibit a strong electron

withdrawing effect, comparable to that of a CF_3 group [8].

Quantum chemical calculations at the B3PW91/6-311G(3d,p) level of theory predict for a bis(*s*-triazinyl) derivative (I) (cf. Eq. (15)) that the phosphinous acid isomer to be favored above the corresponding phosphane oxide isomer. Besides the strong electron withdrawing effect of the *s*-triazinyl group, intramolecular OH–N bridges with distances of 216 and 286 pm (cf. Eq. (15)) seem to be responsible for the stabilization of the phosphinous acid ($\text{C}_3\text{N}_3\text{H}_2$)POH of $\Delta E_{\text{ZP}} = 22$ kJ/mol (C_1 symmetry at B3PW91/6-311G(3d,p) level) with respect to the corresponding phosphane oxide isomer (C_s symmetry), (cf. Eq. (15)) [8]



Conceivable mesoionic compounds, formed by an intramolecular acid base reaction of the acidic function of the phosphinous acid ($\text{C}_3\text{N}_3\text{H}_2$)₂POH with an *ortho* or *para* oriented basic function of *s*-triazinyl substituents are less stable by about 80 kJ/mol at the same level of theory [8].

The realization of these predictions implies that our future work will be focused on a general investigation of the *s*-triazinyl phosphorus chemistry.

Acknowledgements

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