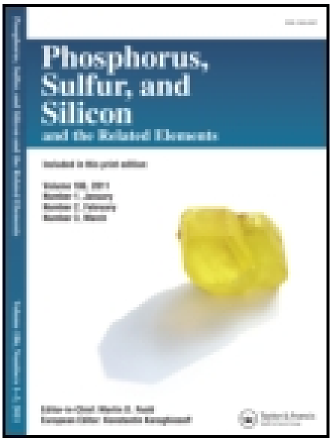

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Evidences for Chelating Complexes of Lithium with Phenylphosphinic and Phenylphosphonic Acids: A Spectroscopic and DFT Study

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EVIDENCES FOR CHELATING COMPLEXES OF LITHIUM WITH PHENYLPHOSPHINIC AND PHENYLPHOSPHONIC ACIDS: A SPECTROSCOPIC AND DFT STUDY

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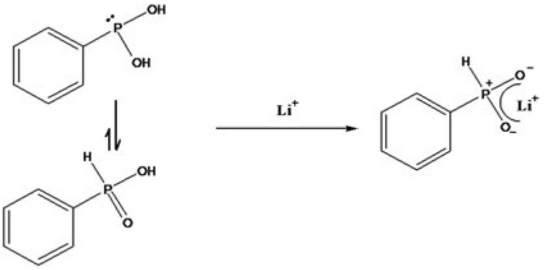
GRAPHICAL ABSTRACT



Abstract *Lithium complexes were prepared with phenylphosphinic and phenylphosphonic acids. The complexes were studied in the solid state using Fourier transform infrared spectroscopy spectroscopy and in solution (methanol) using ^{1}H, ^{13}C, and ^{31}P Nuclear magnetic resonance spectroscopy (NMR) spectroscopy; the most preferred structures of the complexes were determined by density functional theory (DFT) computational method. Although methanol has a strong solvation effect on lithium ions and ligands, which causes dissociation of the complexes, significant changes of the NMR spectra of the complexes (relative to those of the free ligands) were observed. The new spectroscopic results indicate the presence of the phenylphosphinic acid tautomer (**I**: $C_6H_5PH(=O)OH$) rather than that of phenyl-phosphorous acid (**II**: $C_6H_5P(OH)_2$) in deuterated methanol showing PH/PD exchange. On the other hand, tautomer **I** predominates in the complex with lithium without showing PH/PD exchange. The DFT*

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*calculations predict that tautomer **I** is the preferred structure in the case of free ligand and lithium complex. The absence of a PH/PD exchange in the complex is due to the formation of a chelating complex, rather than of a simple salt between lithium ion and the two oxygen atoms of **I**, which prevent tautomerization of **I** into **II**. DFT calculations support the formation of lithium chelating complexes. The lithium ion was found to affect the spectroscopic properties of phenylphosphinic acid more dramatically than those of phenylphosphonic acid.*

Keywords Lithium; chelating complexes; phenylphosphonic acid; phenylphosphinic acid; ^{31}P NMR; FTIR; DFT calculations

INTRODUCTION

Metal phosphonates are a class of hybrid inorganic–organic compounds in which the metal coordinates with phosphonate functional group.[1] Recently, metal organophosphonates have attracted great interest because of their potential applications as ion-exchangers, sensors, or catalysts and due to their intriguing host intercalation chemistry.[2]

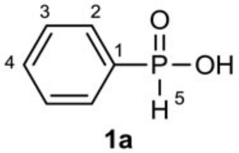
The first study of alkali metal organophosphonates was reported by Rao and Vidyasagar[3] in 2005. They reported the X-ray structures of one-dimensional alkali metal phenyl-phosphonates, which were found to have the formula $M(HO_3PC_6H_5)(H_2O_3PC_6H_5)$, where M=Li, Na, K, Rb, and Cs.[3] The X-ray diffraction study of the complex of lithium with phenylphosphonic acid indicated that lithium is tetrahedrally coordinated by four phosphonate moieties forming one-dimensional chain of $Li(HO_3PC_6H_5)(H_2O_3PC_6H_5)$, with the hydrogen bonding holding the chains together.[3]

However, the first study of alkaline earth metal organophosphonates dates back to 1979, when magnesium phenylphosphonate corresponding to the formula $MgC_6H_5PO_3$ H_2O was reported.[2] Among other alkaline earth metal phenylphosphonates the structures of the calcium, barium, and strontium salts were described. These compounds were found to have various metal/phosphorus ratios depending on the acidity of the reaction medium.[4,5] The powder X-ray patterns indicated that these compounds are layered.[5] Studies on alkali and alkaline earth metal phenylphosphinates are very rare in the literature. Phenylphosphinate complex of lithium was employed as a soil disinfectant; however, there is no detailed investigation of the structure of this compound.[6]

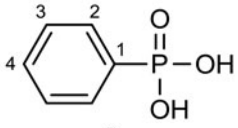
The phosphonate dianion RPO_3^{2-} has a promising structure capable to form units for the self-assembly of polynuclear complexes.[7] Polynuclear transition metal phosphonates have attracted attention because of their ion-exchange and adsorption ability and their proton conductivity, which makes these compounds useful in photochemistry, electro-optics, and catalysis. Several transition metal phenylphosphonates were prepared.[1,8–12] Burkovskaya et al.[7] reported the X-ray structure of decanuclear phenylphosphonate bridged Co(II) complexes. Furthermore, Wang et al.[8] reported a single chain cobalt phenylphosphonate complex $[Co(phen)(4,4'\text{-}bpy)(C_6H_5PO_3H)_2]_n$ 0.5 H_2O (phen=1,10-phenanthroline, 4,4′-bpy=4,4′-bipyridine). Supramolecular copper(II) phenyl-phosphonate complexes, e.g., $[Cu(II)(phen)Cl][C_6H_5PO(OH)_2)((OH)O_2PC_6H_5)]$, were also reported.[12] The structure of trimethyltin(IV) derivatives of phenylphosphonic acid was found to consist of infinite polymeric one- or two-dimensional networks depending on reaction conditions.[13]

The solid-state chemistry of phenylphosphonates constitutes a significant part of this research area, and to the best of our knowledge there are no studies of metal phosphonates in solutions. The aim of the present work is to investigate the nature of interaction between lithium and phenylphosphinic (**1a**) and phenylphosphonic acid (**2a**) in their complexes in the solid state using Fourier transform infrared spectroscopy (FTIR), and in solution using

^{1}H, ^{31}C, and ^{31}P nu**clear magnetic resonance** (NMR) spectroscopy, as well as by density functional theory (DFT) computational techniques.



1a



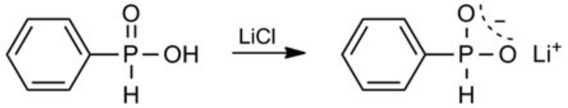
2a

RESULTS AND DISCUSSION

IR Absorption Spectra

The IR spectra of phenylphosphinic acid ligand **1a** and its lithium complex **1** are shown in Figure 1; the IR data are summarized in Table 1. The broad band at 2100–2800 cm^{-1} in the spectrum of the ligand was assigned to ν(O—H) of the hydrogen bonded hydroxy group. This band disappeared upon complexation with lithium. A sharp strong band at 2345 cm^{-1}, assigned to ν(P—H), is observed in the spectrum of the complex. The P—H vibration was reported to cause a weak band at 2408 cm^{-1} in the case of 2,4,6-trimethyl-phenylphosphinic acid.[14] Furthermore, the band at 1676 and 1589 cm^{-1} in the spectrum of the ligand **1a**, assigned to δ(O—H), disappeared upon complexation with lithium. All these observations support the suggestion that the proton of the hydroxy group was replaced by Li$^+$. The bands at 1199, 1152, and 1102 cm^{-1} in the ligand, which were assigned to ν(O—P=O), were shifted to lower frequency upon complexation with Li$^+$. This is due to the decrease of bond order of O—P=O bands in the complexes because of the delocalization of the electrons of the double bond over two P—O bonds (Scheme 1).

