Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2019

Rotational Spectroscopy of Organophosphorous Chemical Agents: Cresyl and Phenyl Saligenin Phosphate

ELECTRONIC SUPPLEMENTARY INFORMATION

Rizalina Tama Saragi,[a] Marcos Juanes,[a] José Luis Abad,[b] Alberto Lesarri,*[a] Ruth Pinacho[c] and José Emiliano Rubio[c]

[a]Departamento de Química Física y Química Inorgánica – IU CINQUIMA , Facultad de Ciencias, Universidad de Valladolid, 47011 Valladolid (Spain). E-mail: lesarri@qf.uva.es

[b]Departamento de Química Biológica, Instituto de Química Avanzada de Cataluña (IQAC-CSIC), Consejo Superior de Investigaciones Científicas (CSIC), 08034 Barcelona (Spain)

[c]Departamento de Electrónica, Escuela Técnica Superior de Ingeniería de Telecomunicación, Universidad de Valladolid, 47011 Valladolid, (Spain)

EXPERIMENTAL AND COMPUTATIONAL METHODS

CBDP (2-(2-cresyl)-4H-1-3-2-benzodioxaphosphorin-2-oxide) and PSP (2-(2-phenyl)-4H-1-3-2-benzodioxaphosphorin-2-oxide) were synthesized as enantiomeric mixtures using the procedure previously described by Faria *et al.*[1] at the IQAC-CSIC. In both cases, a two-step procedure was performed in the same way than other phosphate triester preparations. Thus, in the first step, cresyl (phenyl) phosphorodichloridate was obtained by treatment of o-cresol (phenol, 1 equiv) with $POCl_3$ (1 equiv) in the presence of anhydrous NEt_3 (1 equiv) using dry diethyl ether (Et_2O) as solvent at −78 °C under argon atmosphere. The precipitate was filtered out, and the organic solvent was concentrated to obtain the desired intermediate as an oil. In the second step, the obtained phosphorodichloridates reacted with 1 equiv of 2-hydroxybenzyl alcohol under argon atmosphere using dry CH_2Cl_2 as solvent in presence of anhydrous NEt_3 (3 equiv) at 0 °C and then the mixture was kept at room temperature for 2 h. Formation of the desired compounds were monitored by TLC (UV detection, c. a. $R_f = 0.25$, hexanes; AcOEt 7:3). After this period, the organic phase was washed with water, and the resulting solution was concentrated under reduced pressure to yield a residue containing the desired cyclic phosphate triester. Both compounds were purified by flash SiO_2 column chromatography using a stepwise gradient with hexanes/AcOEt (0–30%, 1% each SiO_2 solvent volume). The overall yield was around 55%.

NMR data:

2-(2-cresyl)-4H-1-3-2-benzodioxaphosphorin-2-oxide (CBDP)

^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.25 (m, 2 H), 7.22–7.05 (m, 6 H), 5.55–5.40 (m, 2 H), 2.21 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0 (d, $J = 7.0$ Hz), 148.7 (d, $J = 8.0$ Hz), 131.52, 129.9 (d, $J = 2.0$ Hz), 129.1 (d, $J = 6.5$ Hz), 127.2 (d, $J = 1.5$ Hz), 125.5 (d, $J = 1$ Hz), 125.4 (d, $J = 1$ Hz), 124.6, 120.5 (d, $J = 10.0$ Hz), 119.7 (d, $J = 2.5$ Hz), 118.8 (d, $J = 9$ Hz), 69.2 (d, $J = 7.5$ Hz), 16.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ −15.8.

2-(2-phenyl)-4H-1-3-2-benzodioxaphosphorin-2-oxide (PSP)

^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 3 H), 7.19 (m, 3 H), 7.15 (m, 1 H), 7.07 (m, 2 H), 5.55–5.40 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0 (d, J = 7.0 Hz), 149.8 (d, J = 7.0 Hz), 129.9, 129.9 129.9, 125.6 (d, J = 1 Hz), 125.3 (d, J = 1 Hz), 124.6, 120.3 (d, J = 10.0 Hz), 119.9 (d, J = 5.0 Hz), 118.7 (d, J = 9.1 Hz), 69.2 (d, J = 7.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ −15.8.

