

The Supporting Information to

The Benchmark of ^{31}P NMR parameters in Phosphate; the Case Study on Structurally Constrained and Flexible Phosphate

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The Supporting Information includes

Supporting Tables S1-S12

Supporting Figures S1-S15

Table S1. The NMR parameters measured in DEP and cDEP. Solvent was D_2O . Only absolute values of J-constants are given.

pH	1.04	13.55	pH	0.65	~14.0
charge	0	-1	charge	0	-1
$\delta(\text{P})$	0.80	1.34	$\delta(\text{P})$	-2.99	-2.68
$\delta(\text{C1})$	66.06	65.00	$\delta(\text{C1})$	79.29	79.76
$\delta(\text{C2})$	18.20	18.35	$\delta(\text{C2})$	34.46	34.46
			$\delta(\text{C3})$	22.78	22.84
$\delta(\text{H1})$	4.01	3.92	$\delta(\text{H1})$	3.94	3.90
$\delta(\text{H2})$	1.28	1.25	$\delta(\text{H3})$	0.99	0.99
$^2\text{J}_{\text{P,C1}}$	5.6	5.5	$^2\text{J}_{\text{P,C1}}$	5.45	5.4
$^3\text{J}_{\text{P,C2}}$	6.7	6.8	$^3\text{J}_{\text{P,C2}}$	4.7	4.6
$^3\text{J}_{\text{P,H1}}$	7.6	7.3	$^3\text{J}_{\text{P,H1}}$	11.85	11.8
$^4\text{J}_{\text{P,H2}}$	0.9	0.8			
$^3\text{J}_{\text{H1,H2}}$	7.1	7.1			

Table S2. The $\sigma(^{31}\text{P})$ NMR shielding in ppm and $^2J_{\text{P,C}}$ NMR scalar J-coupling including FC, SD, PSO and DSO contribution in Hz calculated for the global energy minimum of DEP molecule optimized with the 6-31+G(d) atomic basis, B3LYP method and PCM water solvent.

Basis set ^{a)}	$\sigma(^{31}\text{P})$	$^2J_{\text{P,C}}^{\text{FC}}$	$^2J_{\text{P,C}}^{\text{SD}}$	$^2J_{\text{P,C}}^{\text{PSO}}$	$^2J_{\text{P,C}}^{\text{DSO}}$	$^2J_{\text{P,C}}$
6-31+G(d)	362.12	-5.76	0.00	-0.47	0.05	-6.18
cc-pVDZ	383.37	-4.71	0.01	-0.48	0.05	-5.13
cc-pVTZ	305.84	-5.66	0.00	-0.49	0.05	-6.10
cc-pVQZ	330.95	-6.34	-0.01	-0.47	0.05	-6.78
cc-pV5Z	279.84	-6.53	0.00	-0.53	0.04	-7.02
Iglo-II	302.87	-7.59	0.01	-0.50	0.05	-8.04
Iglo-III	293.67	-7.15	0.01	-0.53	0.04	-7.63
aug-cc-pVDZ	364.24	-6.65	0.00	-0.45	0.05	-7.06
aug-cc-pVTZ	306.02	-6.86	-0.01	-0.43	0.05	-7.25
aug-cc-pVQZ	312.58	-6.21	0.00	-0.46	0.05	-6.62
pcS-1	308.60	n.c.	n.c.	n.c.	n.c.	n.c.
pcS-2	281.61	n.c.	n.c.	n.c.	n.c.	n.c.
pcS-3	279.48	n.c.	n.c.	n.c.	n.c.	n.c.
pcS-4	279.80	n.c.	n.c.	n.c.	n.c.	n.c.
pcJ-1	n.c.	-7.35	n.c.	n.c.	n.c.	n.c.
pcJ-2	n.c.	-6.97	n.c.	n.c.	n.c.	n.c.
pcJ-3	n.c.	-6.82	n.c.	n.c.	n.c.	n.c.
pcJ-4	n.c.	-6.82	n.c.	n.c.	n.c.	n.c.

^{a)} The atomic basis used in NMR calculation. N.c. stands for not calculated.

Table S3. The $\sigma(^{31}\text{P})$ NMR shielding in ppm and $^2J_{\text{P,C}}$ NMR scalar J-coupling including FC, SD, PSO and DSO contribution in Hz calculated for the global energy minimum of DEP molecule optimized with the atomic basis used in NMR calculations, B3LYP method and PCM water solvent.

Basis set ^{a)}	$\sigma(^{31}\text{P})$	$^2J_{\text{P,C}}^{\text{FC}}$	$^2J_{\text{P,C}}^{\text{SD}}$	$^2J_{\text{P,C}}^{\text{PSO}}$	$^2J_{\text{P,C}}^{\text{DSO}}$	$^2J_{\text{P,C}}$	$\sigma - \sigma_{\text{optNMR}}^{\text{b)}$	$^2J - ^2J_{\text{optNMR}}^{\text{b)}$
6-31+G(d)	362.12	-5.76	0.00	-0.47	0.05	-6.18	0	0
cc-pVDZ	373.69	-4.33	-0.01	-0.47	0.06	-4.76	9.68	-0.37
cc-pVTZ	312.46	-5.21	0.00	-0.49	0.05	-5.65	-6.62	-0.45
cc-pVQZ	339.34	-5.86	-0.01	-0.47	0.05	-6.29	-8.39	-0.49
cc-pV5Z	291.66	-5.97	0.00	-0.53	0.04	-6.45	-11.82	-0.57
Iglo-II	311.86	-6.90	0.00	-0.49	0.05	-7.35	-8.99	-0.69
Iglo-III	302.09	-6.50	0.00	-0.52	0.05	-6.97	-8.42	-0.66
aug-cc-pVDZ	355.31	-6.69	-0.01	-0.45	0.05	-7.10	8.93	0.04
aug-cc-pVTZ	311.35	-6.63	-0.01	-0.42	0.05	-7.02	-5.33	-0.23
aug-cc-pVQZ	321.31	-5.70	0.00	-0.45	0.04	-6.11	-8.73	-0.51

^{a)} The atomic basis used in both NMR calculation and geometry optimization. ^{b)} NMR parameter calculated for the global energy minimum optimized with 6-31+G(d) basis (Table S1) minus the NMR parameter for DEP geometry optimized with the basis used in NMR calculation (this table).

Table S4. The $\sigma(^{31}\text{P})$ NMR shielding in ppm and $^2J_{\text{P,C}}$ NMR scalar J-coupling including FC, SD, PSO and DSO contribution in Hz calculated for the global energy minimum of cDEP molecule optimized with the 6-31+G(d) atomic basis, B3LYP method and PCM water solvent.

Basis set ^{a)}	$\sigma(^{31}\text{P})$	$^2J_{\text{P,C}}^{\text{FC}}$	$^2J_{\text{P,C}}^{\text{SD}}$	$^2J_{\text{P,C}}^{\text{PSO}}$	$^2J_{\text{P,C}}^{\text{DSO}}$	$^2J_{\text{P,C}}$
6-31+G(d)	363.32	-4.57	-0.04	-0.37	0.09	-4.89
cc-pVDZ	385.31	-4.14	-0.05	-0.38	0.09	-4.47
cc-pVTZ	306.51	-4.48	-0.04	-0.38	0.08	-4.82
cc-pVQZ	332.48	-5.85	-0.06	-0.39	0.08	-6.20
cc-pV5Z	282.02	-5.91	-0.05	-0.44	0.08	-6.32
Iglo-II	305.10	-6.76	-0.04	-0.41	0.08	-7.13
Iglo-III	295.84	-6.43	-0.05	-0.43	0.08	-6.83
aug-cc-pVDZ	368.93	-6.18	-0.05	-0.37	0.09	-6.51
aug-cc-pVTZ	315.18	-5.97	-0.06	-0.31	0.08	-6.26
aug-cc-pVQZ	307.06	-5.62	-0.05	-0.37	0.08	-5.96
pcS-1	311.03	n.c.	n.c.	n.c.	n.c.	n.c.
pcS-2	283.50	n.c.	n.c.	n.c.	n.c.	n.c.
pcS-3	281.64	n.c.	n.c.	n.c.	n.c.	n.c.
pcS-4	281.94	n.c.	n.c.	n.c.	n.c.	n.c.
pcJ-1	n.c.	-6.55	n.c.	n.c.	n.c.	n.c.
pcJ-2	n.c.	-6.26	n.c.	n.c.	n.c.	n.c.
pcJ-3	n.c.	-6.15	n.c.	n.c.	n.c.	n.c.
pcJ-4	n.c.	-6.16	n.c.	n.c.	n.c.	n.c.