The infrared spectra of phenylphosphonic acid ligand **2a** and its lithium complex **2** are shown in Figure 2; the IR data are summarized in Table 1. The IR characteristics of complex **2** strictly differ from those of complex **1**. The broad band at 3300–2200 cm^{-1} in the spectrum of ligand, which was assigned to ν(O—H) (hydrogen bonded hydroxy group), remained broad upon complexation with lithium. The band assigned to δ(O—H) at 1593 cm^{-1} in the spectrum of ligand shifted to higher frequency upon complexation with lithium. Furthermore, the bands assigned to ν(O—P=O) at 1221, 1145, 1080, 1016, and 940 cm^{-1} in the spectrum of ligand **2a** were shifted to higher frequency upon complexation with Li$^+$ due to the strong hydrogen bonding of PO_3H in complex **2**, which is further supported by the broad band at about 2800–2200 cm^{-1}.[2,4] The FTIR study of complex **2** is consistent with the reported[3] X-ray structure of complex $(Li(HO_3PC_6H_5)$à$(H_2O_3PC_6H_5))$ (**2**), where hydrogen bonding plays an important role in connecting the chains of lithium cations and phenylphosphonate anions together.



Scheme 1

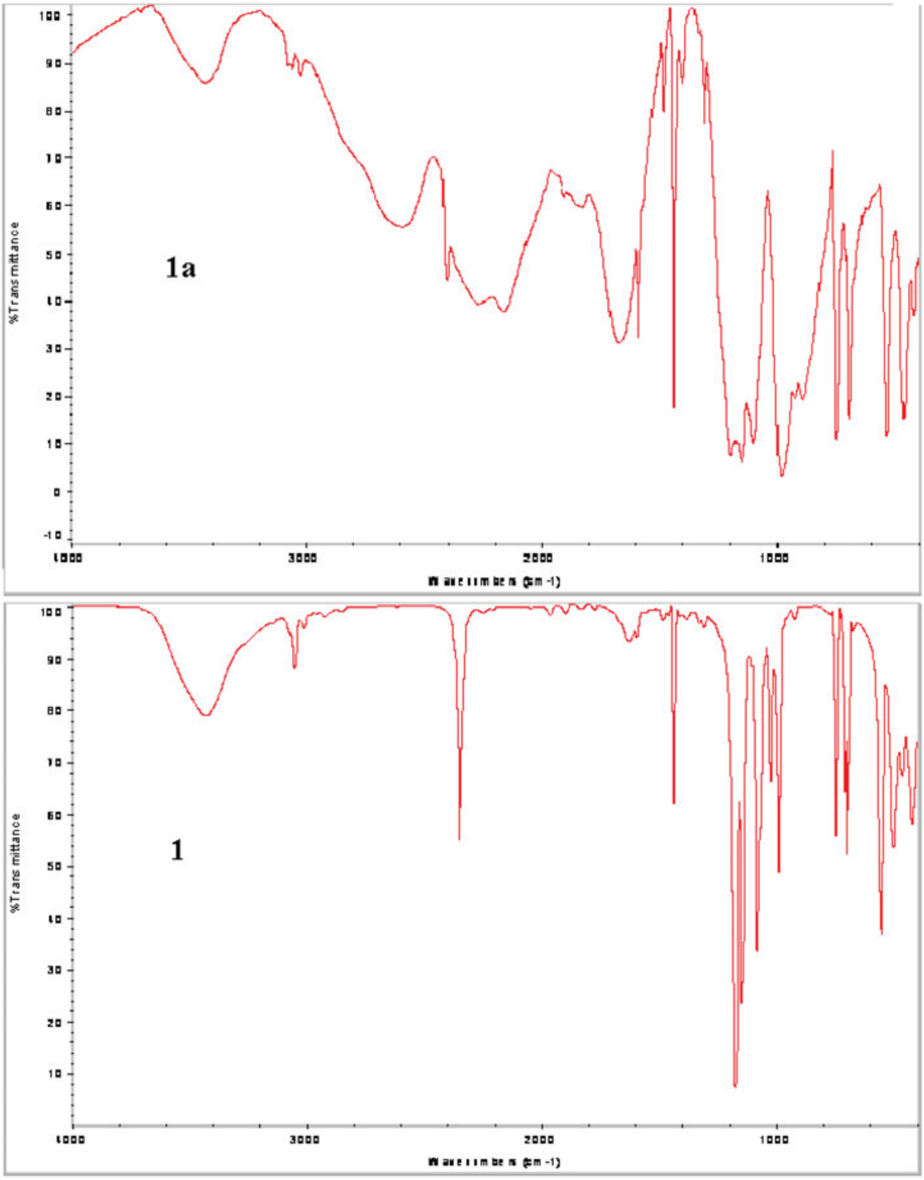


Figure 1 FTIR spectra of **1a** and its complex with lithium **1**. (Color figure available online).

NMR Spectra

The ^{1}H, ^{13}C, and ^{31}P NMR spectra of complexes **1** and **2** were investigated and the chemical shifts and coupling constants (J_{HH}, J_{PC}, and J_{PH}) were analyzed and compared with those of the corresponding ligands. Although methanol has a strong solvation effect on lithium ions and ligands, which causes dissociation of complexes, significant changes in the NMR spectra of the complexes (relative to those of free ligands) were observed. This

Table 1 IR spectral data of ligand **1a** and its complex **1** and ligand **2a** and its complex **2**

	Absorption bands (cm^{-1})			
Assignments*	**1a**	**1**	**2a**	**2**
ν(C—H)	3078 (w) 3072 (w)	3047, 3003 (w)	—	3052 (w)
ν(O—H)	2800–2100 (br)	—	2200–3300 (br)	2200–3200 (br)
ν(P—H)	—	2345 (s)	—	—
δ(OH)	1676 (br), 1589 (s)	—	1593 (m)	1628 (br)
ν(C=C)	1440 (s)	1433 (s)	1439 (s)	1437 (s)
ν(O—P=O)	1199 (s), 1152 (s), 1102 (s)	1175 (s), 1147 (s), 1084 (s)	1221(s), 1145 (s), 1080 (s), 1016 (s), 940 (s)	1285 (m), 1165 (s), 1059 (s), 1024 (m)
δ(O—P=O)	533 (s), 463 (m), 422 (m)	553 (s), 501 (m), 464 (m), 422 (m)	550 (s), 521 (m), 488 (m), 420 (m)	589 (s), 543 (m), 512 (m), 461 (m)

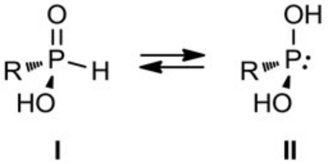
*Assignments were made according to references 2, 4, 15, 17, 18.

reflects the presence of strong interactions between lithium ions and phenylphosphinic and phenylphosphonic acids.

^{1}H NMR Spectra

The ^{1}H NMR chemical shifts and the $^1J_{PH}$ coupling constant of ligand **1a** and its lithium complex **1** are presented in Table 2; the ^{1}H NMR spectra are shown in Figure 3. The chemical shifts of the *ortho*, *meta*, and *para* protons of ligand **(1a)** were assigned to the peaks at 7.75–7.82, 7.52–7.57, and 7.61–7.64 ppm, respectively. The chemical shift values follow the following order: *ortho* > *para* > *meta*, which is consistent with the resonance effect of the electron-withdrawing phosphinyl group. All peaks of the aromatic protons were shifted upfield upon complexation with Li^+. This is due to expected decrease of electron withdrawal strength of phosphinyl group on formation of Li^+ salt.