The rotational spectrum was investigated with a chirped-pulsed Fourier transform microwave (FT-MW) spectrometer at the UVa (BrightSpec) working in the frequency range 2-8 GHz, which follows Pate's design.[2] The samples, which were viscous liquids at room temperature, were located in a heating reservoir inside the injection nozzle in separate experiments. A temperature in the range 110-150°C was sufficient to vaporize the compounds. The sample expanded near-adiabatically into the evacuated chamber (ca. 10^{-6} mbar) through a pulsed (solenoid-driven) injection valve. Neon at stagnation pressures of ca. 1.0 bar was used as carrier gas, using a circular nozzle with a diameter of 1.3 mm. The jet was probed with a microwave chirped pulse, recording the resulting transient molecular emission in the time domain. The excitation pulse (4 μs) was created by an arbitrary waveform generator, amplified to 20 W and radiated through a horn antenna, perpendicular to the propagation of the jet expansion. A molecular transient emission (spanning 40 μs) was then detected through a second collinear horn, recorded with a digital oscilloscope (20 MSamples/s) and Fourier-transformed to produce the frequency domain spectrum. Five excitation cycles were used per gas pulse. Typical linewidths of the rotational transitions (FWHM) reach ca. 100 kHz. All frequency oscillators are locked to a rubidium standard, providing frequency accuracies below 5 kHz.

The analysis of the spectrum used simulation programs by Plusquellic[3] (JB95) and Kisiel[4] (AABS). Spectral fittings used Pickett's CALPGM programs.[5]

The initial conformational search used a fast molecular mechanics method based in the Merck's MMFFs force field algorithm.[6] A combination of dedicated Montecarlo/low-mode search algorithms[7] implemented in Macromodel[8] produced a first set of plausible conformations using a general unrestrained search. Further reoptimization of all structures used either B3LYP[9] with the Grimme D3(BJ)[10] dispersion correction (Becke-Johnson damping function) or the conventional second-order Moller-Plesset[11] (MP2) perturbation method. Two sets of triple-ζ basis sets were tested, including

Ahlrichs' balanced functions[12] (def2-TZVP) and a mixed scheme with Dunning's tight d-augmented correlation-consistent basis set[13] (cc-pV(T+d)Z) for the phosphorous atom and cc-pVTZ for all other atoms. All density-functional and ab initio calculations were implemented in Gaussian09.[14]

REFERENCES

[1] M. Faria, I. Fuertes, E. Prats, J. L. Abad, F. Padrós, C. Gomez-Canela, J. Casas, J. Estévez, E. Vilanova, B. Piña, D. Raldúa, *Sci. Rep*. 2018, **8**, 4844/1-14.

[2] a) S. T. Shipman, B. H. Pate, in *Handbook of High Resolution Spectroscopy*, ed. M. Quack and F. Merkt, Wiley, New York, 2011, pp. 801–828. b) C. Pérez, S. Lobsiger, N. A. Seifert, D. P. Zaleski, B. Temelso, G. C. Shields, Z. Kisiel, B. H. Pate, *Chem. Phys. Lett.* 2013, **571**, 1-15.

[3] David F. Plusquellic, R D. Suenram, B Mate, J O. Jensen, A C. Samuels, *J. Chem. Phys*. 2001, **115**, 3057-3067.

[4] Z. Kisiel, L. Pszczolkowski, I. R. Medvedev, M. Winnewisser, F. C. De Lucia, E. Herbst, *J. Mol. Spectrosc*. 2005, **233**,231-243.

[5] H. M. Pickett, J. Mol. Spectrosc. 1991, **148**, 371-377.

[6] T. A. Halgren, *J. Comp. Chem*. 1999, **20**, 720-729. b) T. A. Halgren, *J. Comp. Chem.* 1999, **20**, 730-748.