^{a)} The atomic basis used in NMR calculation. N.c. stands for not calculated.

Table S5. The $\sigma(^{31}\text{P})$ NMR shielding in ppm and $^2J_{\text{P,C}}$ NMR scalar J-coupling including FC, SD, PSO and DSO contribution in Hz calculated for the global energy minimum of cDEP molecule optimized with the atomic basis used in NMR calculations, B3LYP method and PCM water solvent.

Basis set ^{a)}	$\sigma(^{31}\text{P})$	$^2J_{\text{P,C}}^{\text{FC}}$	$^2J_{\text{P,C}}^{\text{SD}}$	$^2J_{\text{P,C}}^{\text{PSO}}$	$^2J_{\text{P,C}}^{\text{DSO}}$	$^2J_{\text{P,C}}$	$\sigma - \sigma_{\text{optNMR}}^{\text{b)}$	$^2J - ^2J_{\text{optNMR}}^{\text{b)}$
6-31+G(d)	363.32	-4.57	-0.04	-0.37	0.09	-4.89	0	0
cc-pVDZ	375.51	-3.86	-0.07	-0.37	0.09	-4.20	9.80	-0.27
cc-pVTZ	312.86	-4.19	-0.05	-0.37	0.09	-4.53	-6.35	-0.29
cc-pVQZ	340.56	-5.50	-0.06	-0.38	0.08	-5.85	-8.08	-0.35
cc-pV5Z	293.71	-5.49	-0.06	-0.43	0.08	-5.90	-11.69	-0.42
Iglo-II	313.86	-6.29	-0.05	-0.40	0.09	-6.66	-8.76	-0.47
Iglo-III	304.25	-5.98	-0.05	-0.43	0.08	-6.38	-8.41	-0.45
aug-cc-pVDZ	360.13	-6.32	-0.05	-0.37	0.09	-6.65	8.80	0.14
aug-cc-pVTZ	320.92	-5.85	-0.06	-0.31	0.08	-6.13	-5.74	-0.13
aug-cc-pVQZ	315.07	-5.26	-0.05	-0.36	0.08	-5.60	-8.01	-0.36

^{a)} The atomic basis used in both NMR calculation and geometry optimization. ^{b)} NMR parameter calculated for the global energy minimum optimized with 6-31+G(d) basis (Table S3) minus the NMR parameter for DEP geometry optimized with the basis used in NMR calculation (this table).

Table S6. The relative $\Delta\sigma(^{31}\text{P})$ NMR shift in ppm and relative $\Delta^2J_{\text{P,C}}$ NMR spin-spin coupling in Hz calculated with different atomic bases, B3LYP method and PCM water solvent.

Basis set ^{a)}	$\Delta\delta(^{31}\text{P})^{\text{b)}}$	$\Delta\delta(^{31}\text{P})^{\text{c)}}$	$\Delta(\Delta\delta(^{31}\text{P}))^{\text{d)}}$	$\Delta^2J_{\text{P,C}}^{\text{e)}}$	$\Delta^2J_{\text{P,C}}^{\text{f)}}$	$\Delta(\Delta^2J_{\text{P,C}})^{\text{g)}}$
6-31+G(d)	-1.20	-1.20	0.00	-1.29	-1.29	0.00
cc-pVDZ	-1.94	-1.82	-0.12	-0.66	-0.56	-0.10
cc-pVTZ	-0.67	-0.40	-0.27	-1.28	-1.12	-0.16
cc-pVQZ	-1.53	-1.22	-0.31	-0.58	-0.44	-0.14
cc-pV5Z	-2.18	-2.05	-0.13	-0.70	-0.55	-0.15
Iglo-II	-2.23	-2.00	-0.23	-0.91	-0.69	-0.22
Iglo-III	-2.17	-2.16	-0.01	-0.80	-0.59	-0.21
aug-cc-pVDZ	-4.69	-4.82	0.13	-0.55	-0.45	-0.10
aug-cc-pVTZ	-9.16	-9.57	0.41	-0.99	-0.89	-0.10
aug-cc-pVQZ	5.52	6.24	-0.72	-0.66	-0.51	-0.15
pcS-1	-2.43	n.c.	n.c.	n.c.	n.c.	n.c.
pcS-2	-1.89	n.c.	n.c.	n.c.	n.c.	n.c.
pcS-3	-2.16	n.c.	n.c.	n.c.	n.c.	n.c.
pcS-4	-2.14	n.c.	n.c.	n.c.	n.c.	n.c.

^{a)} The atomic basis used in NMR calculation. ^{b)} Geometry was optimized with the 6-31+G(d) basis. ^{c)} Geometry was optimized with the basis used in NMR calculation. ^{d)} $\Delta\delta(^{31}\text{P})$ for geometry optimized with 6-31+G(d) basis minus the $\Delta\delta(^{31}\text{P})$ for geometry optimized with the basis used in NMR calculation. ^{e)} $^2J_{\text{P,C}}$ in DEP minus $^2J_{\text{P,C}}$ in cDEP optimized with the 6-31+G(d) basis. ^{f)} $^2J_{\text{P,C}}$ in DEP minus $^2J_{\text{P,C}}$ in cDEP optimized with the basis used in NMR calculation. ^{g)} $\Delta^2J_{\text{P,C}}$ for geometry optimized with the 6-31+G(d) basis minus $\Delta^2J_{\text{P,C}}$ for geometry optimized with the basis used in NMR calculation. N.c. stands for not calculated.

Table S7. Estimate of MD-averaged $\sigma(^{31}\text{P})$ NMR shielding in ppm and MD-averaged $^2J_{\text{P,C}}$ NMR scalar J-coupling including FC, SD, PSO and DSO contributions in Hz calculated using first twenty MD snapshots for the DEP molecule.

Basis set ^{a)}	$\sigma(^{31}\text{P})$	$^2J_{\text{P,C}}^{\text{FC}}$	$^2J_{\text{P,C}}^{\text{SD}}$	$^2J_{\text{P,C}}^{\text{PSO}}$	$^2J_{\text{P,C}}^{\text{DSO}}$	$^2J_{\text{P,C}}$	$\sigma_{\text{MD}} - \sigma_{\text{gm}}^{\text{b)}}$	$^2J_{\text{MD}} - ^2J_{\text{gm}}^{\text{b)}}$
6-31+G(d)	359.93	-5.00	-0.01	-0.52	0.05	-5.49	-2.19	0.69
cc-pVDZ	383.11	-4.05	-0.02	-0.54	0.05	-4.56	-0.26	0.57
cc-pVTZ	303.38	-4.33	-0.02	-0.60	0.05	-4.91	-2.46	1.19
cc-pVQZ	329.22	-5.32	-0.02	-0.55	0.04	-5.85	-1.73	0.93
cc-pV5Z	278.59	-5.54	-0.02	-0.62	0.04	-6.14	-1.25	0.88
Iglo-II	301.47	-6.10	-0.01	-0.60	0.04	-6.66	-1.40	1.38
Iglo-III	291.74	-5.88	-0.01	-0.62	0.04	-6.47	-1.93	1.16
aug-cc-pVDZ	362.97	-6.03	-0.02	-0.53	0.05	-6.53	-1.27	0.53
aug-cc-pVTZ	305.32	-6.07	-0.03	-0.54	0.04	-6.58	-0.70	0.67
aug-cc-pVQZ	311.14	-5.01	-0.02	-0.54	0.04	-5.53	-1.44	1.09

^{a)} Atomic basis used in NMR calculation. Geometry of the MD snapshots optimized with the 6-31+G(d) basis, B3LYP method and PCM water solvent. ^{b)} MD-averaged NMR parameter (this table) minus the NMR parameter calculated for the global energy minimum (gm) optimized with the 6-31+G(d) basis, B3LYP method and PCM water solvent (Table S1).