Phosphinic acid (**I**, R—PH(=O)OH) exists in equilibrium with the tautomer (**II**, R—P(OH)$_2$) (Scheme 2).[14,15] The doublet at 7.51 ppm with a value of $^1J_{PH} = 563$ Hz in the ^{1}H NMR spectrum of ligand **1a** was assigned to the proton attached to phosphorus. The intensity of this peak was very small compared with that of the peaks of phenyl protons ($\approx$2% of the expected value relative to the aromatic protons). If we take PH/PD exchange into consideration, then tautomer **I** may exist in the case of free ligand **1a** in methanol. However, resemblance between the signal patterns of aromatic protons of the experimental ^{1}H NMR spectrum of **1a** and that of calculated for tautomer **II** might indicate



Scheme 2 Tautomerization equilibrium in phosphinic acids.

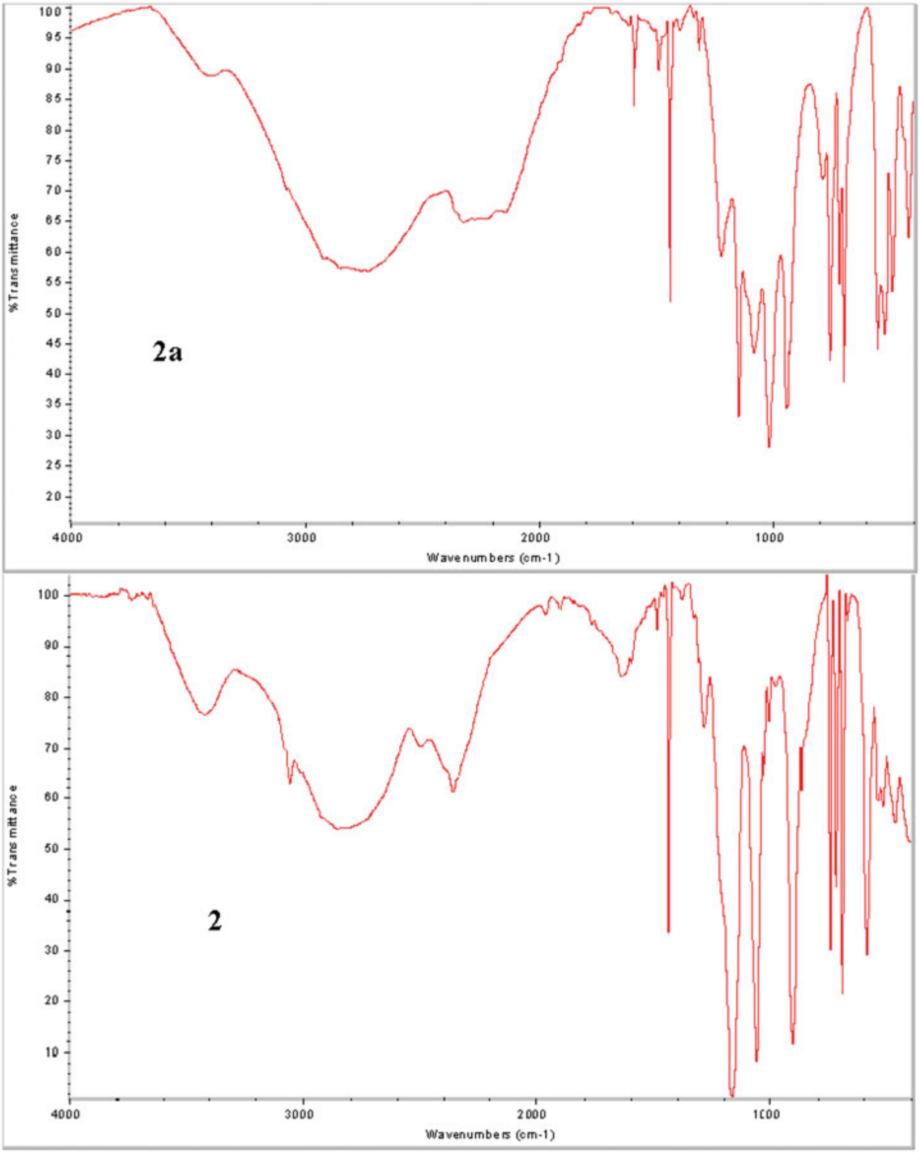


Figure 2 FTIR spectra of **2a** and its complex with lithium **2**. (Color figure available online).

the predominance of tautomer **II** (Figure 3). Orthaber et al.[14] detected only tautomer **I** in the case of 2,4,6-trimethylphenylphosphinic acid in d^6-acetone with $^1J_{PH} = 562$ Hz.

Upon complexation with Li$^+$, the chemical shift of P—H proton was not affected; the coupling constant $^1J_{PH}$ decreased to 511 Hz, however. More important, the integrated intensity of the signal increased to 27% of the expected value upon complexation with Li$^+$. Thus, tautomeric P—H form predominates in the lithium complex **1**. Resemblance between the signal pattern of the aromatic protons of the experimental ^{1}H NMR spectrum of **1** and that calculated for the P—H tautomer supported this finding (Figure 3). This is

Table 2 ^{1}H NMR chemical shifts (at 400.1 MHz, in ppm relative to TMS) and coupling constants (Hz) of ligands **1a** and **2a** and their complexes in CD_3OD

Assignment	**1a**	**1a** tautomer **I** calculated	**1a** tautomer **II** calculated	**1**	**2a**	**2a** calculated	**2**
H-2 (m, 1H) *o*-H	7.75–7.82	7.76–7.87	7.68–7.72	7.69–7.74	7.76–7.82	7.67–7.73	7.77–7.82
H-3 (m, 1H) *m*-H	7.52–7.57	7.47–7.53	7.22–7.26	7.41–7.45	7.44–7.49	7.39–7.43	7.33–7.35
H-4 (m, 1H) *p*-H	7.61–7.64		7.34–7.38		7.52–7.56	7.51–7.55	
P-H (d, 1H)	7.51 ($^1J_{PH}$ = 563 Hz)	5.7 ($^1J_{PH}$ = 320 Hz)		7.51 ($^1J_{PH}$ = 511 Hz)			

further supported by the observation found in the FTIR study described above, where a strong peak due to P—H stretching was observed in the case of the complex. The formation of a chelate complex between lithium ion and the two oxygen atoms of ligand **1a** prevents transfer of the hydrogen atom of P—H moiety to the oxygen atom of the carbonyl group and thus prevents PH/PD exchange with the deuterated solvent methanol. This indicates the formation of chelating complex rather than a simple salt between the lithium ion and the anion of **1a**.