[7] I. Kolossváry, W. C. Guida, *J. Comput. Chem.* 1999, **20**, 1671-1684.

[8] Macromodel, Schrödinger Release 2015-2: MacroModel, Schrödinger, LLC, New York, NY, 2015.

[9] C. Lee, W. Yang, R. G. Parr, *Phys Rev. B* 1988, **37**, 785. b) A. D. Becke, *Phys. Rev. A* 1988, **38**, 3098. c) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5848.

[10] a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys*. 2010, **132**, 154104. b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem*. 2011, **32**, 1456-1465.

[11] C. Møller, M. S. Plesset, *Phys. Rev.* 1934, **46**, 618−622.

[12] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys*. 2005, **7**, 3297-3305.

[13] T. H. Dunning, Jr., K. A. Peterson, A. K. Wilson, *J. Chem. Phys.* 2001, **114**, 9244-9253.

[14] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian 09, Revision C.01; Gaussian, Inc., Wallingford, CT, 2009.

Figure S1. A 2 GHz section of the rotational spectrum of cresyl saligenin phosphate (CBDP, lower trace), and a 50 MHz expansion (upper trace) with typical μ_a (blue) and μ_b (red) rotational transitions (labelled with quantum numbers $J'_{K'_a,K'_c} \leftarrow J''_{K''_a,K''_c}$).

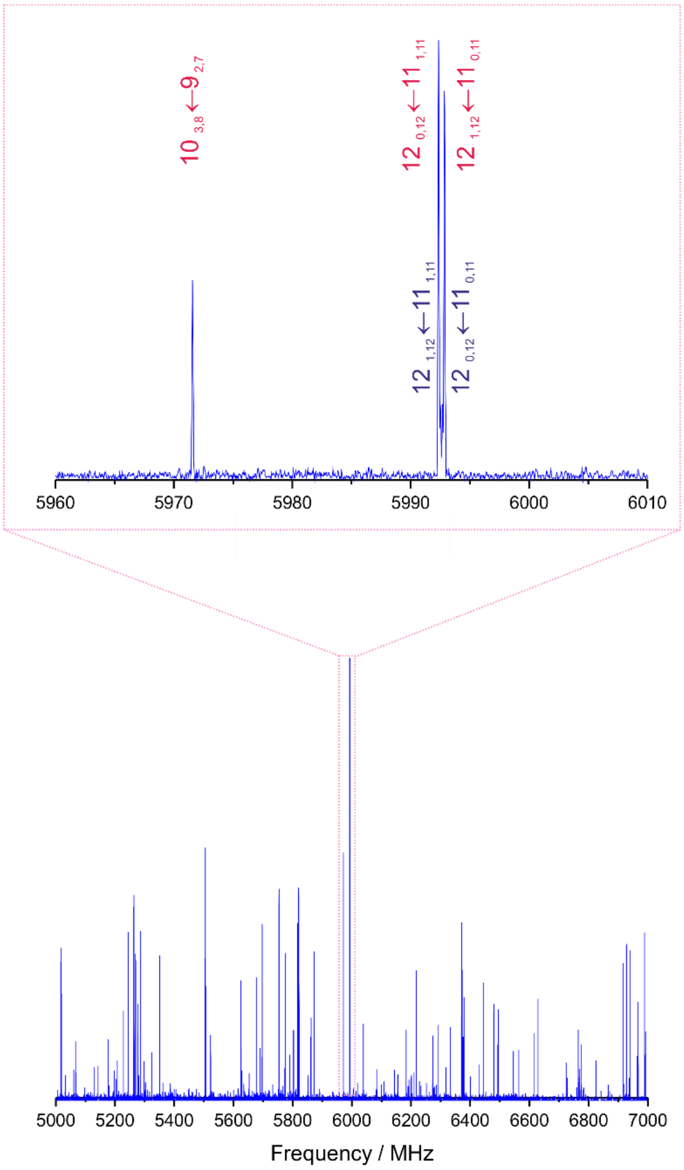


Figure S2. A 2 GHz section of the rotational spectrum of phenyl saligenin phosphate (PSP, lower trace), and a 50 MHz expansion (upper trace) with typical μ_a (blue), μ_b (red) and μ_c (green) rotational transitions (labelled with quantum numbers $J'_{K_a',K_c'} \leftarrow J''_{K_a'',K_c''}$).