Table S8. The $\sigma(^{31}\text{P})$ NMR shielding in ppm calculated for DEP, cDEP, and for the NMR reference molecules with the B3LYP method, PCM water solvent and different atomic bases.

Molecule	Global energy minimum ^{a)}			
	6-31+G(d)	Iglo-III	cc-pV5Z	pcS-4
DEP	362.12	293.67	279.84	279.80
cDEP	363.32	295.84	282.02	281.94
H ₃ PO ₄	366.84	295.70	282.64	281.94
PH ₃	585.30	565.93	552.78	553.67
Molecule	MD-average ^{b)}			MD-average ^{d)}
	6-31+G(d) ^{c)}	6-31+G(d)	Iglo-III	Iglo-III
DEP	360.39 (0.18)	359.68 (0.12)	291.54 (0.13)	308.78 (0.31)
cDEP	362.87 (0.21)	362.29 (0.13)	295.40 (0.13)	313.17 (0.34)
H ₃ PO ₄	n.c.	363.58 (0.10)	292.40 (0.10)	291.43 (0.40)
PH ₃	n.c.	580.25 (0.79)	559.60 (0.93)	568.57 (1.00)

^{a)} Geometry optimization with the B3LYP method, 6-31+G(d) basis and PCM water solvent. Calculation of $\sigma(^{31}\text{P})$ with the B3LYP method and PCM water solvent. ^{b)} The mean statistical value of $\sigma(^{31}\text{P})$ calculated for MD snapshots optimized with the B3LYP method, 6-31+G(d) basis and PCM water solvent with the S_M deviation from the mean in parenthesis. ^{c)} The calculation for MD snapshots including explicit water molecules within the first hydration shell of only DEP and cDEP. The MD-averaged $\sigma(^{31}\text{P})$ for NMR reference was calculated neglecting explicit hydration. Geometry was optimized with the B3LYP method, 6-31+G(d) basis and PCM water. ^{d)} The NMR calculations employing the MD-calculated geometries. N.c. stands for not calculated.

Table S9. The ^{31}P chemical shielding and $\delta(^{31}\text{P})$ and $\Delta\delta(^{31}\text{P})$ NMR chemical shifts in ppm calculated employing different methods, Iglo-III basis and PCM water solvent. The geometries were optimized with the methods, 6-31+G(d) basis and PCM water implicit solvent.

Molecule	Calculation Method									Experiment
	B3LYP	MD-B3LYP ^{a)}	BP86	MD-BP86 ^{a)}	BPW91	M06-2X	PBE0	MP2	HF	
$\sigma(^{31}\text{P})$										
DEP	293.67	291.54 (0.13)	283.13	281.21 (0.13)	284.39	305.95	310.26	330.44	366.53	-
cDEP	295.84	295.40 (0.13)	286.01	286.04 (0.14)	287.18	308.68	312.69	332.85	368.04	-
H ₃ PO ₄	295.70	292.40 (0.10)	284.21	280.06 (0.22)	285.30	309.81	311.51	336.67	368.84	-
$\delta(^{31}\text{P})$										
DEP	2.03	0.86 (0.23)	1.08	-1.15 (0.35)	0.91	3.87	1.25	6.23	2.32	1.34
cDEP	-0.14	-3.00 (0.23)	-1.80	-5.98 (0.36)	-1.88	1.13	-1.17	3.82	0.81	-2.68
$\Delta\delta(^{31}\text{P})$										
DEP wrt cDEP	-2.17	-3.86 (0.26)	-2.88	-4.83 (0.27)	-2.79	-2.74	-2.43	-2.41	-1.51	-4.02
MD-averaged $\Delta\delta(^{31}\text{P})$ ^{b)}										
DEP wrt cDEP	-3.86	n.c.	-4.83	n.c.	-4.59	-4.54	-4.23	-4.21	-3.31	-4.02

^{a)} MD-average of the NMR shift calculated using MD snapshots with the S_M deviations in parenthesis.

^{b)} MD-average calculated from the static NMR shift assuming estimated dynamical correction to $\Delta\delta(^{31}\text{P})$ -1.8 ppm. N.c. stands for not calculated.

Table S10. The ^{31}P chemical shielding and NMR chemical shifts in ppm calculated with the KT2 DFT method, Jensen's pcS-n, n = 1, 2, 3, 4 and Iglo-III atomic bases, and implicit PCM water solvent.

Molecule	pcS-1	pcS-2	pcS-3	pcS-4	Iglo-III
$\sigma(^{31}\text{P})$					
DEP	335.29	312.97	310.83	310.15	324.80
cDEP	338.41	315.80	313.83	313.13	327.79
H_3PO_4	336.23	314.83	311.62	310.96	325.48
$\text{PH}_3^{\text{a)}$	600.50	589.34	591.13	591.16	602.08
$\delta(^{31}\text{P})$					
DEP	0.93	1.85	0.78	0.80	0.67
cDEP	-2.18	-0.96	-2.21	-2.17	-2.31
$\delta(^{31}\text{P})_{\text{PH}_3}$					
DEP	-0.89	10.27	14.20	14.90	11.17
cDEP	-4.00	7.44	11.20	11.92	8.18
$\Delta\delta(^{31}\text{P})$					
cDEP wrt DEP	-3.11	-2.82	-2.99	-2.98	-2.98

^{a)} The calculations neglecting PCM implicit water solvent.

Table S11. The ^{31}P chemical shielding and NMR chemical shifts in ppm calculated with the KT3 DFT method, Jensen's pcS-n, n = 1, 2, 3 and Iglo-III bases and implicit PCM water solvent.

Molecule	pcS-1	pcS-2	pcS-3	Iglo-III
$\sigma(^{31}\text{P})$				
DEP	342.69	322.67	318.39	331.89
cDEP	345.35	325.07	320.99	334.47
H_3PO_4	343.28	324.40	319.12	332.59
$\text{PH}_3^{\text{a)}$	590.09	583.69	583.49	593.17
$\delta(^{31}\text{P})$				
DEP	0.58	1.73	0.72	0.69
cDEP	-2.06	-0.67	-1.87	-1.88
$\delta(^{31}\text{P})_{\text{PH}_3}$				
DEP	-18.70	-5.07	-1.00	-4.81
cDEP	-21.35	-7.48	-3.60	-7.40
$\Delta\delta(^{31}\text{P})$				
cDEP wrt DEP	-2.65	-2.40	-2.59	-2.58

^{a)} The calculations neglecting PCM implicit water solvent.

Table S12. The scalar $^2J_{\text{P,C}}$ couplings in Hz calculated with the Iglo-III (DSO, PSO, SD) and cc-pV5Z (FC) bases. The geometries were optimized with the same method, 6-31+G(d) basis and PCM water implicit solvent.

Molecule	Method of calculation					Experiment
	B3LYP	BP86	BPW91	M06-2X	PBE0	
Global energy minimum –static calculation						
DEP	-7.01	-6.60	-6.86	-6.77	-6.52	5.5
cDEP	-6.31	-5.87	-6.03	-6.64	-6.34	5.4
MD-average ^{a)}						
DEP	-5.95 (0.07)	-5.73 (0.07)	-5.89 ^{a)}	-5.80 ^{a)}	-5.55 ^{a)}	5.5
cDEP	-5.89 (0.02)	-5.48 (0.03)	-5.62 ^{a)}	-6.23 ^{a)}	-5.93 ^{a)}	5.4
MD corrected plus correction due to explicit hydration ^{b)}						
DEP	-5.82	-5.60	-5.35	-5.67	-5.42	5.5
cDEP	-5.55	-5.14	-5.28	-5.89	-5.59	5.4

^{a)} For the B3LYP and BP86 calculated in explicit MD snapshots where the MD correction to $^2J_{\text{P,C}}$ in DEP with the B3LYP and BP86 was 1.06 Hz and 0.87 Hz, and in cDEP it was 0.39 Hz and 0.42 Hz, respectively. For other methods assumed MD correction calculated as average correction with B3LYP and BP86; that was for DEP and cDEP 0.97 Hz and 0.41 Hz, respectively.

^{b)} The MD-calculated correction of $^2J_{\text{P,C}}$ due to explicit hydration was 0.13 Hz and 0.34 Hz in DEP and cDEP, respectively. The calculation was described in main text (Table 3).

