

Investigations of the Tautomeric Equilibria between Phosphane Oxides and Their Corresponding Phosphinous Acids Bearing Electron-Withdrawing Perfluoroaryl Groups

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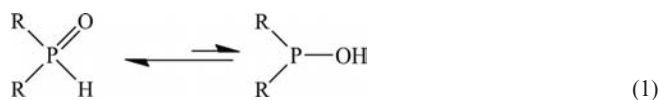
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The unusual form of a phosphinous acid can be stabilized by strongly electron-withdrawing substituents such as trifluoromethyl and pentafluoroethyl groups. The less electron-withdrawing pentafluorophenyl group favors the phosphane oxide tautomer $(R_f)_2P(O)H$ in the solid state, whereas in solution a solvent-dependent equilibrium with the phosphinous acid tautomer $(R_f)_2POH$ is observed. The increasing donating ability of the solvent leads to an increasing amount of the corresponding phosphinous acid tautomer. In accord with quantum chemical calculations, the electron-withdrawing effects of the *p*-tetrafluoropyridyl and 2,4-bis(trifluoromethyl)phenyl groups exceed the pentafluorophenyl group and should therefore be ideally suited to stabilize the corresponding

phosphinous acid tautomer $(R_f)_2POH$. The syntheses of bis-(tetrafluoropyridyl)- and bis[2,4-bis(trifluoromethyl)phenyl]-phosphane oxide enabled the investigation of the solvent-dependent tautomerism by NMR spectroscopy. Introduction of the tetrafluoropyridyl group shifts the tautomeric equilibrium significantly towards the phosphinous acid. Surprisingly, the comparably electron-withdrawing but more bulky 2,4-bis(trifluoromethyl)phenyl group favors the oxide tautomer. The experimental results have been confirmed by DFT calculations. In summary, electron-withdrawing substituents stabilize the phosphinous acid tautomer, whereas it is destabilized by space-demanding groups by an increased C–P–C angle.

Introduction

Trivalent phosphinous acids, R_2POH , are related to pentavalent phosphane oxides, $R_2P(O)H$, by tautomerism. For electron-donating alkyl and aryl groups R the tautomeric equilibrium is completely shifted towards the phosphane oxide, see Equation (1).

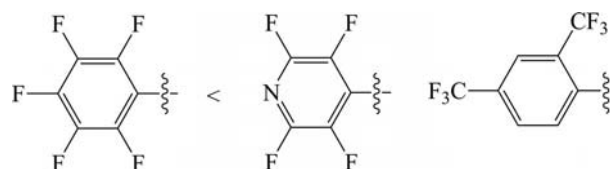


To stabilize the unfavored phosphinous acid structure the introduction of strongly electron-withdrawing substituents, such as trifluoromethyl and pentafluoroethyl groups, is necessary.^[1,2] The employment of the weaker electron-demanding pentafluorophenyl group favors the phosphane oxide tautomer $[(F_5C_6)_2P(O)H, \mathbf{1}]$ in the solid state whereas in solution a solvent-dependent equilibrium is observed.^[3,4] With increasing solvent donicity (DN),^[5] an increasing amount of the phosphinous acid tautomer is observed.

The aim of this work was to stabilize the phosphinous acid tautomer by introducing more strongly electron-with-

drawing aryls than the pentafluorophenyl group. The electron-withdrawing effect of a variety of differently substituted phenyl groups can be classified on the basis of the C–O or C–N bond lengths in the corresponding phenolate or amide ions ($Ar-O^-$ and $Ar-NH^-$), respectively, which are accessible by DFT calculations.^[6] According to these, an increase in the electron-withdrawing effect of the aromatic group leads to a shortened C–O and C–N distance in the corresponding ions.

The difference between the C–E bond lengths in the XC_6H_4-E derivatives and the parent compound C_6H_5-E is denoted by $\Delta(E)_{m,p}$. For $E = O^-$ and NH^- , the values of $\Delta(E)_{m,p}$ exhibit the same tendency as the corresponding Hammett constants. Therefore the values $\Delta(E)_{m,p}$ are useful for classifying the electron-withdrawing effect of various kinds of substituents on phenyl or aryl groups. We calculated the electron-withdrawing effect to increase in the series below.^[6]



Based on this theoretical model an increased stabilization of the phosphinous acid was expected by introducing the