The chemical shifts of different protons of ligand **2a** and its complex **2** as well as the $^1J_{PH}$ coupling constants are presented in Table 2; the corresponding ^{1}H NMR spectra

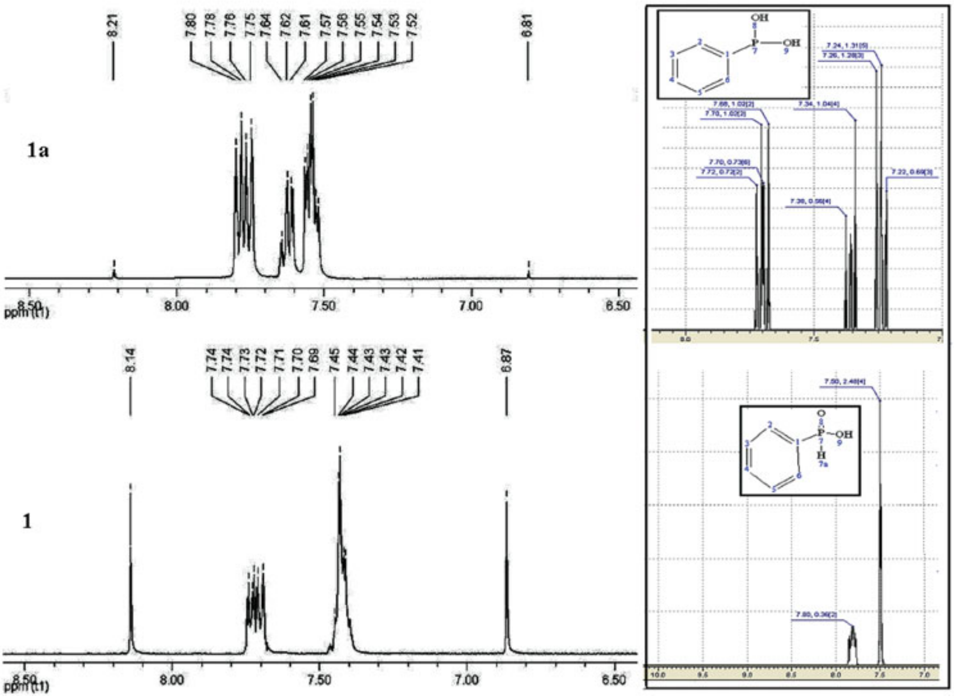


Figure 3 Left: Experimental ^{1}H NMR (at 400.1 MHz) spectra of **1a** and its complex with lithium **1** in CD_3OD. Chemical shifts are given in ppm relative to TMS. Right: Calculated ^{1}H NMR spectra for tautomer **I** and **II** in the aromatic region. (Color figure available online).

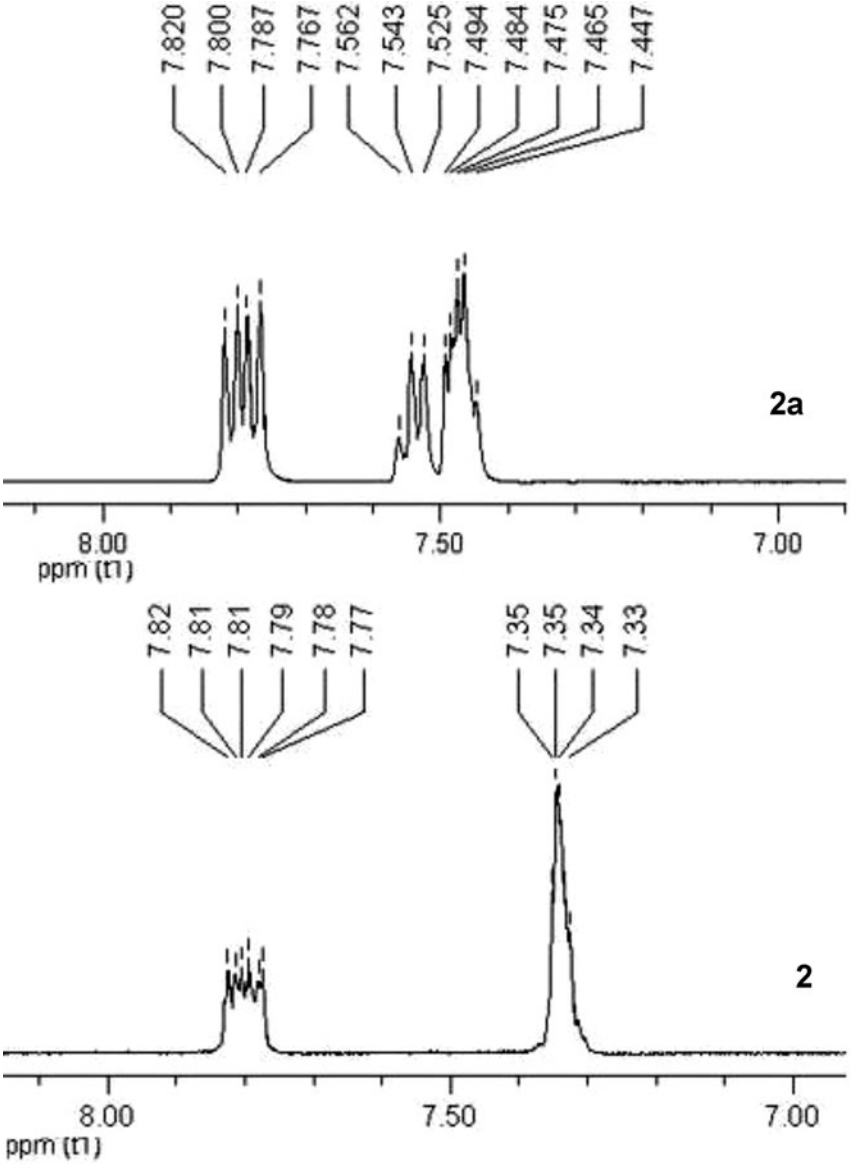


Figure 4 ^{1}H NMR spectra (at 400.1 MHz) of **2a** and its complex with lithium **2** in CD_3OD. Chemical shifts are given in ppm relative to TMS.

are shown in Figure 4. The chemical shifts of the *ortho*, *meta*, and *para* protons of **2a** were assigned to the peaks at 7.76–7.82, 7.44–7.49, and 7.52–7.56 ppm, respectively. The signals of the *meta* and *para* protons of ligand **2a** are shifted upfield upon complexation with Li^+, while the signals of the *ortho* protons are not affected. This may reflect a weaker interaction between cation and anion in **2a** as compared with **1a**.

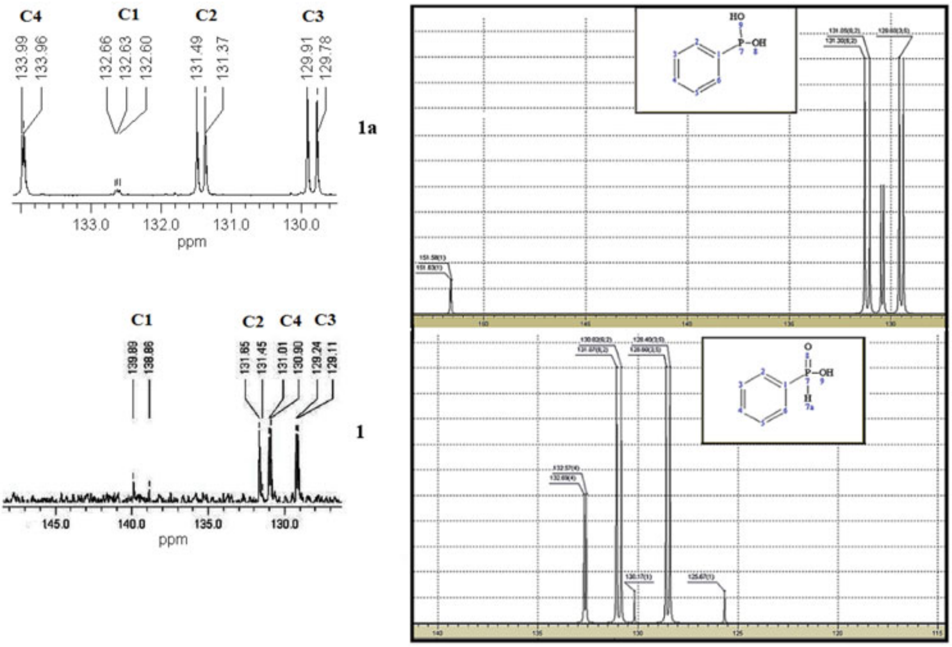


Figure 5 Left: Experimental $^{13}C\{^1H\}$ NMR spectra of **1a** and its complex with lithium **1** at 100.8 MHz in CD_3OD. Chemical shifts are given in ppm relative to TMS. Right: Calculated ^{13}C NMR spectra for tautomers **I** and **II**. (Color figure available online).

