The Supporting Information to

Structural Interpretation of the ^{31}P NMR Chemical Shifts in Thiophosphate and Phosphate; Key Effects due to Spin-Orbit and Explicit Solvent

Jiří Fukal[a], Ondřej Páv[a], Miloš Buděšínský[a], Ivan Rosenberg[a], Jakub Šebera[a], Vladimír Sychrovský[a,b]*

[a] Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, v.v.i., Flemingovo náměstí 2, 166 10, Praha 6, Czech Republic

[b] Department of Electrotechnology, Electrical Engineering, Czech Technical University, Technická 2, 166 27, Praha 6, Czech Republic

including Supporting Figures S1-S9 and Supporting Tables S1-S19.

The Supporting Figures S1-S9

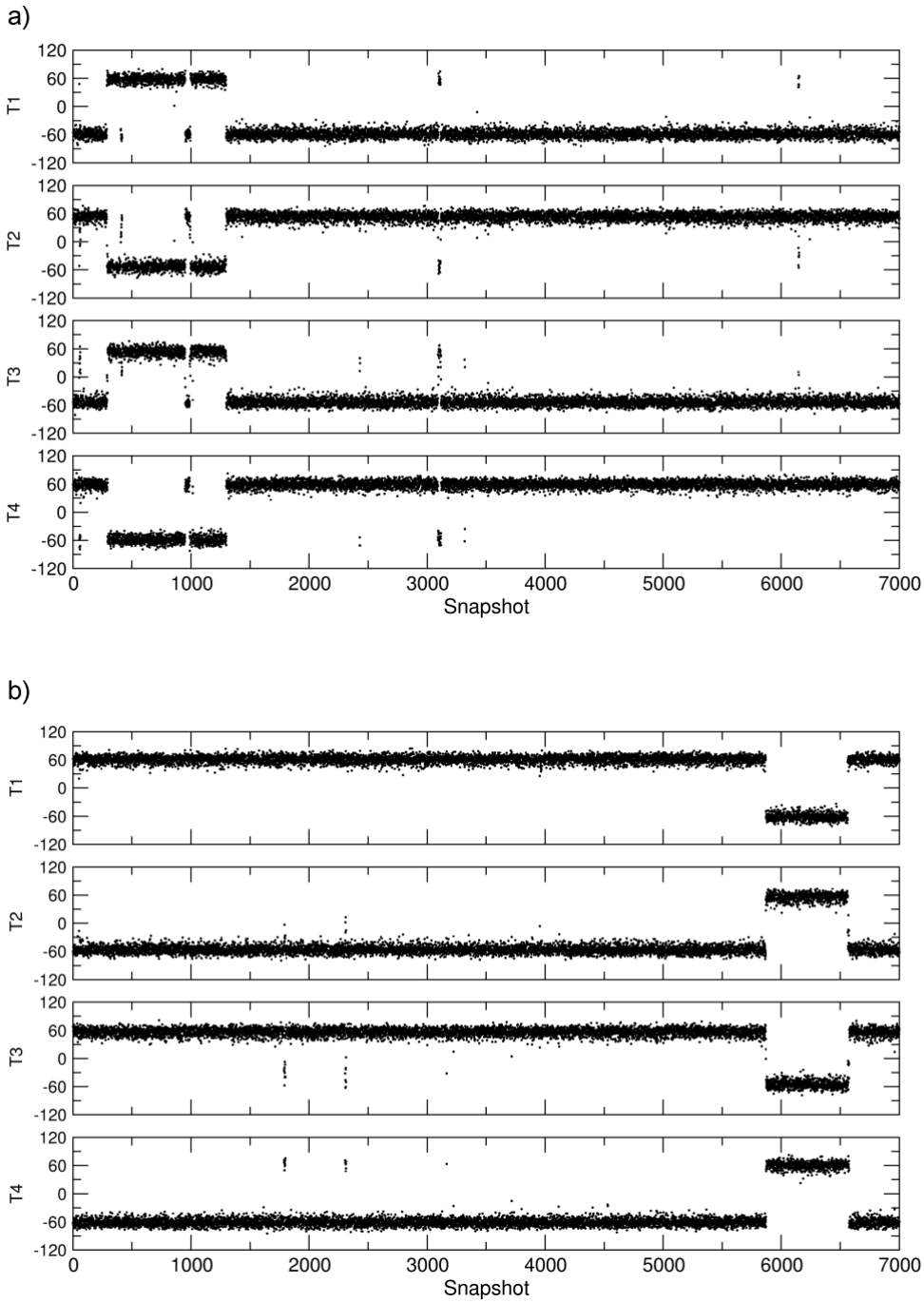

Figure S1. The MD-calculated interconversions between ax-cPT and eq-cPT conformers of the cPT molecule at the temperature 400 K illustrated with the magnitudes of T1÷T4 inner-ring torsion angles in degrees. The starting conformation of cPT in MD simulation was ax-cPT (a) and eq-cPT (b). The MD snapshots are depicted with the ps time step.

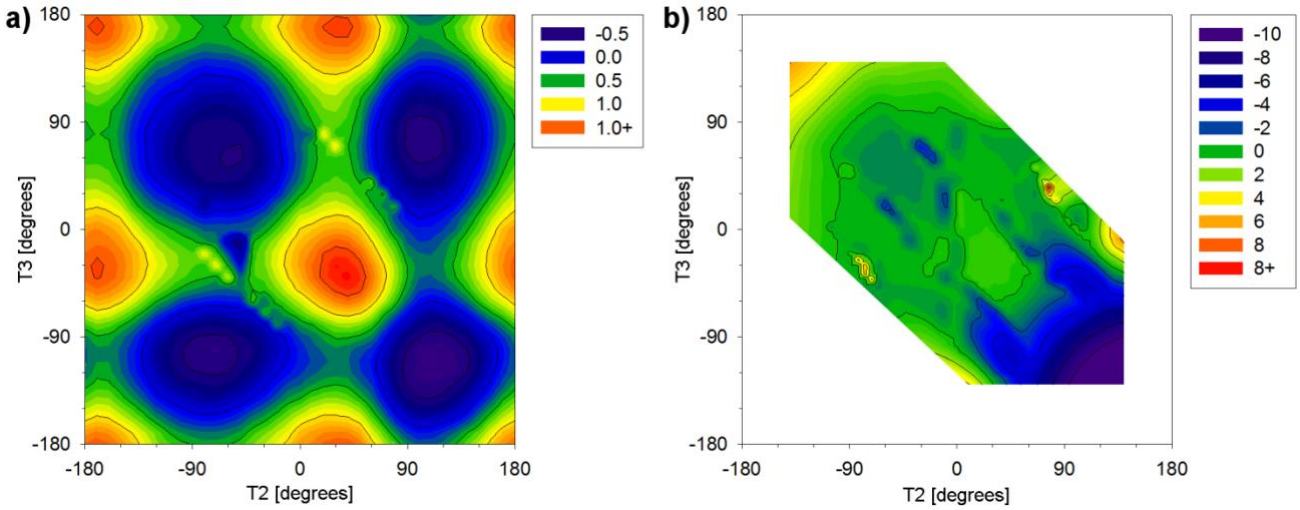

Figure S2. The effect of thiophosphate modification on the potential energy surface describing dependence of energy on T2 and T3 torsion angles. The differential surfaces were calculated as E (in P) − E (in PT) (a) and E (in cP) − E (in cPT) (b) where E was the energy relative to the energy minimum calculated with the B3LYP method, 6-31+G(d) basis and PCM water solvent.