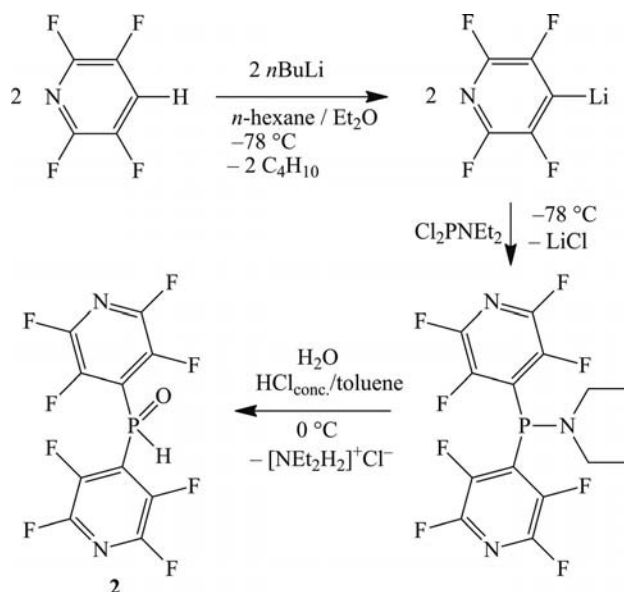
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more strongly electron-withdrawing *p*-tetrafluoropyridyl and 2,4-bis(trifluoromethyl)phenyl groups. Herein we describe the synthesis of the corresponding phosphane oxides (R_f)₂P(O)H and our study of the electronic as well as the steric effects of the chosen aryl groups R_f on the formation of the corresponding phosphinous acid tautomer (R_f)₂P–OH.

Results and Discussion

Bis(tetrafluoropyridyl)phosphane oxide has previously been generated by the hydrolysis of $P(C_5NF_4)_3$ under basic conditions.^[3] In this paper we describe an efficient synthesis of the phosphane oxide (C_5NF_4)₂P(O)H starting from *p*-tetrafluoropyridine. Metalating *p*- C_5NF_4H with *n*-butyllithium and the subsequent addition of dichloro(diethylamino)phosphane, Cl_2PNEt_2 , selectively resulted in the formation of bis(tetrafluoropyridyl)(diethylamino)phosphane, (C_5NF_4)₂PNEt₂ (Scheme 1). Evaporating the solvent and distillation of the residue afforded the product as a yellow liquid in 88% yield. Cleavage of the P–N bond and hydrolysis to give bis(tetrafluoropyridyl)phosphane oxide (**2**) was achieved in a two-phase system of conc. hydrochloric acid and toluene (Scheme 1). The product was obtained in a yield of 70% as a colorless solid that melts at 94 °C. The vibrational spectrum of the solid supports the phosphane oxide structure: the band at $\tilde{\nu} = 2430\text{ cm}^{-1}$ (KBr) for the P–H stretching vibration compares well with the corresponding band of (C_6F_5)₂P(O)H at $\tilde{\nu} = 2472\text{ cm}^{-1}$.^[3,7]

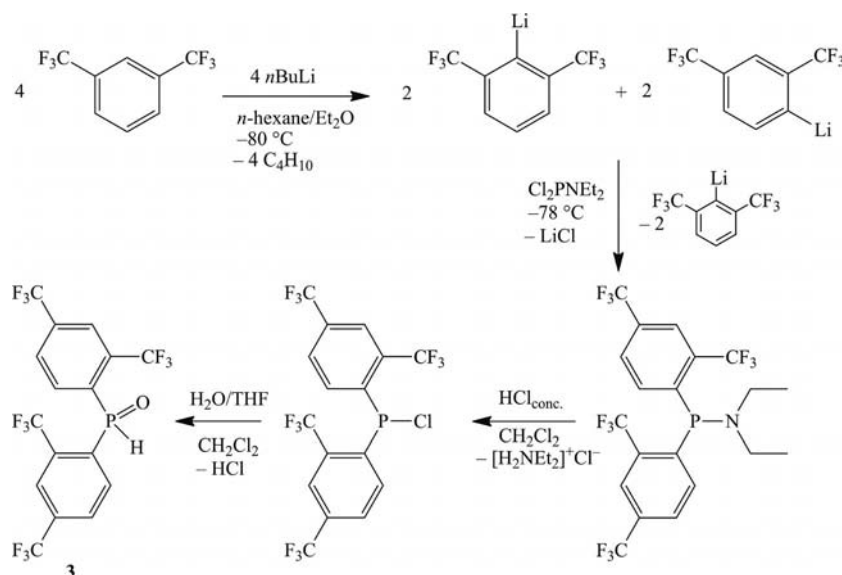
A solvent-dependent equilibrium between the bis(tetrafluoropyridyl)phosphane oxide (**2**) and the corresponding acid tautomer **2a** was observed.^[3,7] As expected, the introduction of the stronger electron-withdrawing C_5NF_4 substituent led to a significant shift of the equilibrium towards the phosphinous acid. Although with the C_6F_5 derivative



Scheme 1. Reaction of dichloro(diethylamino)phosphane with lithiated tetrafluoropyridine and subsequent hydrolysis of the intermediate to give bis(tetrafluoropyridyl)phosphane oxide (**2**).

no phosphinous acid was detected in CH_3CN solution, 78% of the tetrafluoropyridyl derivative exists as the phosphinous acid tautomer.^[7]