^{13}C NMR Spectra

The ^{13}C NMR spectra of ligand **1a** and its complex with Li^+ **1** are shown in Figure 5; the values of the chemical shifts for different carbon atoms are compiled in Table 3. All the signals of carbon atoms were observed as doublets due to coupling with the phosphorus atom. A doublet pattern observed for the ^{13}C NMR signals of the aromatic carbon atoms was also reported by Orthaber et al.[14] for 2,4,6-trimethyl-phenylphosphinic acid with $^1J_{PC} = 138$ Hz and $^2J_{PC} = 12$ Hz. As it is evident from Table 3, the coupling constant J_{PC}

Table 3 $^{13}C\{^1H\}$-NMR chemical shifts (at 100.8 MHz, ppm, relative to TMS) and coupling constants (Hz) of ligands **1a** and **2a** and their complexes **1** and **2** in CD_3OD

Carbon atom	**1a**	**1a** tautomer **I** calculated	**1a** tautomer **II** calculated	**1**	**2a**	**2a** calculated	**2**
C-1	132.6	127.9	151.6	139.4	132.9	137.8	—*
$^1J_{PC}$	3	181	2	103	185	181	
C-2	131.4	131.0	131.2	131.6	131.6	131.3	131.4
$^2J_{PC}$	12	10	10	20	10	10	9
C-3	129.9	128.5	129.5	129.2	129.1	128.0	128.2
$^3J_{PC}$	13	8	8	13	15	8	13
C-4	134.0	132.6	130.4	131.0	132.5	134.3	130.1
$^4J_{PC}$	3	5	5	11	3	5	3

*No peaks were detected.

Table 4 ^{31}P NMR chemical shifts (at 161.3 MHz, ppm, relative to 85% phosphoric acid) and coupling constants (Hz) of ligands **1a** and **2a** and their complexes **1** and **2** in CD_3OD

1a	2,4,6-trimethyl-phenylphosphinic acid in d^6-acetone[15]	2,3,5,6-tetrafluoro-phenylphosphinic acid in d^6-acetone[15]	**1**
47.4 (tt)	24.2	2.2 (initial doublet turns into triplet)	37.9 (dt)
47.8 (dt)			
$^1J_{PD} = 86$ Hz		$^1J_{PD} = 92$ Hz	
$^1J_{PH} = 572$ Hz	$^1J_{PH} = 562$ Hz	$^1J_{PH} = 630$ Hz	$^1J_{PH} = 510$ Hz
$^3J_{PH} = 14$ Hz			$^3J_{PH} = 13$ Hz
2a		**2**	
39.4 (t)		35.3 (t)	
$^3J_{PH} = 14$ Hz		$^3J_{PH} = 11$ Hz	

decreases as we move from C2 to C4. The comparison of the ^{13}C NMR spectrum of **1a** with those calculated for tautomers **I** and **II** does not confirm the existence of any of the two tautomers exclusively (Figure 5).

Resemblance between the ^{13}C NMR data of lithium phenylphosphinate **1** (139.4, $^1J_{PC} = 103$ Hz; 131.6, $^2J_{PC} = 20$ Hz; 129.2, $^3J_{PC} = 13$ Hz; 131.0, $^4J_{PC} = 11$ Hz) and those calculated for tautomer **I** (127.9, $^1J_{PC} = 181$ Hz; 131.0, $^2J_{PC} = 10$ Hz; 128.5, $^3J_{PC} = 8$ Hz; 132.6, $^4J_{PC} = 5$ Hz) indicates that most probably tautomer **I** predominates in the complex (Table 3 and Figure 5).

The ^{13}C NMR spectra of ligand **2a** and its complex **2** are shown in Figure 6. The values of the chemical shifts for different carbon atoms are given in Table 3. The chemical shifts of C2, C3, and C4 of ligand **2a** are shifted upfield upon complexation with Li^+ (Table 3).

^{31}P NMR Spectra

The chemical shifts and selected P,H coupling constants for ligands **1a** and **2a** and their lithium complexes **1** and **2** are presented in Table 4; the corresponding ^{31}P NMR spectra are shown in Figures 7 and 8.

The NMR signal of the phosphorus atom in ligand **1a** undergoes significant upfield shift upon complexation with Li^+ (9.5 ppm). In the case of ligand **1a** two signals are observed: a doublet of triplets and a much more intense triplet of triplets. These two signals indicate that phenylphosphinic acid undergoes PH/PD exchange with deuterated methanol. The 1:1:1 triplet results from the coupling of phosphorus with deuterium atom ($^1J_{PD} =$ 86 Hz). This value is comparable with $^1J_{PD} = 92$ Hz reported in the case of 2,3,5,6-tetrafluoro phenylphosphinic acid.[14] Each line of the 1:1:1 triplet is further split into a 1:2:1 triplet resulting from the coupling of phosphorus with the two aromatic *ortho* hydrogen atoms ($^3J_{PH} = 14$ Hz). The less intense doublet of triplets is caused by the coupling of the phosphorus atom with the directly attached hydrogen atom ($^1J_{PH} = 572$ Hz) and further coupling with the aromatic *ortho* hydrogen atoms ($^3J_{PH} = 14$ Hz). Thus, the triplet of triplets indicates significant PH/PD exchange in **1a**, while the doublet of triplets results from the molecules of **1a** with unexchanged P—H.

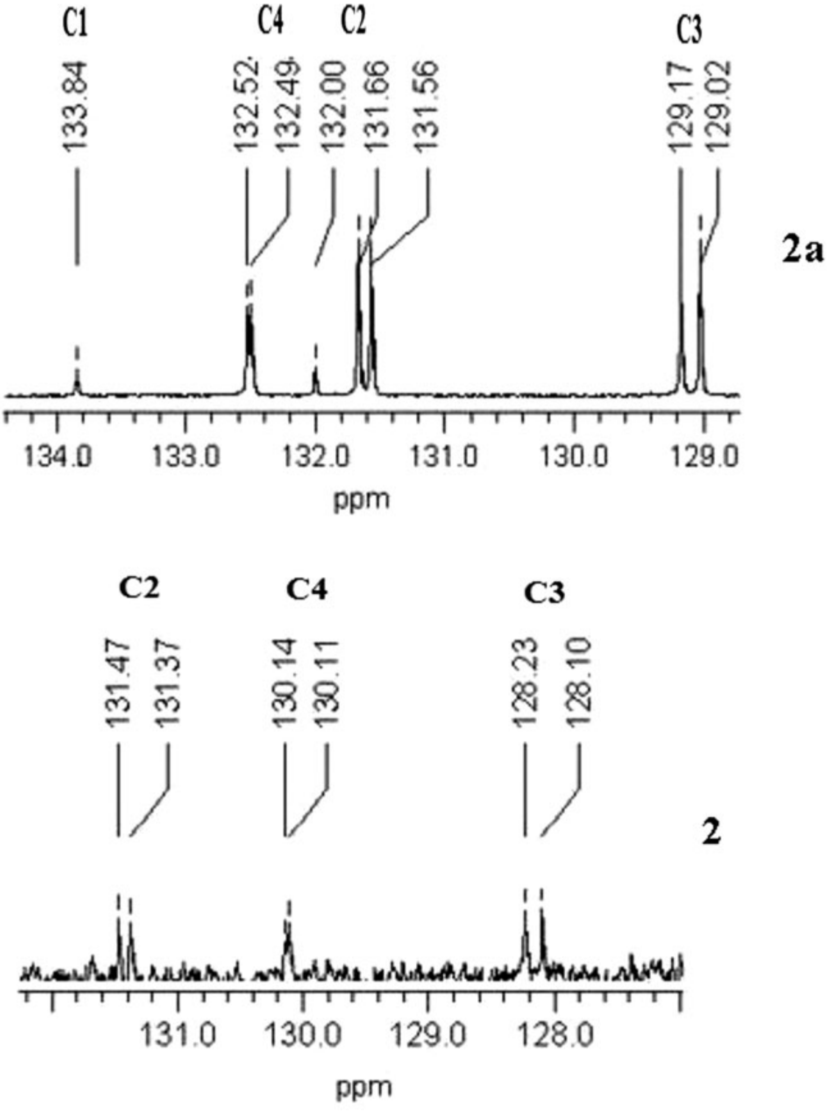


Figure 6 $^{13}C\{^{1}H\}$ NMR spectra of **2a** and its complex with lithium **2** at 100.8 MHz in CD_3OD. Chemical shifts are given in ppm relative to TMS.