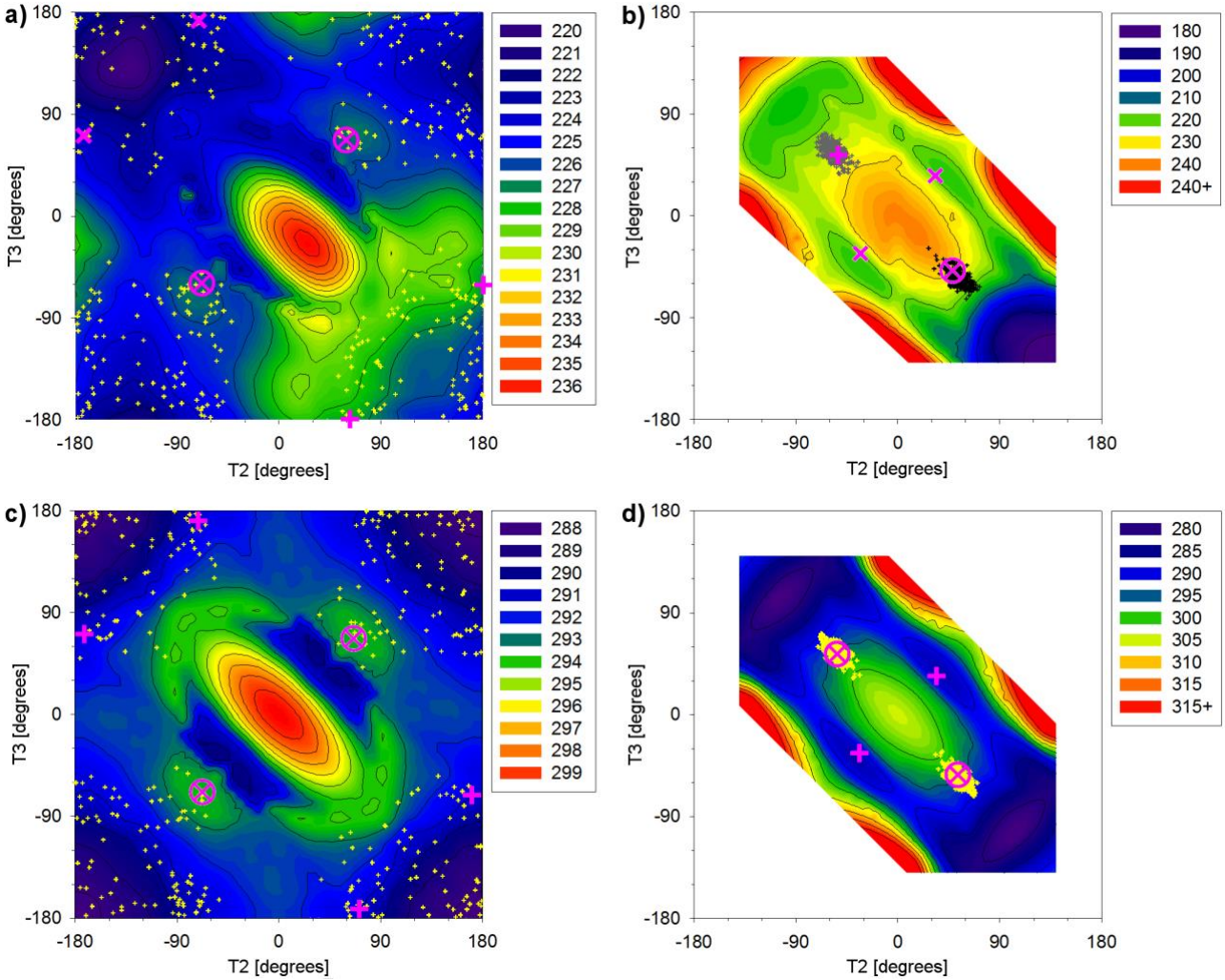

Figure S3. The dependence of σ(^{31}P) NMR shielding on T2 and T3 torsion angles calculated for PT (a), cPT (b), P (c) and cP (d) molecules. Geometries were optimized with the B3LYP method, 6-31G+(d) basis and PCM water on the 10° x 10° geometrical grid. The grid-points within 30° x 30° geometrical grid for P and cP were calculated previously.[25] NMR with the B3LYP, Iglo-III and PCM water solvent. Magnitudes of the σ(^{31}P) in ppm are indicated with colors in the right-upper boxes. The global energy minima were indicated with the crosses within circle. The local energy minima

were indicated with the two kinds of crosses to distinguish their different energies. The snapshot geometries used in MD-averaging of σ(^{31}P) were indicated with yellow dots, for the ax-cPT and eq-cPT with black and grey dots, respectively. The unfilled area for cP and cPT was not calculated (explanation is given in the main text).

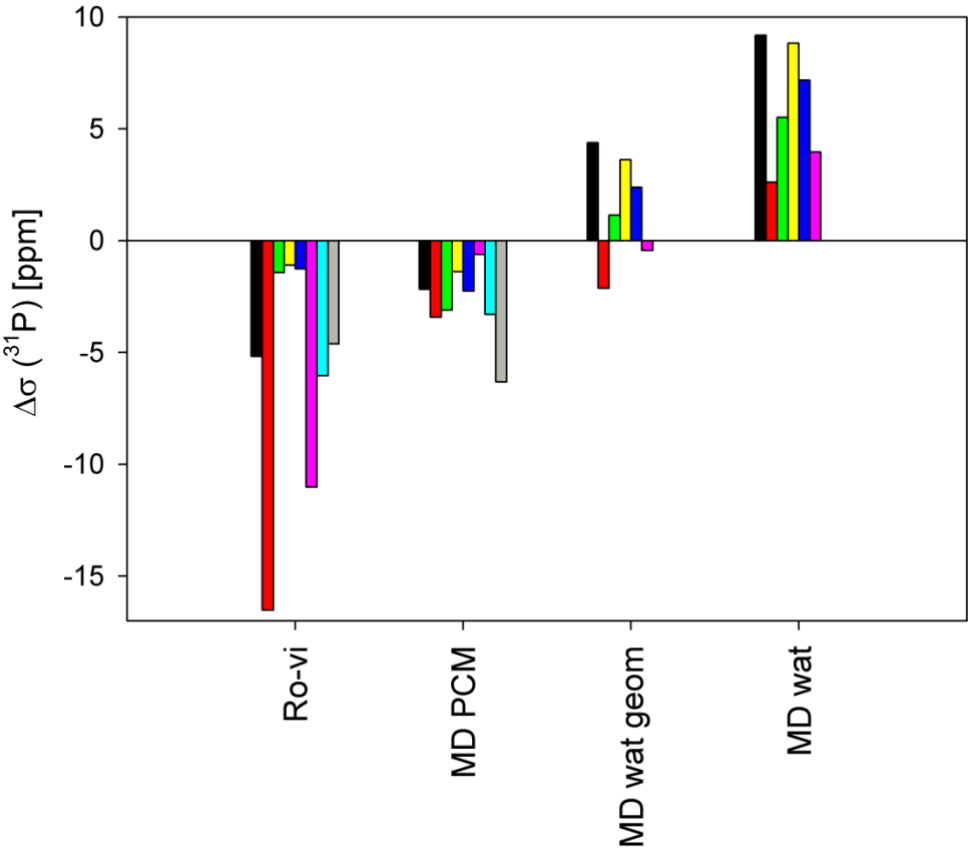

Figure S4. The effects due to molecular dynamics and explicit solvent on σ(^{31}P) NMR shielding calculated in PT (black), P (red), ax-cPT (green), eq-cPT (yellow), cPT (ax and eq average, blue), cP (magenta), H_3PO_4 (cyan), PH_3 (grey); Δσ = σ (including molecular dynamics) – σ (static calculation). The ro-vibrational averaging employed B3LYP and Iglo-III for the geometries optimized with B3LYP and 6-31+G(d) (ro-vi). The MD averaging employed B3LYP and PCM water, Iglo-III in NMR calculations, 6-31+G(d) in geometry optimizations, the explicit waters were neglected (MD PCM), included only in geometry optimization (MD wat geom), included in geometry optimization and NMR calculation (MD wat). All the PH_3 calculations were carried out neglecting solvent.