In addition to the tetrafluoropyridyl group, the 2,4-bis(trifluoromethyl)phenyl group is also more electron-demanding than the pentafluorophenyl group and therefore should be suitable for shifting the tautomeric equilibrium towards the phosphinous acid. Bis[2,4-bis(trifluoromethyl)phenyl]phosphane oxide (**3**) is accessible on a multigram scale by a known protocol starting from 1,3-bis(trifluoromethyl)benzene.^[8] The reaction of 1,3-bis(trifluoromethyl)benzene with *n*-butyllithium in the absence of auxiliary li-



Scheme 2. Reaction of dichloro(diethylamino)phosphane with lithiated 1,3-bis(trifluoromethyl)benzene, P–N bond cleavage to the intermediate chlorophosphane, and its eventual hydrolysis to bis[2,4-bis(trifluoromethyl)phenyl]phosphane oxide (**3**).

gands, such as TMEDA, resulted in the formation of a mixture of 2,4- and 2,6-bis(trifluoromethyl)phenyllithium (Scheme 2).^[8–12] For a selective synthesis of bis[2,4-bis(trifluoromethyl)phenyl]phosphane derivatives we utilized the steric demand of the diethylamino group to discriminate between the two aryllithiums.^[8] In keeping with this, the reaction of dichloro(diethylamino)phosphane with an excess of 2,4- and 2,6-bis(trifluoromethyl)phenyllithium led to the selective formation of the aminophosphane. Cleavage of the P–N bond in a chloroform/conc. hydrochloric acid mixture afforded the corresponding diarylchlorophosphane. Surprisingly, no hydrolysis to the corresponding secondary phosphane oxide **3** was observed under these conditions, contrary to the hydrolysis of the corresponding diphenyl-, bis(pentafluorophenyl)-, and bis(*p*-tetrafluoropyridyl)chlorophosphanes, $R_2\text{P}\text{Cl}$, which hydrolyze under comparable conditions to the corresponding secondary phosphane oxides, $R_2\text{P}(\text{O})\text{H}$.

However, the reaction of a THF solution of [2,4-(CF_3)₂ C_6H_3]₂ PCl with water readily afforded the corresponding phosphane oxide [2,4-(CF_3)₂ C_6H_3]₂ $\text{P}(\text{O})\text{H}$ (**3**) in 87% yield after recrystallization from CH_2Cl_2 solution. The structure of **3** was determined by X-ray diffraction analysis (Figure 1). The colorless [2,4-(CF_3)₂ C_6H_3]₂ $\text{P}(\text{O})\text{H}$ (**3**) crystallizes in the monoclinic space group $C2/c$ (No. 15). The P–O distance of 148.5(1) pm is typical for a P=O double bond and proves the existence of the phosphane oxide isomer in the solid state. H1 was refined isotropically.

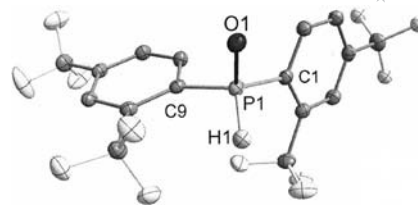


Figure 1. Molecular structure of bis[2,4-bis(trifluoromethyl)phenyl]phosphane oxide (**3**) (ellipsoids are drawn at 50% probability level; all C-bonded hydrogen atoms have been omitted for clarity). Selected bond lengths [pm] and angles [°]: P1–O1 148.5(1), P1–C1 181.7(2), P1–H1 1.29(2), P1–C9 182.3(2), C1–P–C9 106.0(1).

In the solid state, compound **3** exists as the oxide tautomer, whereas in solution a solvent-dependent equilibrium was observed analogous to the pentafluorophenyl- and *p*-tetrafluoropyridyl-substituted derivatives.

Figure 2 shows the ^{31}P NMR spectra of a mixture of [2,4-(CF_3)₂ C_6H_3]₂ $\text{P}(\text{O})\text{H}$ (**3**) and the phosphinous acid [2,4-(CF_3)₂ C_6H_3]₂ $\text{P}\text{--OH}$ (**3a**) in $[\text{D}_6]\text{DMSO}$. The resonance of the phosphinous acid **3a** is observed at $\delta = 77.3$ ppm as a doublet of septets with couplings $^3J(\text{P},\text{H})$ and $^4J(\text{P},\text{F})$ of 9 and 57 Hz, respectively. The resonance of the phosphane oxide isomer **3** is upfield-shifted by about 70 ppm and displays the expected $^1J(\text{P},\text{H})$ coupling of 561 Hz (Figure 2, bottom). The $^4J(\text{P},\text{F})$ coupling of the trivalent phosphorus derivative with bis(trifluoromethyl)phenyl substituents decreases significantly on going to the pentavalent phosphane