On complexation of **1a** with Li^+, PH/PD exchange is suppressed due to preventing tautomerization of **I** to **II**. Thus, the coupling of phosphorus with the directly attached proton ($^{1}J_{PH} = 510$ Hz) and with both aromatic *ortho* hydrogen atoms ($^{3}J_{PH} = 13$ Hz) is observed in the spectrum of complex **1** resulting in a doublet of triplets' line pattern.

The NMR signal of phosphorus in ligand **2a** is less strongly shifted (≈4 ppm) to higher field upon complexation with Li^+ than that of ligand **1a**. The coupling constants of ligand **2a** are not affected significantly upon complexation with Li^+.

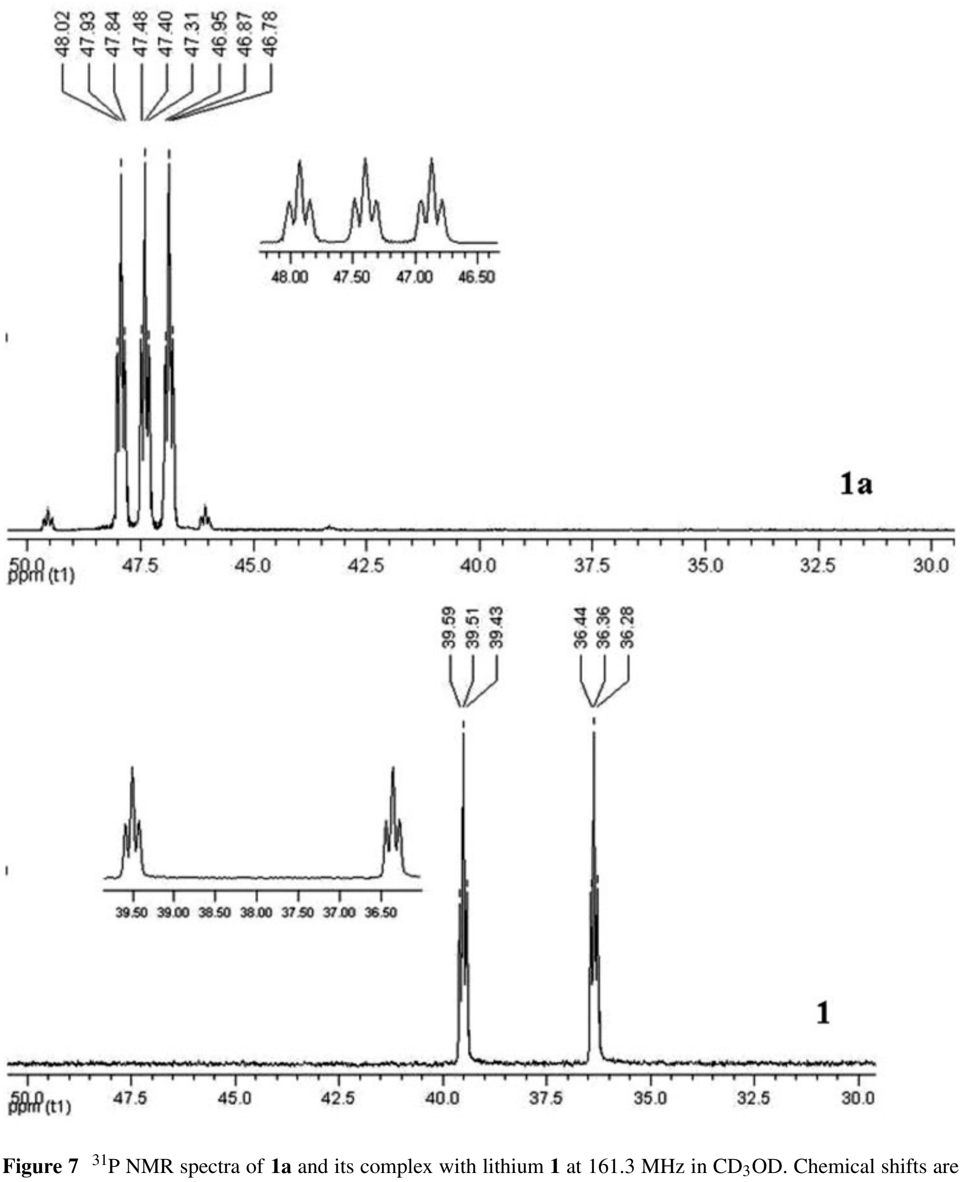


Figure 7 ^{31}P NMR spectra of **1a** and its complex with lithium **1** at 161.3 MHz in CD$_3$OD. Chemical shifts are given in ppm relative to 85% phosphoric acid.

It is worth to mention that no P,Li coupling was observed in the ^{31}P NMR spectra of the studied complexes **1** and **2**. The quartet line patterns reported by Reich et al.[18,19] with $^{1}J_{\mathrm{PLi}}$ values of 45–48 Hz and $^{2}J_{\mathrm{PLi}}$ values of 7.5–11.6 Hz were not detected in the present study. This indicates that the lithium complexes investigated in this study are in a fast dynamic exchange with the corresponding acid anions and lithium cations.