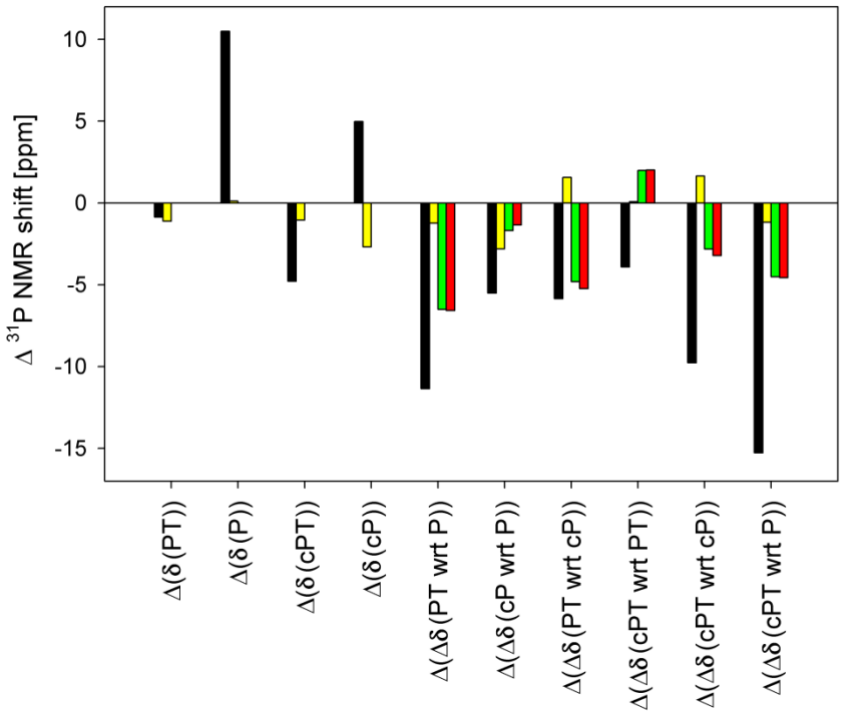

Figure S5. The effect on ^{31}P NMR shifts due to molecular dynamics and solvent calculated as ro-vi average (black), MD-average with PCM water (yellow), MD-average with PCM water for geometries optimized including explicit waters (green) and MD-average including explicit waters (red). The NMR calculations with B3LYP, Iglo-III and PCM water, only the ro-vi calculations neglected solvent. The effect on ^{31}P NMR shift was calculated as ^{31}P NMR shift including effect minus the static ^{31}P NMR shift.

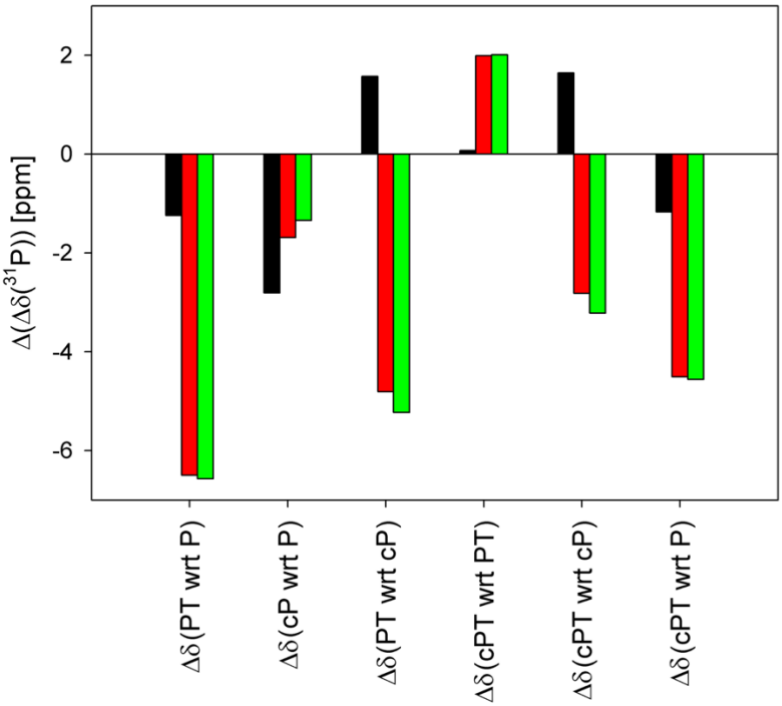

Figure S6. The hydration effect on MD-averaged Δδ(^{31}P) NMR shifts calculated including PCM water (black), explicit waters included in geometry optimization only (red) and explicit waters in geometry optimization and NMR calculations (green). The NMR parameters calculated with B3LYP, Iglo-III, and PCM water. The geometries optimized with B3LYP, 6-31+G(d) and PCM water.