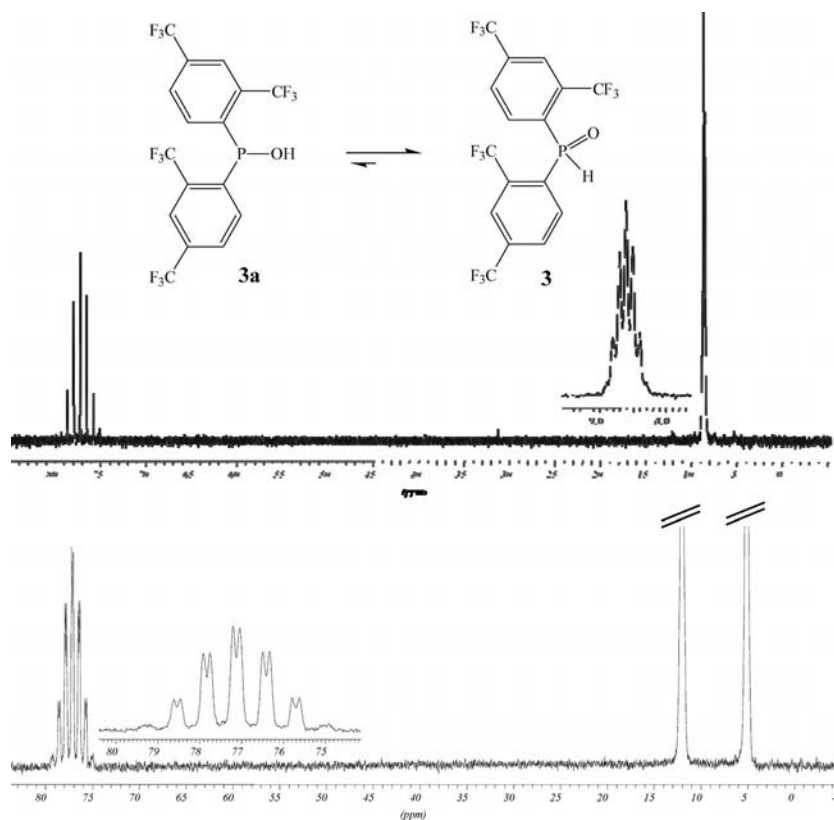


Figure 2. $^{31}\text{P}\{^1\text{H}\}$ NMR (top) and ^{31}P NMR (bottom) spectra of the tautomeric phosphane oxide **3** and the corresponding phosphinous acid **3a** in $[\text{D}_6]\text{DMSO}$ at room temp.

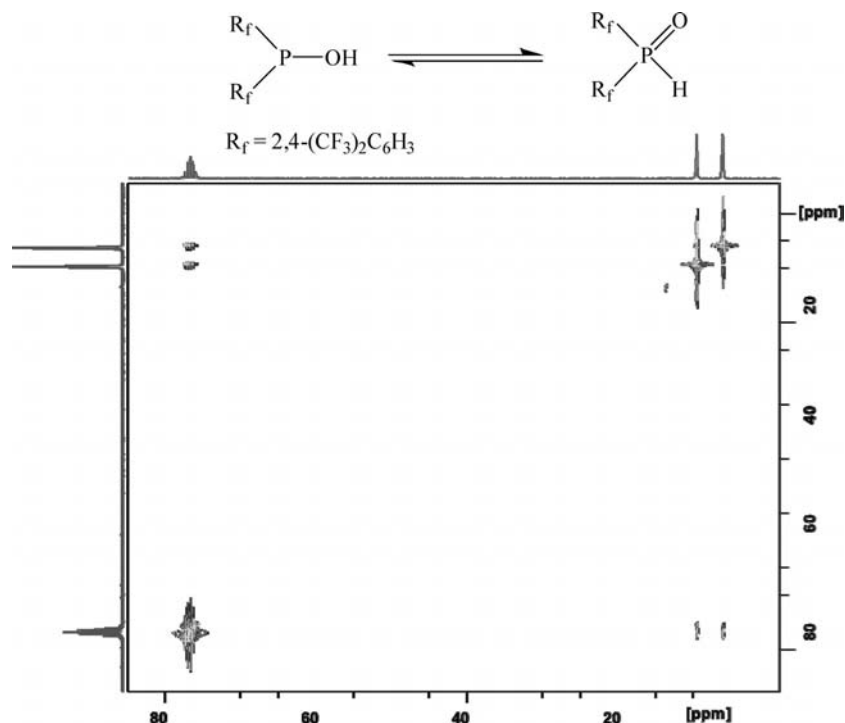


Figure 3. 2D ^{31}P EXSY NMR spectrum of bis[2,4-bis(trifluoromethyl)phenyl]phosphane oxide (**3**) in $[\text{D}_6]\text{DMSO}$ at room temp.

oxide derivative with a $^4J(\text{P},\text{F})$ coupling of only 8 Hz (Figure 2). To prove the dynamic nature of the exchange process between the phosphinous acid and phosphane oxide tautomer a two-dimensional ^{31}P EXSY NMR spectrum was recorded. The observation of cross peaks between the resonances of the phosphinous acid and the oxide isomer proves the tautomeric nature in DMSO solution (Figure 3).