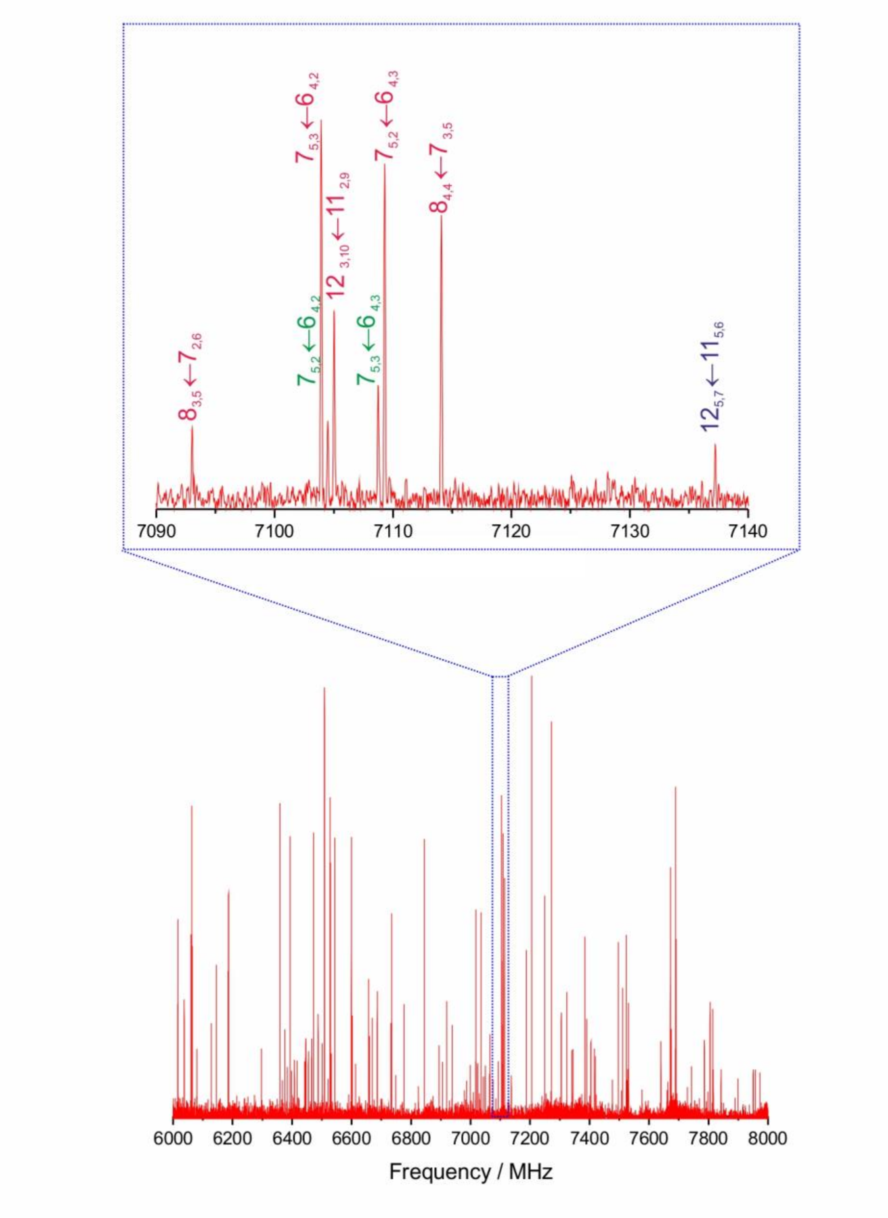


Figure S3. Alternative view to Figure 1 of the molecular conformations of cresyl (CBDP, left column) and phenyl (PSP, right column) saligenin phosphates. The lowest lying conformations of CBDP and PSP exhibit a half-chair conformation of the six-memebered 1,3,2-dioxaphosphorinane ring. A second near-boat phosphorinane conformation is predicted for CBDP. For each ring conformation the phenyl/cresyl rings adopt two possible orientations. Conformational energies calculated according to B3LYP-D3(BJ)/cc-pV(T+d)Z (cc-pVTZ for the C, H, O atoms).