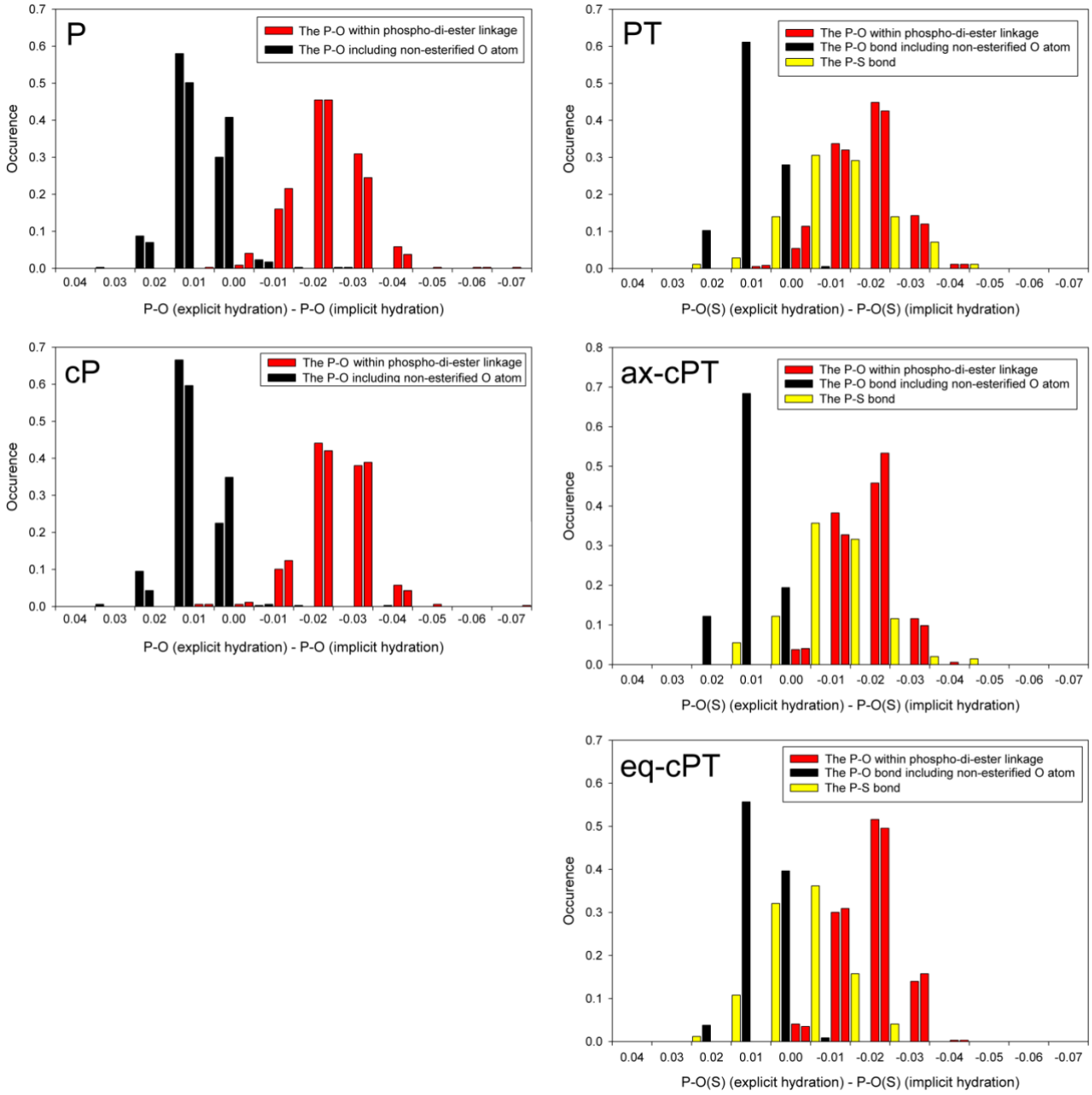

Figure S7. The effect of solvent on MD-averaged geometry of P-O and P-S interatomic distances in Å calculated in P, cP, PT and cPT. The occurrence was calculated as P-O(S) including explicit hydration minus the P-O(S) neglecting explicit hydration. The geometries of MD snapshots optimized with B3LYP, 6-31+G(d), and PCM water.

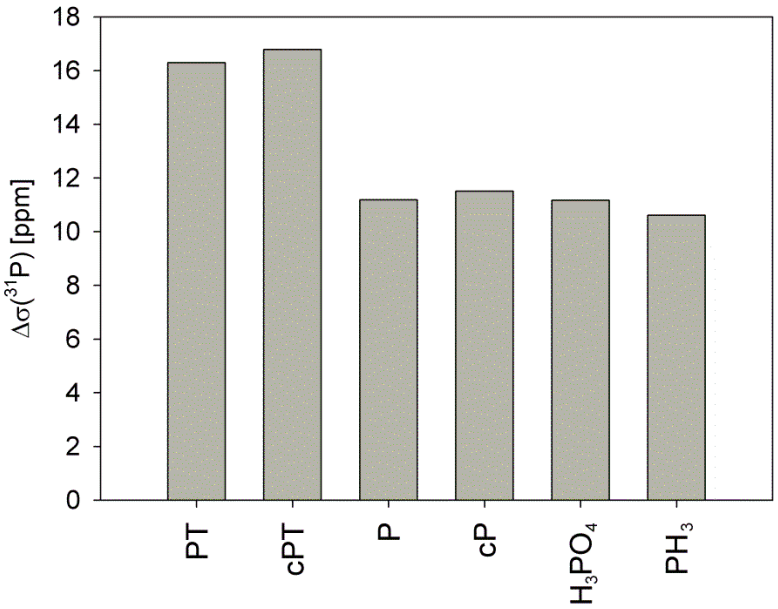

Figure S8. The Spin-orbit (SO) effect on σ(^{31}P) chemical shielding calculated with B3LYP method, QZ4P atomic basis and implicit COSMO-Klamt water solvent. The geometry optimization was with B3LYP, 6-31+G(d) and PCM water. The PH_3 calculated neglecting PCM. Δσ(^{31}P) = σ(^{31}P) (including effect) – σ(^{31}P) (neglecting effect).

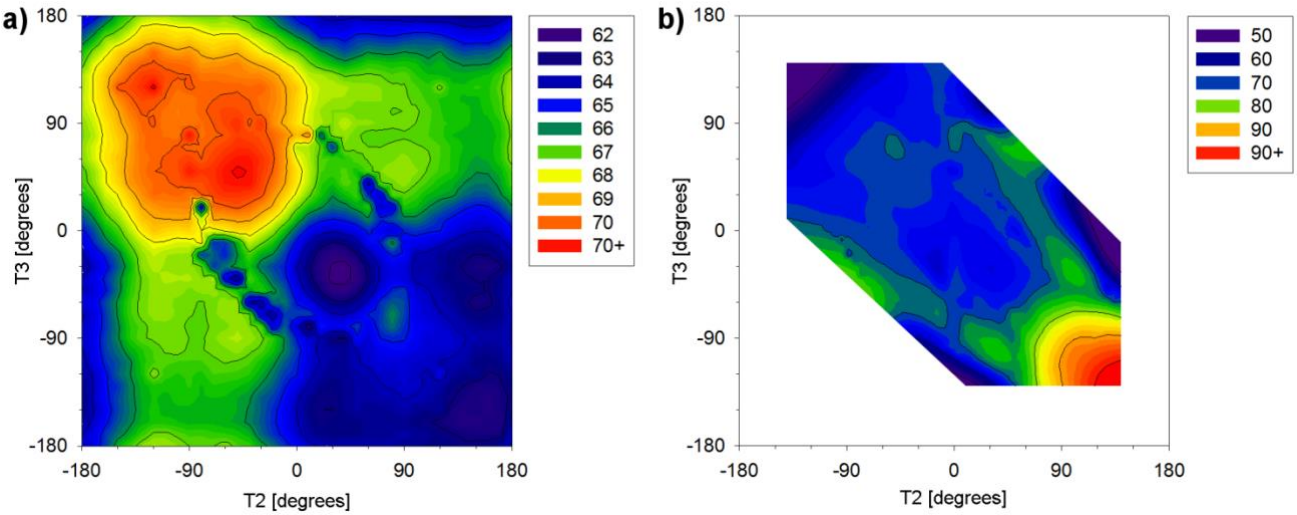

Figure S9. The dependences of heterogenous Δδ(^{31}P) on T2 and T3 torsion angles calculated in opened (left) and structurally locked (right) molecules: Δδ(^{31}P) = σ(^{31}P) (in P) – σ(^{31}P) (in PT) (a) and Δδ(^{31}P) = σ(^{31}P) (in cP) – σ(^{31}P) (in cPT) (b). The NMR parameters calculated with B3LYP, Iglo-III and PCM water solvent. The geometries optimized with the same method and 6-31+G(d) basis.

Supporting Tables S1-S19

Table S1. The ^{31}P NMR shifts of PT and cPT measured in D_2O.

	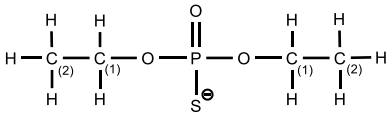			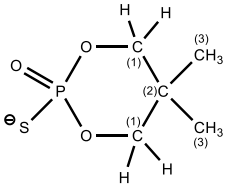	
pH	**1.02**	**13.41**	**pH**	**1.54**	**12.84**
charge	**0**	**-1**	**charge**	**0**	**-1**
δ(P)	57.04	55.41	**δ(P)**	52.44	52.01
δ(C1)	65.73	65.36	**δ(C1)**	78.19	78.93
δ(C2)	18.10	18.16	**δ(C2)**	33.82	34.68
			δ(C3)	22.79; 21.74	23.70; 22.53
δ(H1)	4.00	3.97	**δ(H1)**	4.06; 3.85	4.06; 3.83
δ(H2)	1.27	1.26	**δ(H3)**	1.09; 0.91	1.10; 0.90

Table S2. The geometric parameters of thiophosphate and phosphate calculated with the B3LYP method, 6-31+G(d) atomic basis and PCM water solvent for the global energy minima of the molecules.