Interestingly, in the equilibrium between **3** and **3a** in DMSO solution, only 31% of the phosphinous acid isomer was detected. This value is unexpectedly low in comparison with the pentafluorophenyl- and tetrafluoropyridyl-substituted derivatives. Only in an extremely donating solvent, such as HMPA (hexamethylphosphoramide), does the amount of acid tautomer **3a** exceed the amount of the corresponding phosphane oxide **3** (Table 1). The relative proportion of the acid tautomer with 2,4- $(\text{CF}_3)_2\text{C}_6\text{H}_3$ groups

in all the investigated solvents is significantly lower than those featuring C_6F_5 or C_5NF_4 groups (Table 1).

The relative proportion of the phosphinous acid tautomer decreases along the series tetrafluoropyridyl, pentafluorophenyl, and 2,4-bis(trifluoromethyl)phenyl. This observation contrasts with the estimated electron-withdrawing effects of the chosen aryl groups. As the electronic effects of C_5NF_4 and 2,4- $(\text{CF}_3)_2\text{C}_6\text{H}_3$ are comparable, the stabilization of the corresponding phosphinous acid tautomers and consequently the relative proportions of **2a** and **3a** should also be comparable. Quantum chemical calculations support these experimental findings. The C_5NF_4 -substituted phosphinous acid **2a** is 10.5 kJ/mol lower in energy than the corresponding phosphane oxide **2**, whereas the pentafluorophenyl derivatives **1a** and **1** have similar energies (cf. Table 1).^[3] In contrast, with the 2,4-bis(trifluorometh-

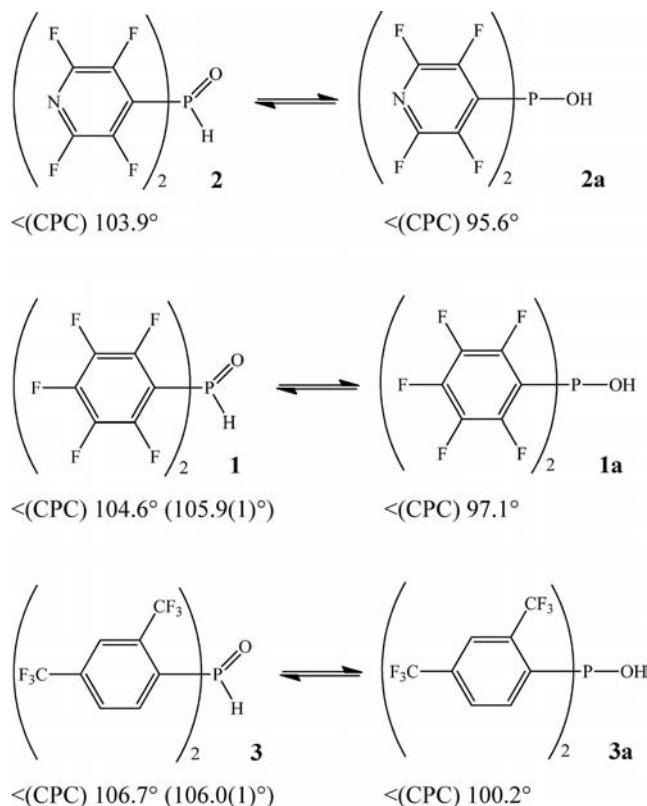
Table 1. Dependence of the amounts of phosphinous acid tautomers **1a**, **2a**, and **3a** on the chosen solvent.^[a]

Solvent	$(\text{C}_5\text{NF}_4)_2\text{P}-\text{OH}$ (2a)	$(\text{C}_6\text{F}_5)_2\text{P}-\text{OH}$ (1a) ^[b]	$[2,4-(\text{CF}_3)_2\text{C}_6\text{H}_3]_2\text{P}-\text{OH}$ (3a)	DN ^[c]
$E_{\text{ZP}}(\text{acid}) - E_{\text{ZP}}(\text{oxide})$ ^[d]	−10.5	−1.7	19.6	
Chloroform	21	0	0	—
Toluene	46	0	0	—
Acetonitrile	78	0	0	14.1
THF	99	55	10	20.0
Diethyl ether	100	60	10	19.2
DMF	100	67	20	24.0
DMSO	n.p.	76	31	29.8
Pyridine	(100)	(80)	36	33.1
NMP	n.p.	90 ^[e]	41	27.3
HMPA	n.p.	n.p.	95	38.8

[a] Percentage distribution from the integration of the ^{31}P NMR resonances; n.p. = not performed [b] Values of $(\text{F}_6\text{F}_5)_2\text{P}-\text{OH}$ are literature-known.^[3] [c] DN = solvent donicity (see ref.^[5]). [d] Calculations were performed at the B3LYP/6-311G(2d,p) level of theory. [e] Recent work.

yl)phenyl groups, the phosphane oxide **3** is stabilized by 19.6 kJ/mol. Thus, the experimental findings as well as the theoretical results underline that the stabilization of phosphinous acids is not only a function of the electronic nature of the aryl substituents but is also equally governed by steric effects.