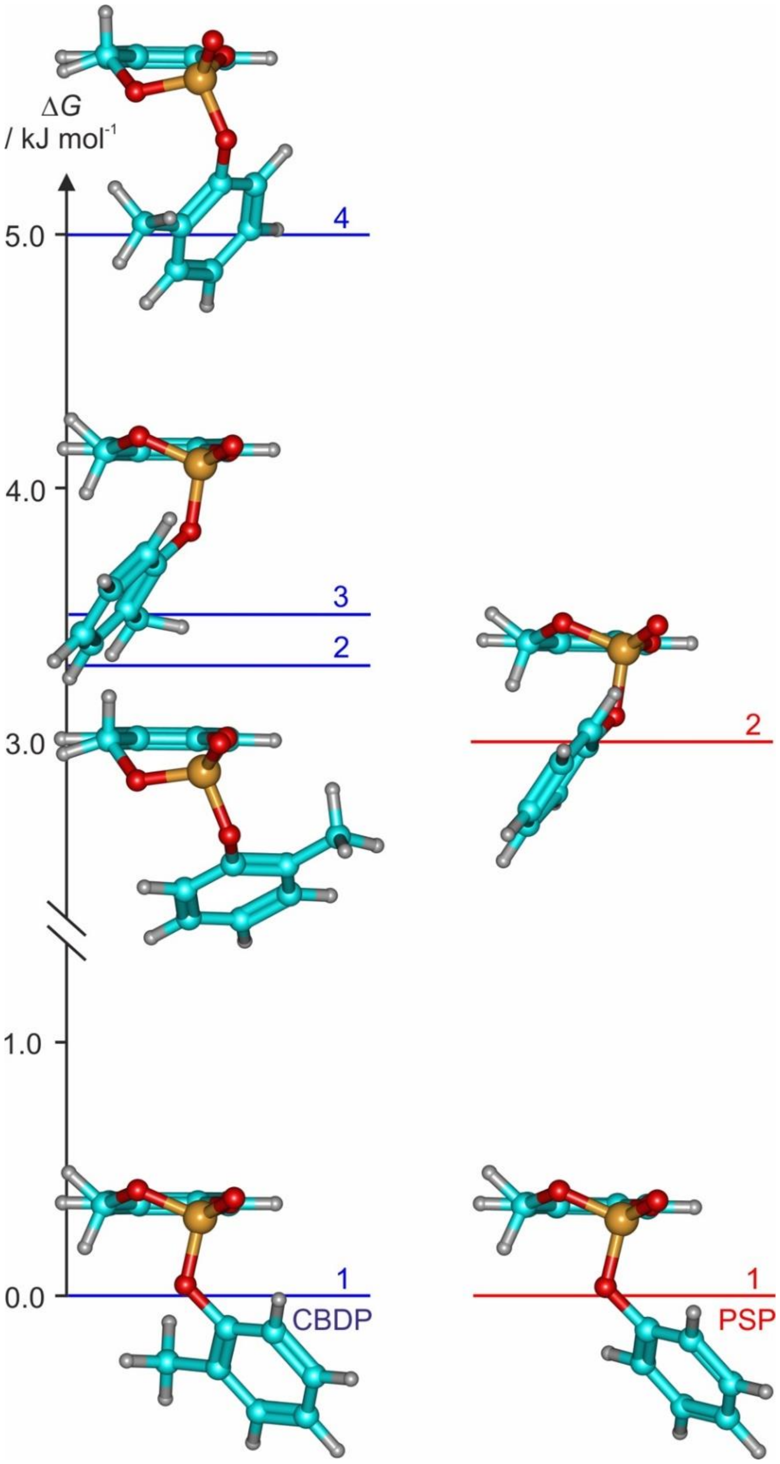


Figure S4. Optimized structure of cresyl saligenin phosphate (CBDP) according to B3LYP-D3(BJ)/cc-PV(T+d)Z calculations (cc-PVTZ for the C, H, O atoms). The figure is rotatable in the pdf file.