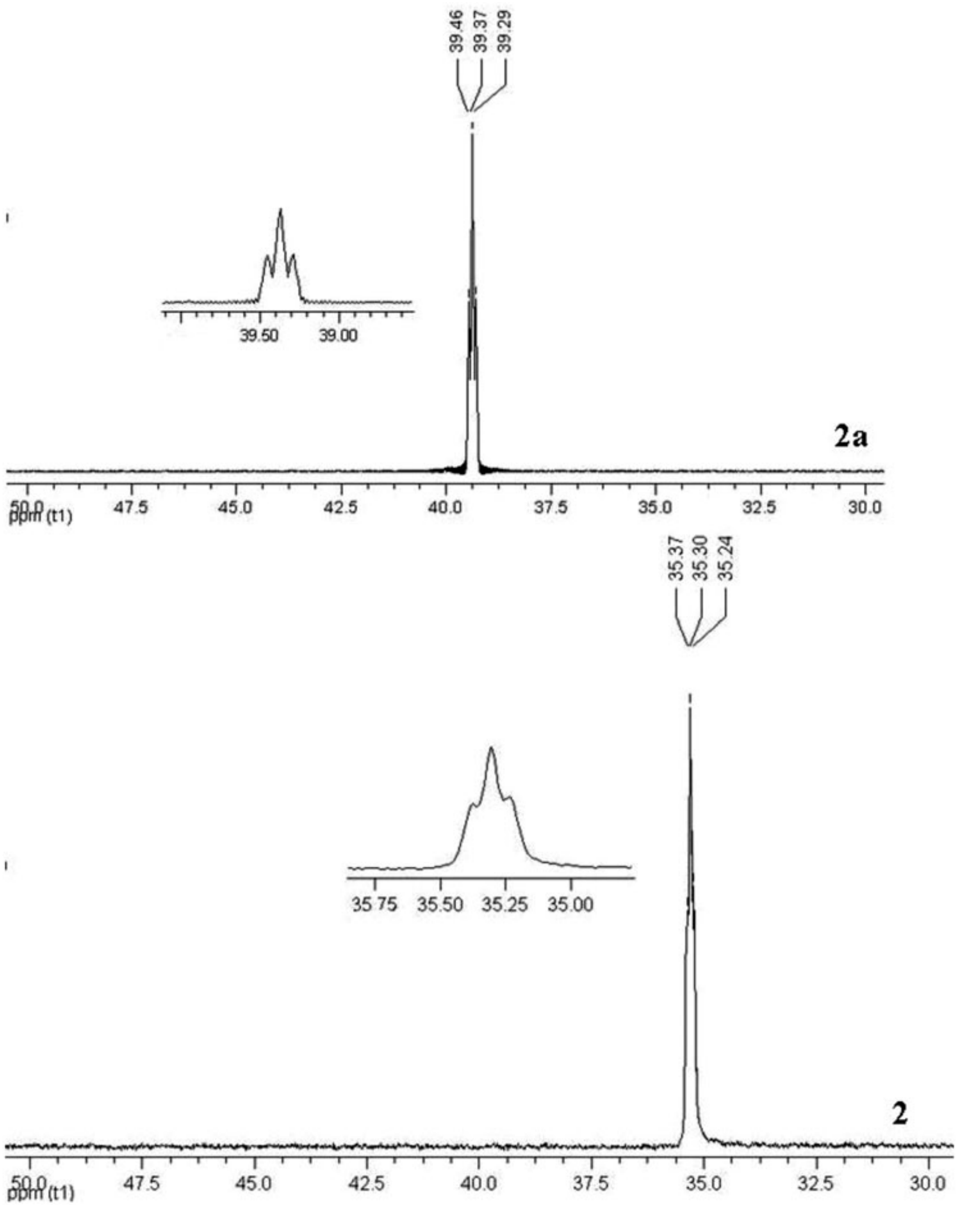
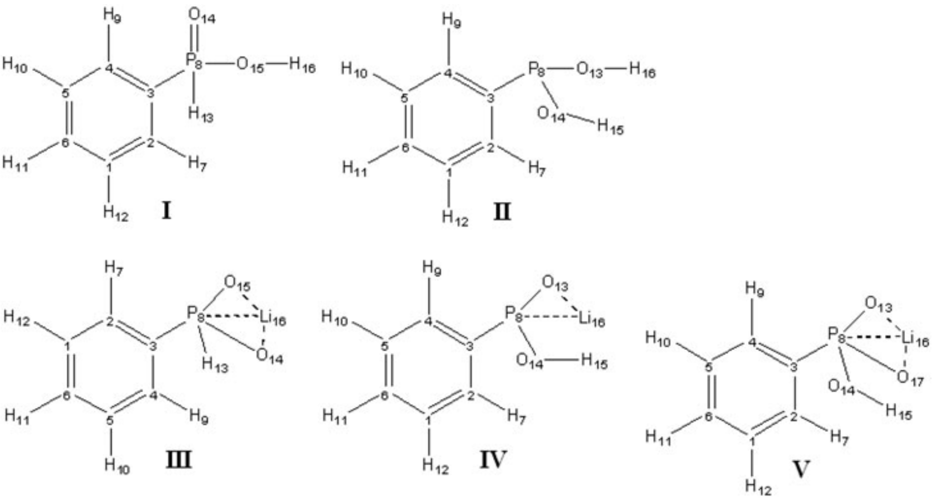


Figure 8 ^{31}P NMR spectra of **2a** and its complex with lithium **2** at 161.3 MHz in CD_3OD. Chemical shifts are given in ppm relative to 85% phosphoric acid.

DFT Calculations

It is worth to mention that all of the phosphorus complexes computationally studied exist in the singlet ground state. Selected atom distances and bond angles computed at B3LYP/6-31G(d) and B3LYP/6-31+G(d) levels of theory are presented in Table 5. The results obtained on the basis of the B3LYP/6-31+G(d) method were found to agree very

Table 5 Selected atom distances (Å) and bond angles (°) for tautomers **I** and **II** of phenylphosphinic acid, and possible structures of lithium complexes **1** and **2** determined by B3LYP/6-31+G(d) calculations*



Structure	I	II	III	IV	V
Atom distance					
C(1)-C(2)	1.396 (1.403)	1.397 (1.395)	1.397 (1.935)	1.397 (1.395)	1.395 (1.394)
C(4)-H(9)	1.086 (1.086)	1.086 (1.085)	1.087 (1.086)	1.087 (1.086)	1.086 (1.086)
C(3)-P(8)	1.814 (1.812)	1.844 (1.842)	1.817 (1.814)	1.856 (1.851)	1.815 (1.813)
P(8)-O(13)	—	1.683 (1.678)	—	1.595 (1.592)	1.539 (1.538)
P(8)-O(14)	1.493 (1.499)	1.667 (1.663)	1.544 (1.542)	1.684 (1.675)	1.639 (1.637)
P(8)-O(15)	1.639 (1.637)	—	1.544 (1.542)	—	—
P(8)-H(13)	1.409 (1.410)	—	1.417 (1.418)	—	—
P(8)-Li(16)	—	—	2.312 (2.303)	2.451 (2.386)	2.305 (2.298)
O(14)-Li(16)	—	—	1.888 (1.884)	—	—
Bond angle					
C(1)-C(2)-H(7)	119.9 (120.0)	119.5 (119.7)	120.3 (120.5)	119.7 (119.9)	120.1 (120.0)
C(4)-C(3)-P(8)	118.8 (118.5)	122.4 (121.7)	120.2 (120.1)	120.7 (120.3)	120.3 (119.7)
C(4)-C(5)-C(6)	120.1 (120.0)	120.3 (120.2)	120.0 (120.0)	120.1 (120.1)	120.1 (120.0)
C(3)-P(8)-O(13)	—	95.5 (95.6)	—	103.4 (103.9)	111.2 (110.5)
C(3)-P(8)-O(14)	113.5 (113.3)	100.2 (99.7)	111.8 (111.3)	99.7 (99.6)	104.7 (105.2)
O(14)-Li(16)-O(15)	—	—	83.2 (83.5)	—	—

*The data in parenthesis is obtained on the basis of B3LYP/6-31G(d).

well and to be consistent with those of the B3LYP/6-31G(d) method (Table 5). For the lithium complex of phenylphosphinic acid **2** with the suggested structure **V**, DFT results show that there are two types of P—O bonds with bond distances of 1.54 Å and 1.64 Å and a C—P distance of 1.82 Å. These results agreed well with the reported X-ray data of the structure of complex **2**, in which the P—O distances are observed in the range of 1.53–1.56 Å[3], and in which the C—P distance lies in the range of 1.78–1.84 Å; this was found experimentally for similar aromatic phosphorus compounds.[20] Note that the frequency tests of the optimized geometry of all structures using B3LYP/6-31+G(d) yielded zero imaginary frequencies and hence the optimized geometry of these phosphorus compounds is true minima. For example, the frequency test analysis of structure **V** showed that the

Table 6 Electronic energies (E_h) for tautomers **I** and **II** of phenylphosphinic acid and possible structures of lithium complexes **1** and **2** calculated at B3LYP/6-31+G(d) level of theory. The change in Gibbs energy (δ G) for the tautomerization of phenyl-phosphinic acid **I** to phenylphosphorous acid **II** was also calculated at the B3LYP/6-31+G(d) level of theory

Structure	E_h (Hartree)	δ G (kcal mol^{-1})
$C_6H_5H(P{=}O)OH$ (I)*	−724.586	$\delta\ G_{I\rightarrow II} = +5.67$ (in gas phase) $\delta G_{I\rightarrow II} = +8.02$ (in methanol)
C_6H_5-$P(OH)_2$ (II)	−724.576	
C_6H_5-PH(=O)OLi (III)	−731.607	
C_6H_5-P(OH)OLi (IV)	−731.563	
C_6H_5-P(=O)(OH)OLi (V)	−806.865	

*For compound numbers, see Table 5.

values were in the range 3170–3180 cm^{-1} for the C—H stretching vibration and 1477 cm^{-1} for the aromatic C=C stretching vibrations. The P—O stretching vibration was found to be within the range of 1000–1213 cm^{-1} and the O—P—O bending vibration was in the range of 408–525 cm^{-1}. All these values are in good agreement with those found in the infrared spectrum of complex **2** (Table 1). Hence, the DFT method applied in this study is suitable to examine the geometrical parameters of the phosphorus compounds investigated.