As predicted from the Lewis structures, DFT calculations confirmed that phosphinous acids exhibit smaller C–P–C angles than the corresponding phosphane oxide isomers (Scheme 3). This leads to the assumption that sterically demanding groups cause a destabilization of the phosphinous acid form.



Scheme 3. Experimental (in brackets) and calculated [B3LYP/6-311G(2d,p)] C–P–C angles of the diarylphosphane oxides **1–3** and the corresponding phosphinous acids **1a–3a**.

To gain a closer insight into the relative energies of the phosphinous acids and their phosphane oxide tautomers, a relaxed potential energy scan was performed by varying the H–P–H angle in the phosphinous acid, $\text{H}_2\text{P–OH}$, and the phosphane oxide, H_3PO . As depicted in Figure 4, for H–P–H angles below 95° the phosphinous acid isomer is energetically favored, whereas H–P–H angles larger than 95° stabilize the phosphane oxide isomer. Further increasing the H–P–H angle leads to an increase in the energy gap between the phosphane oxide structure and the phosphinous acid isomer.

With the optimized H–P–H angles, the phosphane oxide H_3PO is, at the B3LYP/6-311G(3d,p) level of theory, stabilized by 4.3 kJ/mol with respect to the phosphinous acid tautomer $\text{H}_2\text{P–OH}$. Complete basis set extrapolations em-

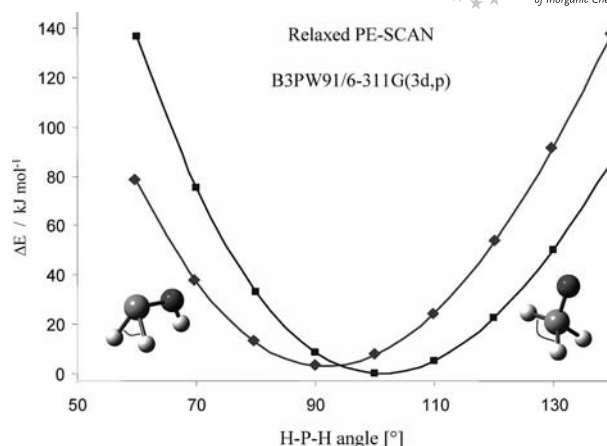


Figure 4. Dependence of the potential energies of $\text{H}_2\text{P–OH}$ and H_3PO on the H–P–H angle [relaxed potential energy scan at the B3PW91/6-311G(3d,p) level of theory].

ploying the coupled-cluster series gave a comparable value.^[13] In solution, the energy gap is significantly larger.^[13] Recently, Peruzzini and co-workers succeeded in generating the phosphane oxide H_3PO in solution by electrochemical methods.^[14] The phosphinous acid tautomer could be trapped by coordination to ruthenium complexes.

Conclusions

Based on DFT calculations, the *p*-tetrafluoropyridyl and 2,4-bis(trifluoromethyl)phenyl groups are more electron-demanding than the pentafluorophenyl ring, which should stabilize the phosphinous acid isomer. The introduction of the *p*-tetrafluoropyridyl group led, as expected, to a shift in the equilibrium towards the phosphinous acid in comparison to the weaker electron-withdrawing pentafluorophenyl group.

The experimental and theoretical investigations of the tautomerism of bis[2,4-bis(trifluoromethyl)phenyl]phosphane oxide, however, indicate that steric effects also influence the tautomeric equilibrium. Thus, the increased spatial demand of the 2,4-bis(trifluoromethyl)phenyl substituent leads to a widened C–P–C angle and therefore to a destabilization of the acid isomer ($\text{R}_2\text{P–OH}$).

Experimental Section

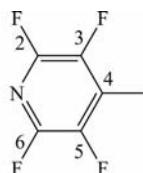
General: Dichloro(diethylamino)phosphane was prepared according to the procedure of Burg and Slota by treating PCl_3 with 2 equiv. of HNEt_2 in hexane solution.^[15] All other chemicals were obtained from commercial sources and used without further purification. Standard high-vacuum techniques were employed throughout the work. Nonvolatile compounds were handled under dry N_2 using Schlenk techniques.

NMR spectra were recorded with a Bruker Model Avance III 300 spectrometer (^3P NMR: 111.92 MHz; ^{19}F NMR: 282.40 MHz; ^{13}C NMR: 75.47 MHz; ^1H NMR: 300.13 MHz) with positive shifts being downfield from the external standards [85% orthophosphoric

acid (^{31}P), CCl_3F (^{19}F), and TMS (^1H)). EI mass spectra were recorded with a Finnigan MAT 95 spectrometer (20 eV). Intensities are referenced to the most intense peak within a spectrum. Isotope patterns for comparison were calculated with the program IsoPro.^[16]

Melting and visible decomposition points were determined by using a HWS Mainz 2000 apparatus. C, H, and N analyses were carried out with a HEKAtech Euro EA 3000 apparatus.