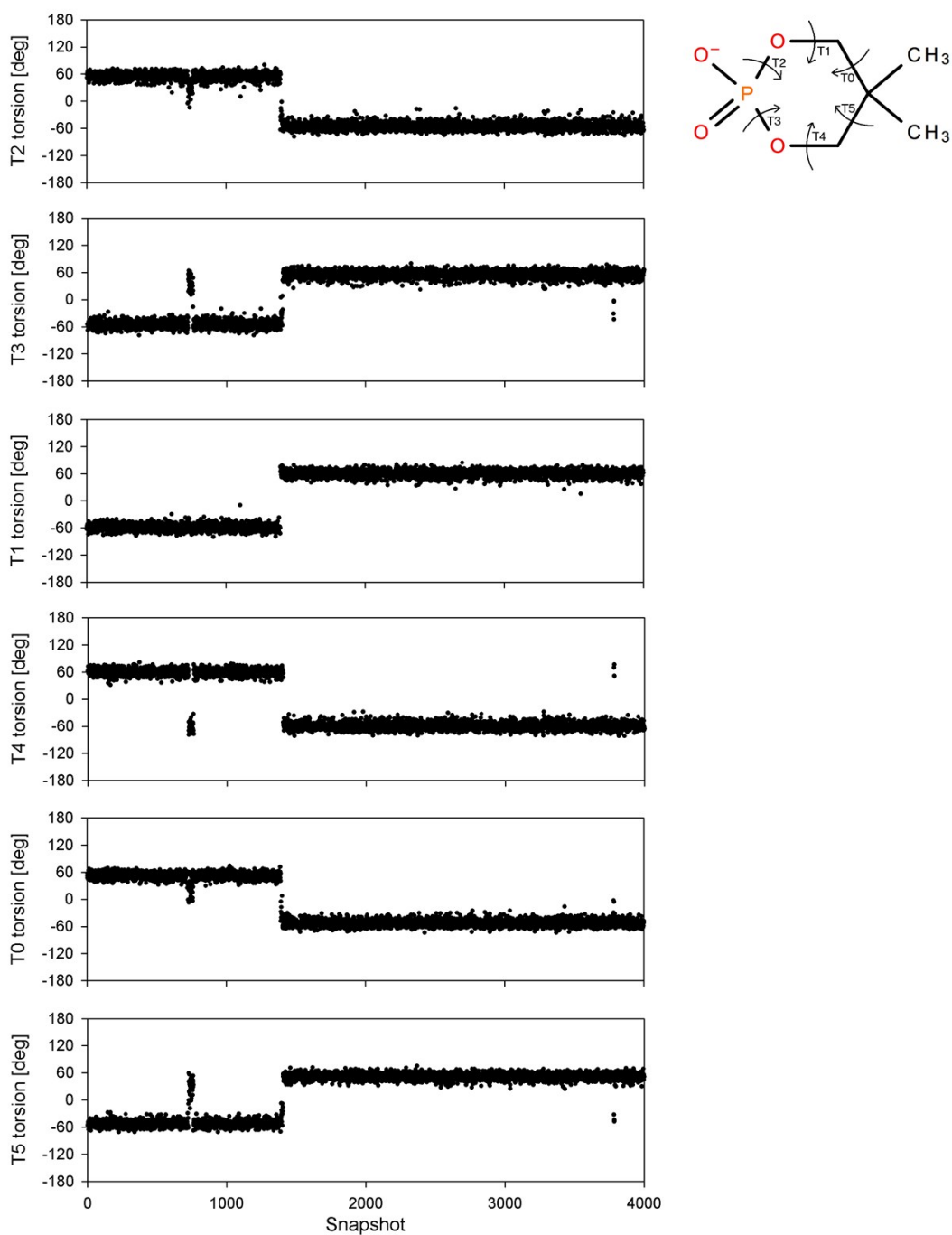


Figure S1. The MD calculated magnitudes of the inner-ring torsion angles T0-T5 depicted in the right-upper corner at temperature 400 K illustrate interconversion between the two energy-minima cDEP stereoisomers.

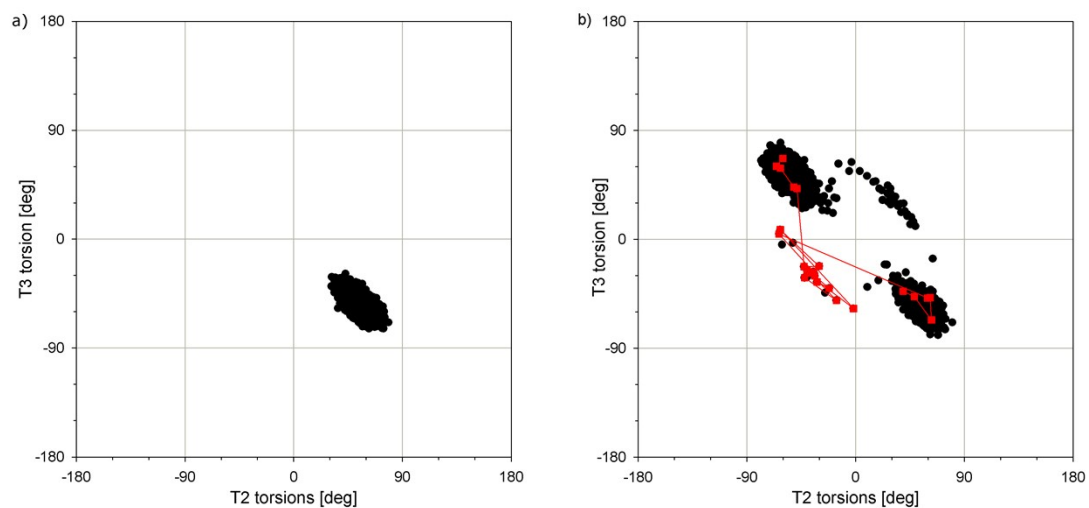


Figure S2. The MD calculated magnitudes of the T2 and T3 torsion angles in cDEP at 300 K (left) and at 400 K (right). The MD snapshot geometries describing conformational interconversion marked in the red were interconnected in a consecutive order in the course of MD calculation.