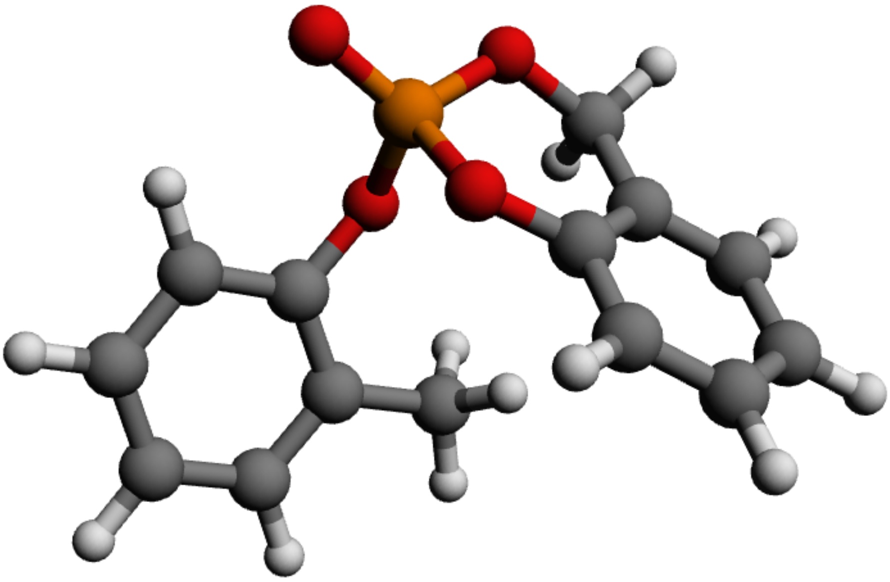


Figure S5. Optimized structure of phenyl saligenin phosphate (PSP) according to B3LYP-D3(BJ)/cc-PV(T+d)Z calculations (cc-PVTZ for the C, H, O atoms). The figure is rotatable in the pdf file.