Molecule	P-O [a]	P-O [a]	O-P-O [a]	P-O(S) [b]	P-O [b]	O-P-O(S) [b]
PT	1.649	1.649	102.8	2.011	1.511	119.4
P [c]	1.654	1.654	102.6	1.513	1.513	121.5
ax-cPT	1.651	1.651	100.3	2.014	1.506	118.8
eq-cPT	1.655	1.655	100.0	1.999	1.514	119.6
cP [c]	1.658	1.658	99.8	1.516	1.508	121.1

[a] The parameters within phospho-di-ester linkage calculated for the global energy minima. [b] The parameters including non-esterified O and S atoms. [c] Ref.[25]. The interatomic distances in Å and the valence angles in degrees.

Table S3. The σ(^{31}P) NMR shielding in PT and P and Δδ(^{31}P) NMR shift of PT with respect to P in ppm calculated for the global energy minima with the B3LYP method and PCM water solvent.

Basis	σ[a]	σ[b]	Δδ[c]	σ[d]	σ[e]	Δδ[f]
Iglo-II	236.91	302.87	65.95	245.77	311.86	66.09
Iglo-III	226.36	293.67	67.31	235.53	302.09	66.56
cc-pVDZ	318.87	383.37	64.50	306.88	373.69	66.81
cc-pVTZ	245.41	305.84	60.43	253.00	312.46	59.46
cc-pVQZ	272.19	330.95	58.76	282.96	339.34	56.38
cc-pV5Z	213.07	279.84	66.77	228.23	291.66	63.43
pcS-0	225.52	288.87	63.35	158.41	239.59	81.19
pcS-1	242.76	308.60	65.84	242.28	309.27	66.99
pcS-2	214.71	281.61	66.90	228.62	292.60	63.98
pcS-3	213.17	279.48	66.31	228.50	291.31	62.81
pcS-4	213.61	279.80	66.19	229.05	291.69	62.65

[a] In PT. [b] In P. [c] Δδ(^{31}P) = σ(^{31}P) (in P) − σ(^{31}P) (in PT), geometry with the 6-31+G(d). [d] In PT. [e] In P. [f] Δδ(^{31}P) = σ(^{31}P) (in P) − σ(^{31}P) (in PT), geometry with the basis in NMR calculation.

Table S4. The $\Delta\delta(^{31}P)$ NMR shifts in ppm calculated with Iglo-III and pcS-4 employing different geometries.

Basis	PT wrt P	cP wrt P	PT wrt cP	cPT wrt PT	cPT wrt cP	cPT wrt P
Iglo-III[a]	67.31	−2.17	69.48	−1.95	67.53	65.36
pcS-4 [a]	66.19	−2.14	68.33	−1.67	66.66	64.52
Iglo-III [b]	64.58	−2.15	66.73	−1.48	65.25	63.10
pcS-4 [b]	63.14	−2.14	65.28	−1.22	64.06	61.92
Iglo-III [c]	64.13	−2.19	66.32	−1.38	64.94	62.75
pcS-4 [c]	62.65	−2.18	64.82	−1.11	63.71	61.53

[a]Geometry with the 6-31+G(d). [b]Geometry with the 6-311++G(3df,3pd). [c]Geometry with the pcS-4. The geometry optimizations and NMR calculations with B3LYP and PCM water. For PT wrt P: $\Delta\delta(^{31}P) = \sigma(^{31}P)$ (in P) − $\sigma(^{31}P)$ (in PT) and accordingly for the others. The calculated $\sigma(^{31}P)$ can be found in Tab. S5.

Table S5. The $\sigma(^{31}P)$ NMR shielding in ppm calculated in PT, P, cP and cPT molecules with Iglo-III and pcS-4 bases, B3LYP method and PCM water solvent.

Basis	PT	P	cP	cPT	ax-cPT	eq-cPT
Iglo-III [a]	226.36	293.67	295.84	228.31	230.78	225.84
pcS-4 [a]	213.61	279.80	281.94	215.28	218.20	212.36
Iglo-III [b]	240.15	304.73	306.88	241.63	244.33	238.93
pcS-4 [b]	227.52	290.66	292.80	228.74	231.89	225.58
Iglo-III [c]	241.63	305.76	307.95	243.01	245.81	240.21
pcS-4 [c]	229.05	291.69	293.87	230.16	233.42	226.91

The geometry optimization with B3LYP, PCM water, and [a] 6-31+G(d), [b] 6-311++G(3df,3pd), [c] pcS-4.

Table S6. The static $\delta(^{31}P)$ NMR shifts in ppm calculated with different methods Iglo-III and PCM water solvent.

Molecule	HF	MP2	BP86	BPW91	M06-2X	PBE0	B3LYP
$\delta(^{31}P)^a$							
PT	62.92	66.89	62.87	61.48	73.65	60.92	69.34
cPT[c]	62.85	65.20	59.79	58.46	71.97	58.63	67.39
P[d]	2.31	6.23	1.08	0.91	3.86	1.25	2.03
cP[d]	0.80	3.82	−1.80	−1.88	1.13	−1.18	−0.14
$\delta(^{31}P)_{PH3}{}^b$							
PT	17.60	52.47	84.10	80.28	89.74	72.34	73.47
cPT[c]	17.52	50.78	81.02	77.26	88.06	70.05	71.52
P[d]	−43.01	−8.19	22.31	19.71	19.95	12.67	6.16
cP[d]	−44.52	−10.60	19.43	16.92	17.22	10.24	3.99

[a] $\delta(^{31}P) = \sigma(^{31}P)$ (in H_3PO_4) − $\sigma(^{31}P)$ (in molecule). [b] $\delta(^{31}P)_{PH3} = \sigma(^{31}P)$ (in PH_3) − $\sigma(^{31}P)$ (in molecule) − 266.1 ppm. PH_3 calculated neglecting solvent. [c] The average value for ax-cPT and eq-cPT. [d] From the Ref.[25]. Geometries optimized with the method in NMR calculation, 6-31+G(d), PCM water. The calculated $\sigma(^{31}P)$ can be found in Tab S8.

Table S7. The static $\Delta\delta(^{31}P)$ NMR shifts in ppm calculated with different methods, Iglo-III and PCM water solvent.

$\Delta\delta(^{31}P)^a$	HF	MP2	MP2[b]	MP2[c]	BP86	BPW91	M06-2X	PBE0	B3LYP
PT wrt P	60.61	60.66	64.17	65.42	61.79	60.57	69.79	59.67	67.31
PT wrt cP	62.12	63.07	66.46	67.39	64.67	63.36	72.52	62.1	69.48
cP wrt P	−1.51[d]	−2.41[d]	-2.29	-1.97	−2.88[d]	−2.79[d]	−2.73[d]	−2.43[d]	−2.17[d]
cPT wrt PT	−0.07	−1.69	-1.91	-1.61	−3.08	−3.02	−1.68	−2.29	−1.95

cPT wrt cP	62.05	61.38	64.55	65.78	61.59	60.34	70.84	59.81	67.53
cPT wrt P	60.54	58.97	62.26	63.81	58.71	57.55	68.11	57.38	65.36

[a] The relative $\Delta\delta(^{31}P)$ NMR shift cP wrt P: $\Delta\delta(^{31}P) = \sigma(^{31}P)$ (in P) − $\sigma(^{31}P)$ (in cP) and accordingly for the others. [b] The B3LYP geometry. [c] NMR with the pcS-2 for B3LYP geometry. [d] From the Ref.[25]. The $\Delta\delta(^{31}P)$ involving cPT employed average values of respective parameters for ax-cPT and eq-cPT. Geometries optimized with the method in NMR calculation, 6-31+G(d), PCM water. The calculated $\sigma(^{31}P)$ can be found in Tab S8.

Table S8. The $\sigma(^{31}P)$ in ppm calculated with different methods, Iglo-III and PCM water.