Bis(tetrafluoropyridyl)(diethylamino)phosphane: At -78°C , a 1.6 M *n*-butyllithium solution (29.0 mL, 46.4 mmol) in hexane was added to a solution of *p*-tetrafluoropyridine (6.8 g, 45.1 mmol) in diethyl ether (170 mL). After stirring the reaction mixture for 1 h at -78°C , the temperature was raised to -30°C for 15 min to complete the reaction. After cooling to -78°C , dichloro(diethylamino)phosphane (3.9 g, 22.4 mmol) in diethyl ether (15 mL) was added. The mixture was warmed to room temperature and the precipitates were removed by filtration. After evaporation of the solvent, the product was obtained by vacuum distillation at 98°C as a yellow liquid in 88% yield (8.1 g, 19.9 mmol). ^1H NMR (300.13 MHz, CDCl_3): δ = 3.20 [dq, $^3J(\text{P,H})$ = 11, $^3J(\text{H,H})$ = 7 Hz, 4 H, CH_2], 1.00 [t, $^3J(\text{H,H})$ = 7 Hz, 6 H, CH_3] ppm. ^{13}C NMR (CDCl_3 , 75.47 MHz): δ = 143.4 [dm, $^1J(\text{C,F})$ = 249 Hz, C-2, C-6], 141.2 [dm, $^1J(\text{C,F})$ = 256 Hz, C-3, C-5], 132.0 [dt, $^1J(\text{P,C})$ = 46, $^{2/3}J(\text{F,C})$ = 20/3 Hz, C-4], 47.4 [tdq, $^1J(\text{C,H})$ = 136, $^2J(\text{P,C})$ = 18, $^2J(\text{C,H})$ = 4 Hz, CH_2], 14.0 [qdt, $^1J(\text{C,H})$ = 126, $^2J(\text{P,C})$ = 4, $^2J(\text{C,H})$ = 3 Hz, CH_3] ppm. ^{19}F NMR (282.40 MHz, CDCl_3): δ = -136.1 (m, 3-F, 5-F), -90.5 (m, 2-F, 6-F) ppm. ^{31}P NMR (111.92 MHz, CDCl_3): δ = 21.2 [quint-quint (tridec), $^3J(\text{P,F})$ = 22, $^3J(\text{P,H})$ = 11 Hz] ppm. MS (EI, 20 eV): m/z (%) = 404 (41) $[(\text{C}_5\text{NF}_4)_2\text{PNHET}_2]^+$, 389 (100) $[(\text{C}_5\text{NF}_4)_2\text{PNHETMe}]^+$, 361 (13) $[(\text{C}_5\text{NF}_4)_2\text{PNMe}]^+$, 332 (4) $[(\text{C}_5\text{NF}_4)_2\text{P}]^+$, 240 (14) $[(\text{C}_5\text{NF}_4)\text{PNEtMe}]^+$. $\text{C}_{14}\text{H}_{10}\text{F}_8\text{N}_3\text{P}$ (403.2): calcd. C 41.70, H 2.49, N 10.42; found C 42.18, H 2.24, N 10.62.



Bis(tetrafluoropyridyl)phosphane Oxide (2): Bis(tetrafluoropyridyl)aminophosphane (2.11 g, 12.0 mmol) was dissolved in toluene (15 mL) and extracted three times with conc. hydrochloric acid (15 mL) at 0°C . The solvent of the resulting organic phase was removed in vacuo to yield 1.27 g (70%, 8.4 mmol) of bis(tetrafluoropyridyl)phosphane oxide (2) as a colorless solid (m.p. 94°C).

NMR spectroscopic data for $(\text{C}_5\text{NF}_4)_2\text{P}(\text{O})\text{H}$ in CD_3CN : ^1H NMR (300.13 MHz, CD_3CN): δ = 8.90 [d, $^1J(\text{P,H})$ = 605 Hz, $(\text{C}_5\text{NF}_4)_2\text{P}(\text{O})\text{H}$] ppm. $^{13}\text{C}\{^{19}\text{F}\}$ NMR (CD_3CN , 75.47 MHz): δ = 121.8 [dd, $^1J(\text{P,C})$ = 91, $^2J(\text{C,H})$ = 13 Hz, C-4] ppm. ^{13}C NMR (CD_3CN , 100 MHz): δ = 142.5 [m, $^1J(\text{C,F})$ \approx 250 Hz, C-3, C-5], 143.5 [m, $^1J(\text{C,F})$ \approx 250 Hz, C-2, C-6] ppm. ^{19}F NMR (282.40 MHz, CD_3CN): δ = -136.7 (m, 3-F, 5-F), -90.6 (m, 2-F, 6-F) ppm. ^{31}P NMR (111.92 MHz, CD_3CN): δ = -19.9 [d, $^1J(\text{P,H})$ = 605 Hz, $(\text{C}_5\text{NF}_4)_2\text{P}(\text{O})\text{H}$] ppm.