Our results indicate that the phenyl ring in all structures still retains its planarity since all C—C—C, C—C—H, and C—C—P bond angles are very close to 120°, and hence the π electrons in the phenyl moiety are still delocalized in these configurations. The optimized geometries of all proposed structures of lithium complexes showed that $P(=O)(O^-)$ anion moiety exists preferably in the delocalized form on three sites (O—P—O) that it interacts strongly with Li^+ ion forming chelating complex as suggested by the spectroscopic study. The structures with Li^+ ion bonded to a single oxygen atom were found to be unstable and directly converted to the delocalized chelating complexes. Similar results were obtained by Remko et al.,[21] where bidentate (specific and not merely electrostatic) bonding of Li^+ and Na^+ (oriented symmetrically) to the two oxygen atoms of carboxylates, sulfates, phosphates, and phosphonates ($Li^+ \ldots O$ distance of 1.858 Å) was found depending on DFT calculations.

To decide which of the structures, **III** or **IV**, is the preferred one for complex **1**, the electronic energy of each possible structure was calculated at the B3LYP/6-31+G(d) level of theory and is listed in Table 6. The results show that the electronic energies of the two structures are relatively close to each other. However, structure **III** exhibits the largest electronic energy, and hence is the most preferred one for complex **1**, as also found in the spectroscopic study.

The change in Gibbs free energy, δ G at 298 K, indicates that the tautomerization of phenylphosphinic acid **I** to phosphorous acid **II** is a non-spontaneous process (+5.67 kcal/mol in gas phase and 8.02 kcal/mol in methanol, Table 6) in gas phase as well as in methanol. This means that structure **I** is the most favorable and stable tautomer. Similar $\delta\ G^{298}$ value was reported for 2,4,6-trimethyl phenylphosphinic acid by Orthaber et al.[14] using DFT calculations, which was found to be +6.5 kcal/mol in the gas phase. For a fluorinated derivative 2,3,5,6-tetrafluoro phenylphosphinic acid, a smaller value was obtained (+1.9 kcal/mol).[14]

CONCLUSIONS

The ^{1}H, ^{13}C, and ^{31}P NMR spectra of the organophosphorus ligands **1a** and **2a** and their lithium complexes indicate that phenylphosphinic acid tautomer $C_6H_5PH(=O)OH$ predominates in deuterated methanol with PH/PD exchange. The phenylphosphinic acid tautomer also predominates in the case of lithium complex in deuterated methanol but without PH/PD exchange due to the formation of lithium chelating complexes. DFT calculations support the predominance of phenylphosphinic acid tautomer in the case of the free ligand and its lithium complex. Furthermore, DFT calculations show preference for chelating lithium complexes with the ligands investigated. The bidentate (specific and not merely electrostatic) bonding of Li^+ with carboxylates, sulfates, phosphates, and phosphonates, which was suggested by Remko et al.[21], was confirmed by the present paper based on spectroscopic and DFT computational techniques. This type of bonding is very important in biopolymers such as nucleotides and glycosaminoglycans.

EXPERIMENTAL

Preparation of Lithium Complex of Phenylphosphinic Acid ($Li(O_2P(H)C_6H_5)$) (1)

The complex $Li(O_2P(H)C_6H_5)$ (**1**) was prepared by mixing 50 mL of acetone (analytical grade, Aldrich) solutions of 0.30 g (7.1×10^{-3} mol) of LiCl (analytical grade, Aldrich) with 50 mL of a solution of 1.006 g (7.1×10^{-3} mol) of phenylphosphinic acid $HO_2P(H)C_6H_5$ (**1a**) (extra pure, Aldrich). The white precipitate was filtered off, washed, and dried at room temperature; m.p. > 360°C; elemental analysis: Calcd.: C, 48.67; H, 4.06; found: C, 48.59; H 4.04%.

Preparation of Lithium Complex of Phenylphosphonic Acid $Li(HO_3PC_6H_5)\cdot(H_2O_3PC_6H_5)$ (2)

The complex $Li(HO_3PC_6H_5)$ċ$(H_2O_3PC_6H_5)$ (**2**) was previously prepared by the reaction of phenylphosphonic acid and Li_2CO_3 in water as a solvent.[3] In the present paper the complex $Li(HO_3PC_6H_5)$ċ$(H_2O_3PC_6H_5)$ (**2**) was prepared by mixing of 50 mL of acetone solution of 0.30 g (7.1×10^{-3} mol) of LiCl with 50 mL of solution of 1.119 g (7.1×10^{-3} mol) of phenylphosphonic acid ($H_2O_3PC_6H_5$) (**2a**) (extra pure, Aldrich). The white precipitate was filtered off, washed, and dried at room temperature; m.p. > 360°C; elemental analysis: Calcd.: C, 44.70; H 4.03; found: C, 44.28; H, 4.08%. The structure of the complex reported by Rao and Vidyasagar[3] is in very good agreement with the obtained elemental analysis of the complex prepared in this work.

^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained using a Bruker-Avance 400 MHz spectrometer operating at 400.1 MHz for ^{1}H, at 100.8 MHz for ^{13}C, and at 161.3 MHz for ^{31}P. The chemical shifts are given in ppm relative to TMS in the case of ^{1}H and ^{13}C and relative to 85% phosphoric acid in the case of ^{31}P as external standards. All samples were dissolved in deuterated methanol. IR spectra were recorded using a MAGNA-IR560 spectrometer (Nicolet Instrument Corporation). Elemental analysis was carried out using eurovector model E.A.3000 instrument employing thin sample tubes. Melting points were measured with a SPM2 Stuart apparatus. All calculated NMR spectra were obtained using ACD/ChemSketch (Advanced Chemistry Development Inc.; Ontario, Canada; http://www.acdlabs.com).

DFT Calculations

The geometrical parameters of phenylphosphinic acid and that of lithium compounds **1** and **2** were fully optimized using the B3LYP method as implemented in the Gaussian 03 suite of programs.[15] The density functional theory calculations (B3LYP) were performed using two types of basis sets: 6-31G(d) and 6-31+G(d), where the first basis set has only polarization function, and the second basis set has polarization and diffuse functions, which are suitable and flexible to examine the geometrical structure of the organophosphorus compounds investigated. To make sure that all of these structures represent a minimum, a frequency test has been performed for each structure, where the electronic energy, including the zero point correction, was calculated on the basis of the B3LYP/6-31+G(d) method. These results were also used to determine the most favorable structures of the complexes. In addition, the change in Gibbs free energy at 298 K, ΔG^{o}_{298}, was calculated for the tautomerization of phenylphosphinic acid **I** to phenylphosphonic acid **II**.

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