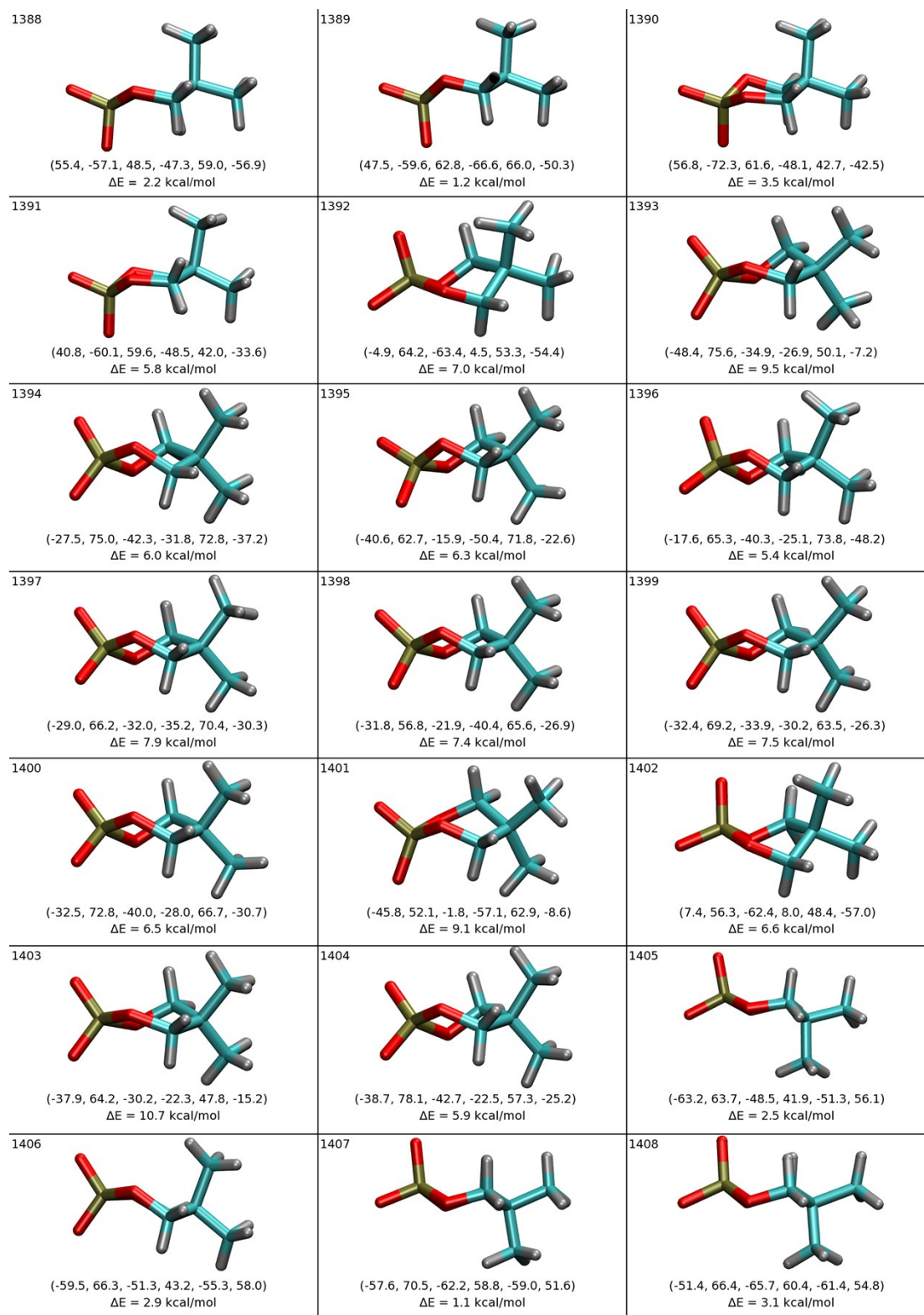


Figure S3. The geometries, MD torsion angles T0, T1, T2, T3, T4, T5 (in parenthesis), and B3LYP/6-31G(d,p) energies relative to the energy of global energy minimum calculated during interconversion between the two cDEP stereoisomers. Energy was calculated for geometry optimized snapshots where T0-T5 torsion angles were fixed. Number of MD snapshot is given in the left-upper corner.

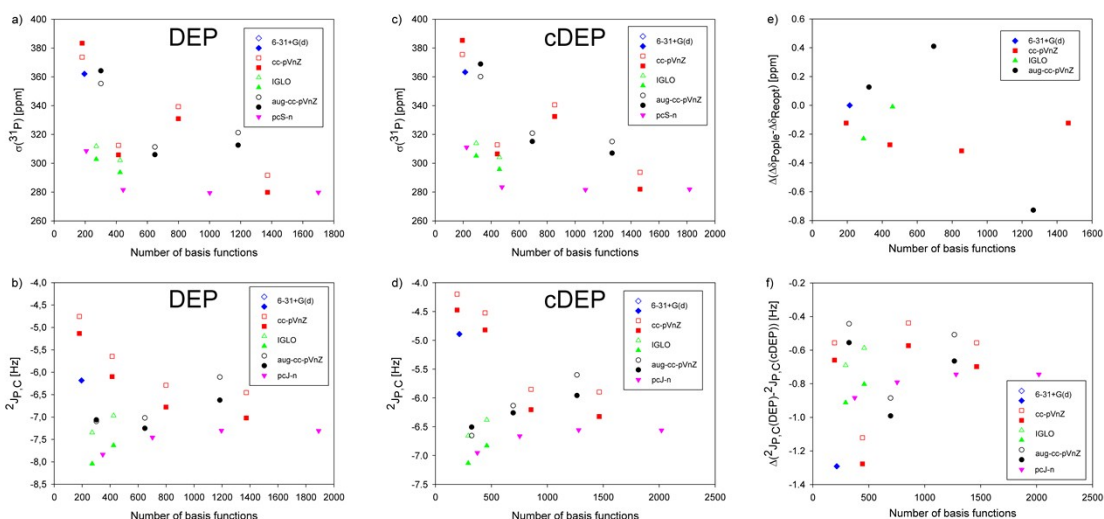


Figure S4. The dependence of the $\sigma(^{31}\text{P})$ NMR shielding and $^2J_{\text{P,C}}$ NMR spin-spin coupling on number of basis functions calculated with the 6-31+G(d), IglO-II, IglO-III, cc-pVnZ ($n = \text{D, T, Q}$ and 5), aug-cc-pVnZ ($n = \text{D, T}$ and Q), and pcS- n and pcJ- n ($n = 1, 2, 3, 4$) atomic bases for the global energy minimum of DEP and cDEP molecules. For pcJ- n calculations of $^2J_{\text{P,C}}$ only the FC term was calculated with the bases, the DSO, PSO, SD terms were calculated with IglO III. Geometry optimization of the molecules was carried out with the 6-31+G(d) atomic basis (filled symbols) and with the atomic basis used in NMR calculation (open symbols), B3LYP method and PCM water solvent. **a)** $\sigma(^{31}\text{P})$ NMR shielding in DEP, **b)** $^2J_{\text{P,C}}$ spin-spin coupling in DEP **c)** $\sigma(^{31}\text{P})$ NMR shielding in cDEP, **d)** $^2J_{\text{P,C}}$ spin-spin coupling in cDEP, **e)** effect of geometry optimization on $\Delta\delta(^{31}\text{P})$ NMR shift, **f)** effect of geometry optimization on $\Delta^2J_{\text{P,C}}$.

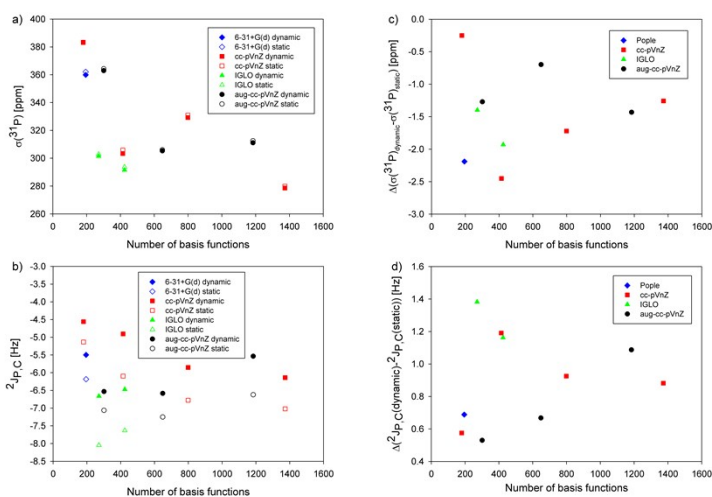


Figure S5. The $\sigma(^{31}\text{P})$ NMR shielding and $^2J_{\text{P,C}}$ NMR spin-spin coupling calculated for the DEP molecule as statistical average using 20 MD snapshots (dynamic) and for the global energy minimum (static) with the 6-31+G(d), IglO-II, IglO-III, cc-pVnZ ($n = \text{D, T, Q}$ and 5) and aug-cc-pVnZ ($n = \text{D, T}$ and Q) bases, B3LYP method, PCM water solvent. All geometries were optimized with the 6-31+G(d) basis, B3LYP method and PCM water solvent. **a)** $\sigma(^{31}\text{P})$ NMR shielding, **b)** $^2J_{\text{P,C}}$ spin-spin coupling, **c)** MD-averaged $\sigma(^{31}\text{P})$ minus the $\sigma(^{31}\text{P})$ for global energy minimum, **d)** MD-averaged $^2J_{\text{P,C}}$ minus the $^2J_{\text{P,C}}$ for global energy minimum.