NMR spectroscopic data for $(\text{C}_5\text{NF}_4)_2\text{P}-\text{OH}$ in CD_3CN : ^1H NMR (300.13 MHz, CD_3CN): δ = 6.60 [s, $(\text{C}_5\text{NF}_4)_2\text{P}-\text{OH}$] ppm. $^{13}\text{C}\{^{19}\text{F}\}$ NMR (CD_3CN , 75.47 MHz): δ = 133.0 [d, $^1J(\text{P,C})$ = 48 Hz, C-4] ppm. ^{13}C NMR (CD_3CN , 75.47 MHz): δ = 141.7 [dm, $^1J(\text{C,F})$ = 256, $^2J(\text{P,C})$ = 12 Hz, C-3, C-5], 143.3 [dm, $^1J(\text{C,F})$ = 246 Hz, C-2, C-6] ppm. ^{19}F NMR (282.40 MHz, CD_3CN): δ = -137.4 (m,

3-F, 5-F), -93.6 (m, 2-F, 6-F) ppm. ^{31}P NMR (111.92 MHz, CD_3CN): δ = 69.9 [quint, $^3J(\text{P,F})$ = 28 Hz, $(\text{C}_5\text{NF}_4)_2\text{P}-\text{OH}$] ppm.

MS (EI, 20 eV): m/z (%) = 348 (100) $[(\text{C}_5\text{NF}_4)_2\text{POH}]^+$, 332 (4) $[(\text{C}_5\text{NF}_4)_2\text{PH}]^+$, 198 (23) $[(\text{C}_5\text{NF}_4)\text{POH}]^+$, 181 (2) $[(\text{C}_5\text{NF}_4)\text{P}]^+$, 151 (12) $[(\text{C}_5\text{NF}_4)\text{H}]^+$, 132 (6) $[(\text{C}_5\text{NF}_3)\text{H}]^+$. $\text{C}_{10}\text{HF}_8\text{N}_2\text{OP}$ (348.1): calcd. C 34.50, H 0.29, N 8.05; found C 34.39, H 0.24, N 7.86.

Solvent-Dependent Equilibria: The ^{31}P NMR spectroscopic investigations of the solvent-dependent equilibria were carried out with 150 mg of each phosphane oxide dissolved in 0.7 mL of the chosen solvent in an NMR tube. The measurements were repeated on two consecutive days to observe possible changes in the integrals.

X-ray Structure Determination: The crystal data for **3** were collected with a Bruker Nonius-Kappa CCD diffractometer using graphite-monochromated $\text{Mo}-K_\alpha$ radiation (71.073 pm). The structure was solved by direct methods and refined by full-matrix least-square cycles (programs SHELXS-97 and SHELXL-97).^[17] Details of the crystallographic measurements can be found in Table 2.

Table 2. Crystal data and refinement characteristics for phosphane oxide **3**.

	[2,4-(CF ₃) ₂ C ₆ H ₃] ₂ P(O)H (3)
Empirical formula	C ₁₆ H ₇ F ₁₂ OP
<i>a</i> [pm]	1985.0(1)
<i>b</i> [pm]	1823.1(1)
<i>c</i> [pm]	2871.7(1)
β [°]	93.06(1)
<i>V</i> [10 ⁶ pm ³]	10377.5(2)
<i>Z</i>	24
<i>D_x</i> [g cm ⁻³]	1.821
Crystal system	monoclinic
Space group	<i>C2/c</i> (No. 15)
Shape/color	column/colorless
Crystal size [mm ³]	0.30 × 0.30 × 0.26
<i>T</i> [K]	100(2)
θ range	3.04/30.00
Index range	$-27 \leq h \leq 27$ $-25 \leq k \leq 25$ $-40 \leq l \leq 40$
Total data collected	126453
Unique data	15098
Observed data (<i>I</i> > 2σ)	11347
μ [mm ⁻¹] (numerical)	0.289
<i>T_{min/max}</i>	0.9287/0.9184
Absorption correction	multi-scan
<i>R₁/wR₂</i> [<i>I</i> > 2σ(<i>I</i>)]	0.043/0.104
<i>R₁/wR₂</i> (all data)	0.064/0.115
Goodness of fit (<i>S_{all}</i>)	1.045
<i>R</i> (int.)/ <i>R</i> (σ)	0.046
$\Delta\rho_{\text{max./min.}}$ [10 ⁶ e pm ⁻³]	0.840/−0.624
<i>F</i> (000)	5616

CCDC-833430 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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