Molecule	B3LYP	BP86	BPW91	M06-2X	PBE0	HF	MP2
PT	226.36	221.34	223.82	236.16	250.59	305.92	269.78
P[a]	293.67	283.13	284.39	305.95	310.26	366.53	330.44
ax-cPT	230.78	226.44	228.83	239.81	254.74	308.76	273.34
eq-cPT	225.84	222.40	224.84	235.86	251.02	303.22	269.60
cPT[b]	228.31	224.42	226.84	237.84	252.88	305.99	271.47
cP[a]	295.84	286.01	287.18	308.68	312.69	368.04	332.85
H_3PO_4	295.70	284.21	285.30	309.81	311.51	368.84	336.67
PH_3[c]	565.93	571.54	570.20	592.00	589.03	589.62	588.35

[a]From the Ref.[25]. [b]The average value of σ in ax-cPT and eq-cPT. [c]The calculations neglecting solvent. Geometries optimized with the method in NMR calculation, 6-31+G(d), PCM water.

Table S9. The effects due to ro-vibrational and MD averaging on σ(^{31}P) NMR shielding in ppm.

Molecule	σ^a	$\sigma_{ro\text{-}vi}{}^b$	σ^c	$\sigma_{MD}{}^d$	$\sigma_{MD}{}^e$	$\sigma_{MD}{}^f$	$\Delta\sigma_{ro\text{-}vi}{}^g$	$\Delta\sigma_{MD}{}^h$	$\Delta\sigma_{MD}{}^i$	$\Delta\sigma_{MD}{}^j$
PT	228.97	223.79	226.36	224.18	230.73	235.54	–5.18	–2.18 (0.12)	4.37 (0.17)	9.18 (0.27)
P	297.75	281.22	293.67[k]	290.25	291.54	296.28	–16.53	–3.42 (0.09)	–2.13 (0.13)[k]	2.61 (0.19)
ax-cPT	234.95	233.52	230.78	227.67	231.92	236.29	–1.43	–3.11 (0.21)	1.14 (0.23)	5.51 (0.31)
eq-cPT	227.72	226.61	225.84	224.45	229.45	234.67	–1.10	–1.39 (0.11)	3.61 (0.14)	8.83 (0.51)
cPT[i]	231.33	230.07	228.31	226.06	230.69	235.48	–1.26	–2.25 (0.32)	2.38 (0.37)	7.17 (0.82)
cP	299.95	288.93	295.84[k]	295.23	295.40	299.79	–11.03	–0.61 (0.11)	–0.44 (0.13)[k]	3.95 (0.21)
H_3PO_4	299.96	293.92	295.70[k]	292.40	n.c.	n.c.	–6.04	–3.30 (0.10)[k]	n.c.	n.c.
PH_3[m]	566.29	561.67	565.93[k]	559.60	n.c.	n.c.	–4.61	–6.33 (0.93)[k]	n.c.	n.c.

[a] The static σ neglecting solvent. [b] The ro-vi corrected σ neglecting solvent. [c] The static σ including PCM water. [d] The MD-averaged σ including PCM water. [e] The MD-averaged σ including PCM water, geometry explicit plus PCM water. [f] The MD-averaged σ including explicit plus PCM water. [g] The ro-vi correction neglecting solvent: $\Delta\sigma_{ro\text{-}vi} = \sigma_{ro\text{-}vi}{}^b - \sigma^a$. [h] The MD correction including PCM: $\Delta\sigma_{MD} = \sigma_{MD}{}^d - \sigma^c$. [i] The MD correction in PCM including the effect of explicit water on geometry: $\Delta\sigma_{MD} = \sigma_{MD}{}^e - \sigma^c$. [j] The MD correction including explicit water plus PCM: $\Delta\sigma_{MD} = \sigma_{MD}{}^f - \sigma^c$. All the geometries with B3LYP and 6-31+G(d). All the NMR calculations with the B3LYP and Iglo-III. [k] From the Ref.[25]. [i] The average for ax-cPT and eq-cPT. [m] The PH_3 calculations were neglecting solvent. The S_M deviations for MD-averaged NMR shielding in the parentheses. n.c. stands for not calculated.

Table S10. The $\delta(^{31}P)$ NMR shifts referenced to H_3PO_4 in ppm.

Molecule	δ^a	$\delta_{ro\text{-}vi}{}^b$	$\delta_{ro\text{-}vi\ corr}{}^{b1}$	$\delta_{MD}{}^c$	$\delta_{exp}{}^d$
PT	69.34	70.13	68.48	68.22 (0.22)	55.41
P	2.03[f]	12.70	12.52	2.15 (0.19)	1.34[f]
cPT[e]	67.39	63.85	62.61	66.34 (0.42)	52.01
cP	–0.14[f]	4.99	4.85	–2.83 (0.21)	–2.68[f]

[a] The static $\delta(^{31}P)$. [b] The ro-vi averaged $\delta(^{31}P)$ neglecting solvent. [b1] The static $\delta(^{31}P)$ including PCM water plus the ro-vi correction. [c] The MD-averaged $\delta(^{31}P)$ neglecting explicit waters. [d] The experiment. [e] The average $\delta(^{31}P)$ for ax-cPT and eq-cPT. [f] From the Ref.[25]. The MD-averaging with B3LYP, Iglo-III, and PCM water for B3LYP, 6-31+G(d), PCM water geometries. The S_M values in parenthesis.

Table S11. The $\delta(^{31}P)_{PH3}$ NMR shifts referenced to PH_3 in ppm.

Molecule	$\delta_{PH3}{}^a$	$\delta_{PH3\ ro\text{-}vi}{}^b$	$\delta_{PH3\ ro\text{-}vi\ corr}{}^{b1}$	$\delta_{PH3\ exp}{}^c$
PT	73.47	71.78	74.04	55.41
P [d]	6.16	14.35	18.08	1.34
cPT	71.52	65.50	68.17	52.01
cP [d]	3.99	6.64	10.41	−2.68

[a] The static $\delta(^{31}P)_{PH3}$, B3LYP, Iglo-III, PCM water for B3LYP, 6-31+G(d), PCM water geometry. [b] The ro-vi averaged $\delta(^{31}P)_{PH3}$, B3LYP, Iglo-III for B3LYP, 6-31+G(d) geometry. [b1] The static $\delta(^{31}P)_{PH3}$, B3LYP, Iglo-III, PCM water for B3LYP, 6-31+G(d), PCM water geometry plus the ro-vi correction. [c] The experiment. [d] From the Ref.[25]. $\delta(^{31}P)_{PH3} = \sigma(^{31}P)$ (PH_3, neglecting solvent) − $\sigma(^{31}P)$ (in molecule) − 266.1 ppm.[67]

Table S12. The effect of molecular dynamics on $\Delta\delta(^{31}P)$ NMR shifts in ppm.