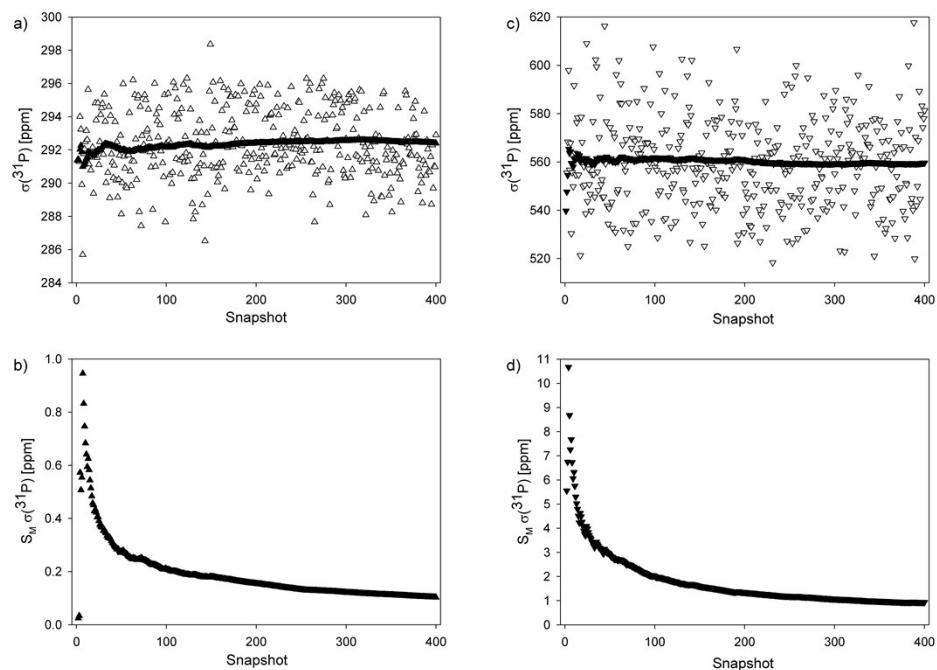


Figure S6. Dynamically averaged $\sigma(^{31}\text{P})$ NMR shielding calculated for the NMR reference molecules with the B3LYP method and Iglo-III basis: a) $\sigma(^{31}\text{P})$ calculated for the MD snapshots of H_3PO_4 (open triangles) and cumulative average of $\sigma(^{31}\text{P})$ (full triangles), b) cumulative S_M for $\sigma(^{31}\text{P})$ of H_3PO_4 , c) $\sigma(^{31}\text{P})$ calculated for the MD snapshots of PH_3 (open triangles) and cumulative average of $\sigma(^{31}\text{P})$ (full triangles), d) cumulative S_M for $\sigma(^{31}\text{P})$ of PH_3 .

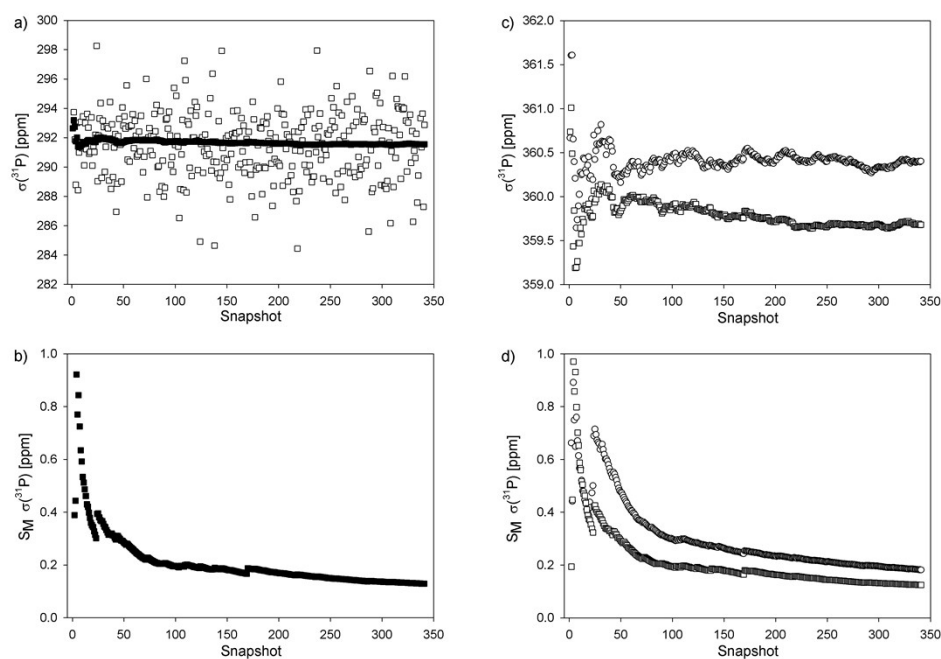


Figure S7. Dynamically averaged $\sigma(^{31}\text{P})$ NMR shielding calculated for the DEP molecule with the B3LYP method and PCM water solvent: a) $\sigma(^{31}\text{P})$ for the MD snapshots (open squares) and cumulative average of $\sigma(^{31}\text{P})$ (full squares) calculated with the Iglo-III basis, b) cumulative S_M for $\sigma(^{31}\text{P})$ calculated with Iglo-III basis, c) $\sigma(^{31}\text{P})$ calculated with the 6-31+G(d) basis for MD snapshots including explicit hydration (circles) and neglecting explicit hydration (squares), d) cumulative S_M calculated with 6-31+G(d) basis for $\sigma(^{31}\text{P})$ including explicit hydration (circles) and neglecting explicit hydration (squares).

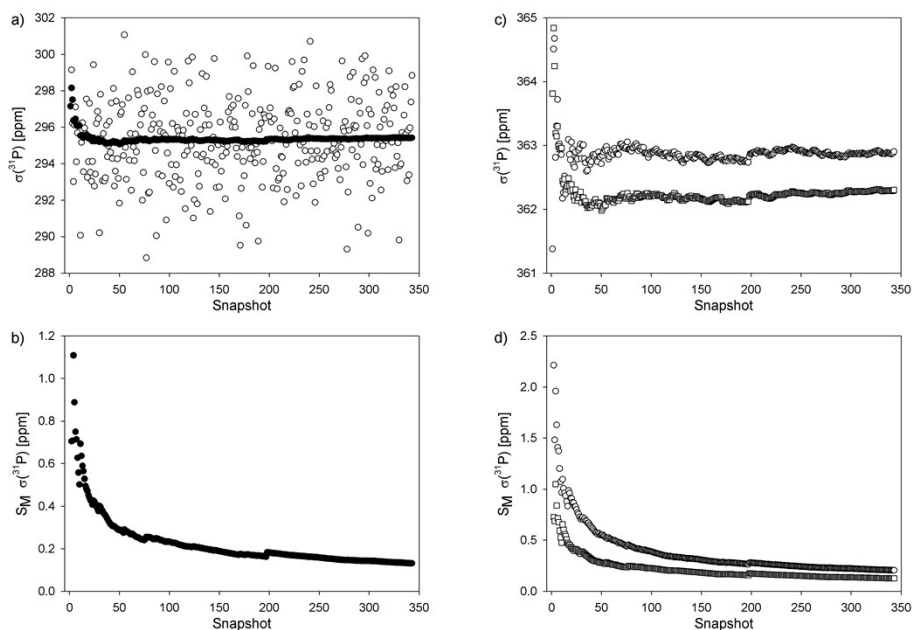


Figure S8. Dynamically averaged $\sigma(^{31}\text{P})$ NMR shielding calculated for the cDEP molecule with the B3LYP method and PCM water solvent: a) $\sigma(^{31}\text{P})$ for the MD snapshots (open squares) and cumulative average of $\sigma(^{31}\text{P})$ (full squares) calculated with the Iglo-III basis, b) cumulative S_M for $\sigma(^{31}\text{P})$ calculated with Iglo-III basis, c) $\sigma(^{31}\text{P})$ calculated with the 6-31+G(d) basis for MD snapshots including explicit hydration (circles) and neglecting explicit hydration (squares), d) cumulative S_M calculated with 6-31+G(d) basis for $\sigma(^{31}\text{P})$ including explicit hydration (circles) and neglecting explicit hydration (squares).