$\Delta\delta(^{31}P)$ [a]	$\Delta\delta^b$	$\Delta\delta_{ro\text{-}vi}{}^c$	$\Delta\delta_{ro\text{-}vi}{}^{c1}$	$\Delta\delta_{MD}{}^d$	$\Delta\Delta\delta_{MD}{}^{d1}$	$\Delta\delta_{MD}{}^e$	$\Delta\Delta\delta_{MD}{}^{e1}$	$\Delta\delta_{MD}{}^f$	$\Delta\Delta\delta_{MD}{}^{f1}$	$\Delta\delta_{exp}{}^g$
PT wrt P	67.31	57.43	55.96	66.07 (0.21)	−1.24	60.81 (0.30)	−6.50	60.74 (0.46)	−6.57	54.07
cP wrt P	−2.17[h]	−7.71	−7.67	−4.98 (0.20)	−2.81	−3.86 (0.26)[h]	−1.69	−3.51 (0.40)	−1.34	−4.02[h]
PT wrt cP	69.48	65.14	63.63	71.05 (0.23)	1.57	64.67 (0.30)	−4.81	64.25 (0.48)	−5.23	58.09
cPT wrt PT[i]	−1.95	-6.28	−5.87	−1.88 (0.44)	0.71	0.04 (0.54)	2.91	0.06 (1.09)	3.24	−3.4
cPT wrt cP[i]	67.53	58.86	57.76	69.71 (0.43)	2.28	64.71 (0.50)	−1.90	64.31 (1.03)	−1.99	54.69
cPT wrt P[i]	65.36	51.15	50.09	64.19 (0.41)	−0.53	60.85 (0.50)	−3.59	60.80 (1.01)	−3.33	50.67

[a] PT wrt P: $\Delta\delta(^{31}P) = \sigma(^{31}P)$ (in P) – $\sigma(^{31}P)$ (in PT) and accordingly for the others. [b] The static $\Delta\delta(^{31}P)$. [c] The ro-vi averaged $\Delta\delta(^{31}P)$ neglecting solvent. [c1] The static $\Delta\delta(^{31}P)$ including PCM water plus the ro-vi correction. [d] The MD-averaged $\Delta\delta(^{31}P)$ neglecting explicit waters. [d1] The MD correction for static $\Delta\delta(^{31}P)$: $\Delta\Delta\delta = \Delta\delta^d - \Delta\delta^b$. [e] The MD-averaged $\Delta\delta(^{31}P)$ for geometry optimized including explicit water. [e1] The MD correction for static $\Delta\delta(^{31}P)$: $\Delta\Delta\delta = \Delta\delta^d - \Delta\delta^e$. [f] The MD-averaged $\Delta\delta(^{31}P)$ calculated including explicit water. [f1] The MD correction for static $\Delta\delta(^{31}P)$: $\Delta\Delta\delta = \Delta\delta^d - \Delta\delta^f$. [g] The experiment. [h] From the Ref.[25]. [i] The average $\Delta\delta(^{31}P)$ for ax-cPT and eq-cPT. The MD-averaging with B3LYP, Iglo-III, and PCM water for the B3LYP, 6-31+G(d), PCM water geometries. The ro-vibrational averaging neglecting solvent. The S_M values in parenthesis.

Table S13. The interatomic distances in Å and valence angles in degrees calculated for the atoms within phospho-di-ester linkage.

Molecule	P-O [a]	P-O [b]	P-O [c]	O-P-O [a]	O-P-O [b]	O-P-O [c]
PT	1.649	1.625	1.647	102.8	98.7	100.5
P	1.654	1.627	1.653	102.6	98.2	100.5
ax-cPT	1.651	1.652	1.630	100.3	99.0	100.5
eq-cPT	1.655	1.657	1.634	100.0	98.7	99.9
cP	1.658	1.657	1.628	99.8	99.2	100.7

[a] The global energy minima. [b] The MD average in PCM solvent. [c] The MD average including explicit water solvent. The optimizations with B3LYP, 6-31+G(d) and PCM water solvent.

Table S14. The interatomic distances in Å and bond angles in degrees calculated for the non-esterified P-O(S) atoms.

Molecule	P-O [a]	P-O [b]	P-O [c]	P-O(S) [a]	P-O(S) [b]	P-O(S) [c]	O-P-O(S) [a]	O-P-O(S) [b]	O-P-O(S) [c]
PT	1.511	1.513	1.516	2.011	2.015	1.994	119.4	118.3	114.8
P	1.513	1.515	1.516	1.513	1.515	1.518	121.5	120.2	116.2
ax-cPT	1.506	1.507	1.511	2.014	2.012	1.993	118.8	118.7	114.8
eq-cPT	1.514	1.513	1.514	2.000	1.999	1.987	119.6	119.7	115.7
cP	1.508	1.508	1.512	1.516	1.515	1.516	121.1	121.1	116.3

[a] The global energy minima. [b] The MD average in PCM solvent. [c] The MD average including explicit water solvent. The optimizations with B3LYP, 6-31+G(d) and PCM water solvent.

Table S15. The effect due to Spin-orbit (SO) on σ(^{31}P) NMR shielding in ppm.

Molecule	$\sigma^{a,a1}$	$\sigma_{SO}{}^{a,a2}$	$\sigma^{b,b1}$	$\sigma_{SO}{}^{b,b2}$	$\Delta\sigma_{SO}{}^{d}$	$\Delta\sigma_{SO}{}^{e}$
PT	231.47	247.55	216.27	233.58	16.08	17.31
P	292.99	304.10	281.56	293.15	11.11	11.59
ax-cPT	235.25	251.59	220.67	238.38	16.34	17.71
eq-cPT	229.51	246.31	214.96	233.01	16.80	18.05
cPT [f]	232.38	248.95	217.82	235.70	16.57	17.88
cP	295.17	306.58	283.73	295.58	11.41	11.85
H_3PO_4	292.81	303.93	282.29	293.80	11.12	11.51
PH_3	560.44	571.55	555.66	566.30	11.11	10.64

[a] The NMR calculation and geometry optimization with B3LYP, QZ4P Slater-type orbitals and COSMO-Klamt water. [a1] Neglecting relativistic effects. [a2] Including SO. [b] The NMR calculation with B3LYP, QZ4P Slater-type orbitals and COSMO-Klamt water for the geometries optimized with B3LYP, 6-31+G(d) Gaussian-type orbitals and PCM water neglecting relativistic affects. [b1] NMR neglecting relativistic effects. [b2] NMR including SO. [d] The relativistic correction employing relativistic geometry: $\Delta\sigma_{SO} = \sigma_{SO}{}^{a,a2} - \sigma^{a,a1}$. [e] The relativistic correction employing nonrelativistic geometry: $\Delta\sigma_{SO} = \sigma_{SO}{}^{b,b2} - \sigma^{b,b1}$. [f] The average value for ax-cPT and eq-cPT.

Table S16. The effect due to Four-component DFT on σ(^{31}P) NMR shielding in ppm calculated with B3LYP method and Iglo-III and pcS-2 atomic bases.

	Iglo-III [a]			pcS-2 [b]		
Molecule	σ^{a1}	σ^{a2}	$\Delta\sigma_{FC}{}^{a3}$	σ^{b1}	σ^{b2}	$\Delta\sigma_{FC}{}^{b3}$
PT	242.06	267.13	25.07	236.32	260.76	24.44
P	307.92	326.75	18.84	301.28	319.56	18.27
ax-cPT	247.78	273.08	25.30	241.72	266.21	24.49
eq-cPT	240.14	265.79	25.66	233.67	258.54	24.82
cPT [c]	243.96	269.43	25.48	237.70	262.38	24.68
cP	310.27	329.26	18.99	303.51	321.98	18.47
H_3PO_4	309.63	328.68	19.05	302.69	321.27	18.57
PH_3	570.64	589.06	18.42	560.96	579.32	18.36

[a] The geometry with B3LYP, 6-311++G(3df,3pd) and PCM water. [a1] The NMR neglecting relativistic effect. [a2] The NMR with Four-component DFT. [a3] The relativistic correction: $\sigma^{a2} - \sigma^{a1}$. [b] The geometry with B3LYP including SO, QZ4P Slater-type orbitals and COSMO-Klamt water. [b1] The NMR neglecting relativistic effect. [b2] The NMR with Four-component DFT. [b3] The relativistic correction: $\sigma^{b2} - \sigma^{b1}$. [c] The average value for ax-cPT and eq-cPT. The PH_3 molecule calculated neglecting solvent.

Table S17. The Spin-orbit (SO) effect and the effect due to Four-component (FC) DFT on relative Δδ(^{31}P) NMR shifts in ppm.