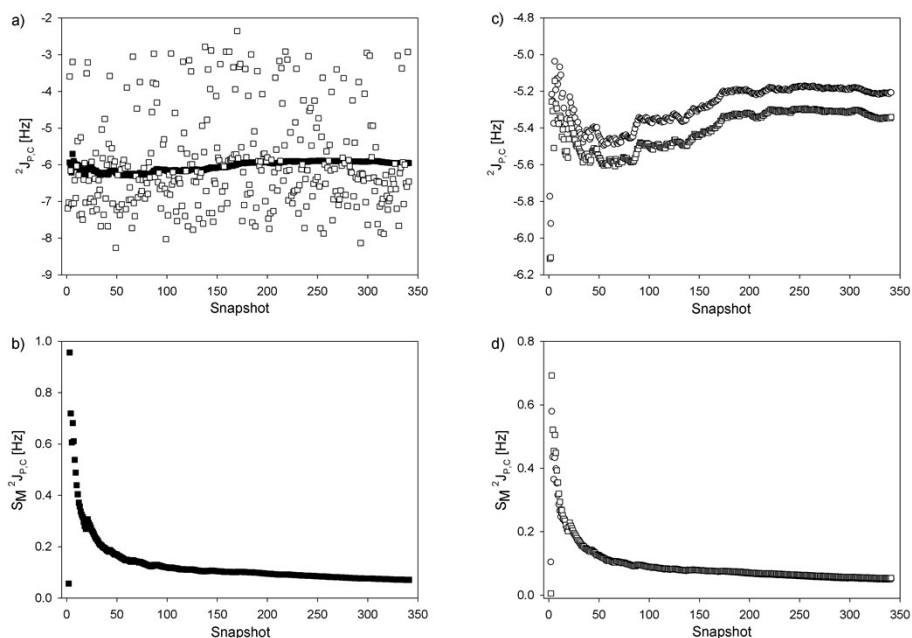


Figure S9. Dynamically averaged ${}^2J_{\text{P,C}}$ NMR coupling calculated for the DEP molecule with the B3LYP method and PCM water solvent: a) ${}^2J_{\text{P,C}}$ for the MD snapshots (open squares) and cumulative average of ${}^2J_{\text{P,C}}$ (full squares) calculated with the Iglo-III basis, b) cumulative S_M for ${}^2J_{\text{P,C}}$ calculated with the Iglo-III basis, c) ${}^2J_{\text{P,C}}$ calculated with the 6-31+G(d) basis for MD snapshots including explicit hydration (circles) and neglecting explicit hydration (squares), d) cumulative S_M calculated for ${}^2J_{\text{P,C}}$ with the 6-31+G(d) basis including explicit hydration (circles) and neglecting explicit hydration (squares).

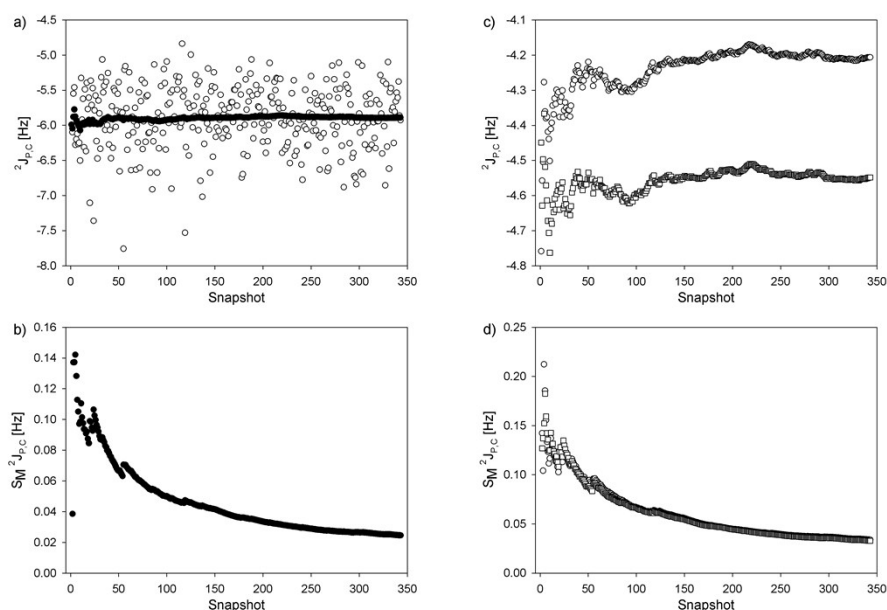


Figure S10. Dynamically averaged ${}^2J_{P,C}$ NMR coupling calculated for the cDEP molecule with the B3LYP method and PCM water solvent: a) ${}^2J_{P,C}$ for the MD snapshots (open squares) and cumulative average of ${}^2J_{P,C}$ (full squares) calculated with the Iglo-III basis, b) cumulative S_M for ${}^2J_{P,C}$ calculated with the Iglo-III basis, c) ${}^2J_{P,C}$ calculated with the 6-31+G(d) basis for MD snapshots including explicit hydration (circles) and neglecting explicit hydration (squares), d) cumulative S_M calculated for ${}^2J_{P,C}$ with the 6-31+G(d) basis including explicit hydration (circles) and neglecting explicit hydration (squares).

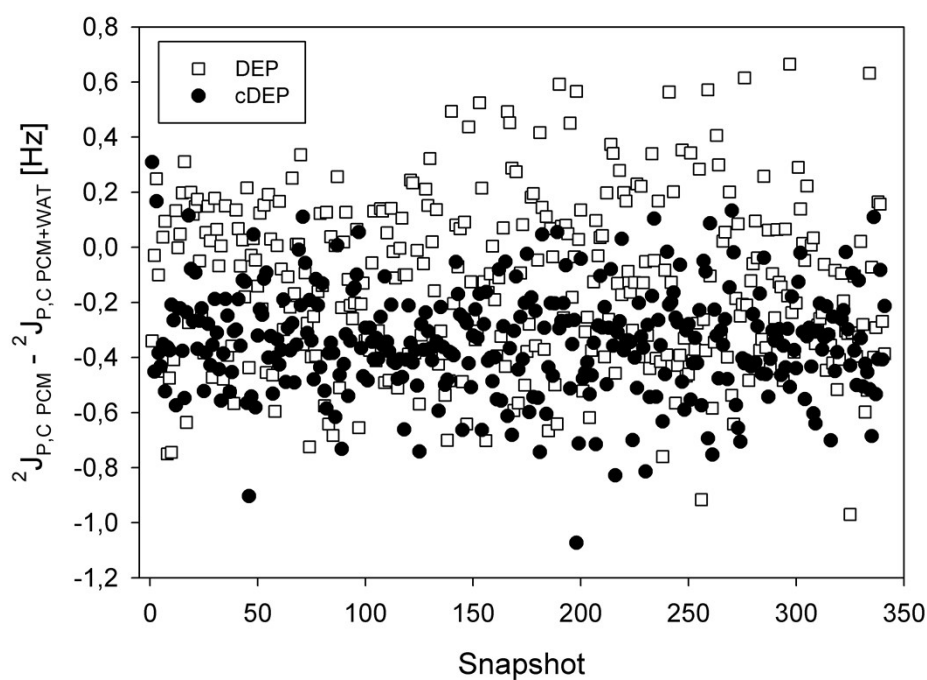


Figure S11. Effect of explicit hydration of MD-snapshots on magnitude of the ${}^2J_{P,C}$ NMR coupling calculated for DEP and cDEP molecules.