$\Delta\delta(^{31}P)$ [a]	$\Delta\delta^{b,b1}$	$\Delta\delta^{b,b2}$	$\Delta\Delta\delta$ [c]	$\Delta\delta^{d,d1}$	$\Delta\delta^{d,d2}$	$\Delta\Delta\delta$ [e]
PT wrt P	61.52	56.55	−4.97	64.96	58.80	−6.16
cP wrt P	−2.18	−2.48	−0.30	−2.23	−2.42	−0.19
PT wrt cP	63.70	59.03	−4.67	67.18	61.22	−5.97
cPT wrt PT	−0.91	−1.40	−0.49	−1.38	−1.63	−0.24
cPT wrt cP	62.79	57.63	−5.16	65.81	59.59	−6.21
cPT wrt P	60.61	55.15	−5.46	63.58	57.18	−6.41

[a] PT wrt P: $\Delta\delta(^{31}P) = \sigma(^{31}P)$ (in P) − $\sigma(^{31}P)$ (in PT) and accordingly for the others. [b] The NMR calculation and geometry optimization with B3LYP, QZ4P Slater-type orbitals and COSMO-Klamt water. [b1] Neglecting relativistic effects. [b2] Including SO. [c] The SO correction for Δδ: $\Delta\Delta\delta = \Delta\delta^{b,b2} -$

$\Delta\delta^{b,b1}$. [d] The NMR with B3LYP and pcS-2 for geometry with B3LYP, QZ4P Slater-type orbitals and COSMO-Klamt water. [d1] NMR neglecting relativistic effect. [d2] NMR with Four-component DFT. [e] The FC correction for Δδ: $\Delta\Delta\delta = \Delta\delta^{d,d2} - \Delta\delta^{d,d1}$. The Δδ for cPT was calculated as average of Δδ for ax-cPT and eq-cPT.

Table S18. The Spin-orbit (SO) effect and the effect due to Four-component (FC) DFT on ^{31}P NMR shifts referenced to H_3PO_4 and PH_3 in ppm.

Molecule	$\delta^{b,b1}$	$\delta^{b,b2}$	$\Delta\delta^{c}$	$\delta^{d,d1}$	$\delta^{d,d2}$	$\Delta\delta^{e}$
cPT [a]	60.43	54.98	−5.45	64.99	58.88	−6.11
cP	−2.36	−2.65	−0.29	−0.81	−0.71	0.09
PT	61.34	56.38	−4.96	66.38	60.51	−5.87
P	−0.18	−0.17	0.01	1.42	1.71	0.29
	$\delta_{PH3}^{b,b1}$	$\delta_{PH3}^{b,b2}$	$\Delta\delta_{PH3}^{c}$	$\delta_{PH3}^{d,d1}$	$\delta_{PH3}^{d,d2}$	$\Delta\delta_{PH3}^{e}$
cPT [a]	61.96	56.50	−5.46	57.16	50.83	−6.32
cP	−0.83	−1.13	−0.30	−8.65	−8.76	−0.11
PT	62.87	57.90	−4.97	58.54	52.46	−6.08
P	1.35	1.35	0.00	−6.42	−6.33	0.08

[a] Average of δ for ax-cPT and eq-cPT. [b] The NMR calculation and geometry optimization with B3LYP, QZ4P Slater-type orbitals and COSMO-Klamt water. [b1] Neglecting relativistic effect. [b2] Including SO. [c] The SO correction for δ: $\Delta\delta = \delta^{b,b2} - \delta^{b,b1}$. [d] The NMR with B3LYP and pcS-2 for geometry with B3LYP, QZ4P Slater-type orbitals and COSMO-Klamt water. [d1] NMR neglecting relativistic effect. [d2] NMR with Four-component DFT. [e] The FC correction for δ: $\Delta\delta = \delta^{d,d2} - \delta^{d,d1}$. The δ was referenced to H_3PO_4. $\delta(^{31}P)_{PH3} = \sigma(^{31}P)$ (PH_3, neglecting solvent) − $\sigma(^{31}P)$ (in molecule) − 266.1 ppm.

Table S19. The corrections due to basis set limit, molecular dynamics and SO calculated for ^{31}P NMR shifts referenced to H_3PO_4 and PH_3 in ppm.

Molecule	δ^{a}	$\Delta\delta^{b}$	$\Delta\delta^{c1}$	s_M^{c1}	$\Delta\delta^{c2}$	s_M^{c2}	$\Delta\delta^{d}$	δ^{e1}	δ^{e2}	Experiment
PT	69.34	–4.67	–12.48	0.22	–1.12	0.27	–4.96	47.23	58.59	55.41
cPT	65.56	–4.45	–9.24	0.26	–0.41	0.28	–5.28	46.60	55.42	52.01
P	2.03	–0.50	–5.91	0.19	0.12	0.23	0.01	–4.37	1.66	1.34
cP	–0.14	–0.47	–7.25	0.21	–2.69	0.23	–0.29	–8.15	–3.59	–2.68
Molecule	δ_{PH3}^{c}	$\Delta\delta_{PH3}^{d}$	$\Delta\delta_{PH3}^{c1}$	s_M^{c1}	$\Delta\delta_{PH3}^{c2}$	s_M^{c2}	$\Delta\delta_{PH3}^{d}$	δ_{PH3}^{e1}	δ_{PH3}^{e2}	Experiment
PT	73.47	–8.54	–15.51	1.05	–4.15	1.10	–4.97	44.45	55.81	55.41
cPT	69.69	–8.31	–12.27	1.09	–3.44	1.33	–5.29	43.82	52.65	52.01
P	6.16	–4.37	–8.94	1.02	–2.91	1.12	0.00	–7.15	–1.12	1.34
cP	3.99	–4.34	–10.28	1.04	–5.72	1.14	–0.30	–10.93	–6.37	–2.68

[a] The static ^{31}P NMR shift with Iglo-III for the global energy minima with 6-31+G(d) including PCM water. [b] The basis-set limit correction for static $\delta(^{31}P)$: Δδ = δ (NMR pcS-4, 6-311++G(3df,3pd) geometry, PCM water) – δ (NMR Iglo-III, 6-31+G(d) geometry, PCM water). [c1] The MD correction for static $\delta(^{31}P)$: Δδ = δ (MD average) – δ^{a} (static), NMR Iglo-III and geometries 6-31+G(d) with PCM water, molecules including explicit waters and references neglecting explicit waters. [c2] The MD correction for static $\delta(^{31}P)$: δ = δ (MD average) – δ^{a} (static), NMR Iglo-III and geometries 6-31+G(d) with PCM water, molecules and references neglecting explicit waters. [d] The Spin-orbit correction for $\delta(^{31}P)$. [e1] The total calculated $\delta(^{31}P)$ NMR shift: $\delta(^{31}P) = \delta^{a} + \Delta\delta^{b} + \Delta\delta^{c1} + \Delta\delta^{d}$. [e2] The total calculated $\delta(^{31}P)$ NMR shift: $\delta(^{31}P) = \delta^{a} + \Delta\delta^{b} + \Delta\delta^{c2} + \Delta\delta^{d}$. All the NMR calculations and geometry optimizations with B3LYP. PH_3 calculated neglecting solvent. The Boltzmann-corrected $\sigma(^{31}P)$ NMR shielding was employed for cPT ^{31}P NMR shifts: $\sigma(^{31}P) = 0.13\ \sigma(^{31}P)$ (in eq-cPT) + $0.87\ \sigma(^{31}P)$ (in ax-cPT). $\delta(^{31}P) = \sigma(^{31}P)$ (in H_3PO_4) − $\sigma(^{31}P)$ (in molecule), $\delta(^{31}P)_{PH3} = \sigma(^{31}P)$ (in PH_3) − $\sigma(^{31}P)$ (in molecule) − 266.1 ppm.