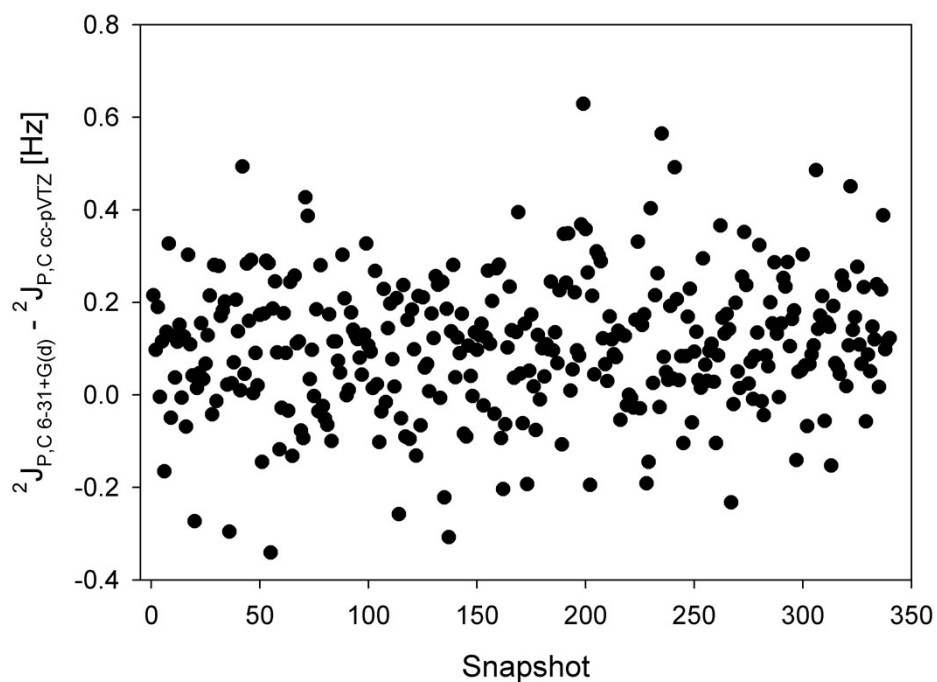


Figure S12. Effect of geometry optimization with 6-31+G(d) and cc-pVTZ bases on ${}^2J_{P,C}$ in MD snapshots of cDEP calculated with Igló-III basis except for the FC J-coupling that was calculated with the cc-pV5Z basis. The MD-averaged ${}^2J_{P,C}$ using cc-pVTZ optimized snapshots was -5.99 Hz.

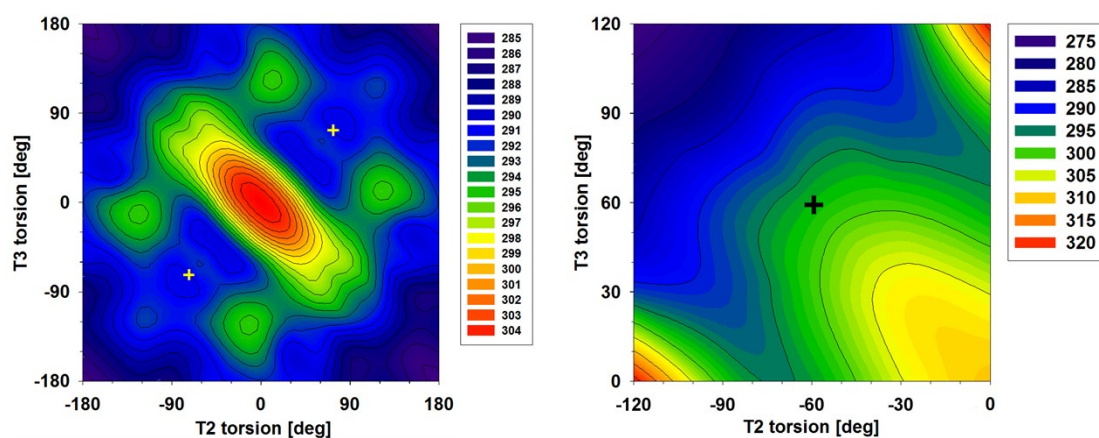


Figure S13. Dependence of the $\sigma(^{31}\text{P})$ NMR shielding on T2 and T3 torsion angles calculated for DEP (left) and cDEP (right). Geometries were optimized with the B3LYP method and 6-31G(d,p) basis on the $30^\circ \times 30^\circ$ geometrical grid and NMR calculations were carried out with the B3LYP method, Igló-III basis and PCM water solvent. Magnitudes of the $\sigma(^{31}\text{P})$ in ppm are indicated with different colors in the right-upper boxes. Geometries of the global energy minima are indicated with crosses.

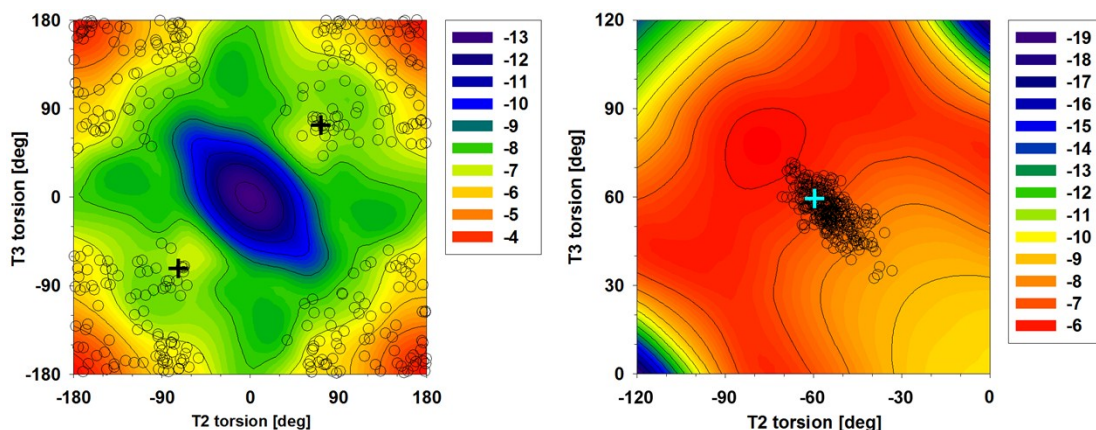


Figure S14. Dependence of the ${}^2J_{p,c}$ NMR spin-spin coupling on T2 and T3 torsion angles calculated for DEP (left) and cDEP (right). Geometries were optimized with the B3LYP method and 6-31G(d,p) basis on the $30^\circ \times 30^\circ$ geometrical grid and NMR calculations were carried out with the B3LYP method, Igló-III basis and PCM water solvent. Magnitudes of ${}^2J_{p,c}$ in Hz are indicated with different colors in the right-upper boxes. The geometries of global energy minima are indicated with crosses. The geometries of MD snapshots are indicated with black open cycles.

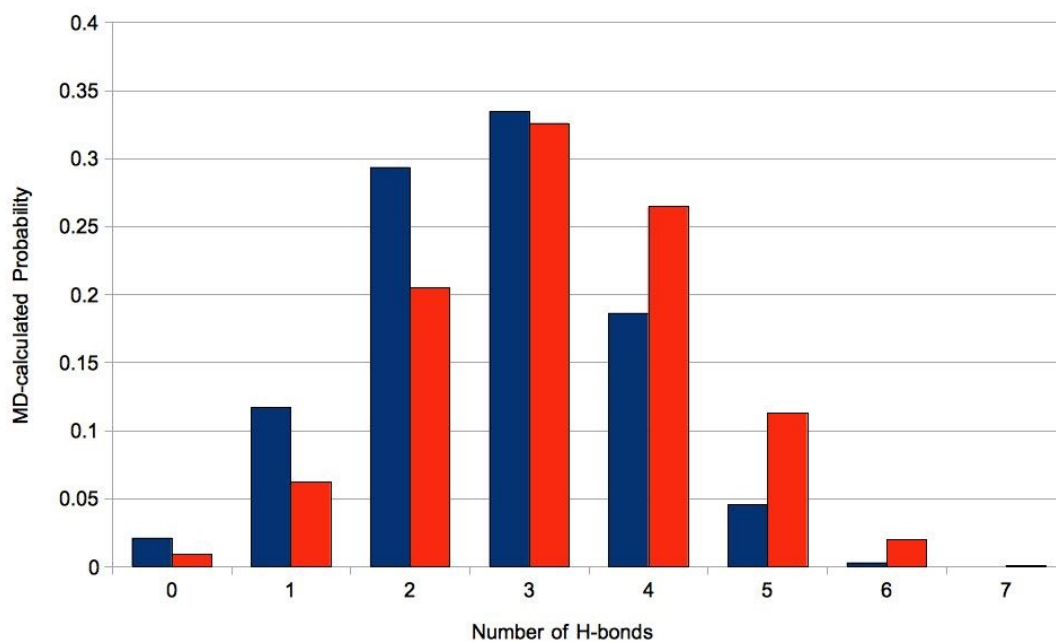


Figure S15. MD-calculated probability of occurrence of H-bonds between the phosphate group and explicit water molecules in DEP (blue) and cDEP (red). Statistically averaged overall number of H-bonds between the two exo oxygen atoms of phosphate and water molecules during complete MD calculations was 2.7 and 3.2 for DEP and cDEP, respectively. The calculations for H-bond donor-acceptor distance 3.0 Å using the VMD 1.8.7 program.