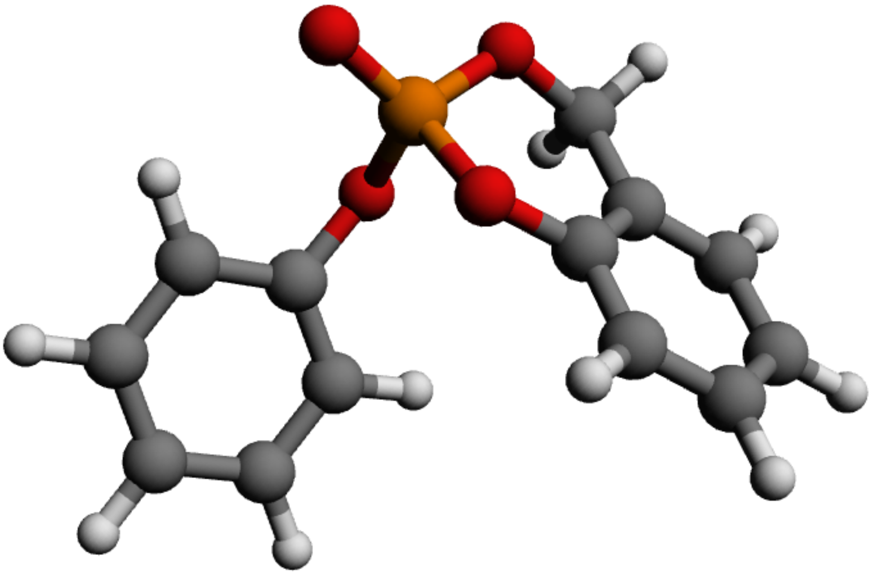
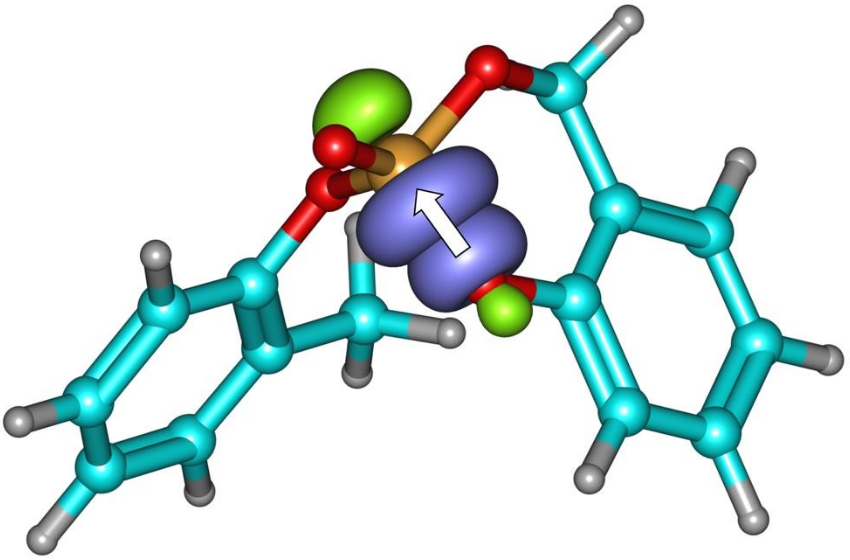


Figure S6. The most relevant donor-acceptor hyperconjugative interaction in cresyl (upper figure) and phenyl (lower figure) saligenin phosphate (B3LYP-D3(BJ)/def2-TZVP), according to second order perturbation theory analysis of the Fock matrix in the NBO basis in Tables S15 and S16 In both molecules the lp$_\sigma$ lone pair at the O(1) atom is predicted to donate to the unoccupied lp$_\sigma$* lone pair at the phosphorous atom.



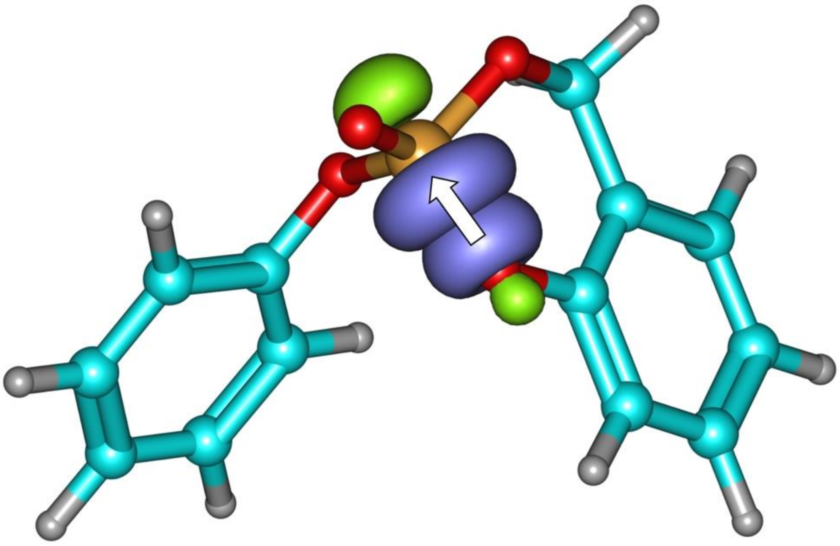


Table S1. Theoretical prediction of the rotational parameters of cresyl saligenin phosphate (CBDP) using the calculation level B3LYP-D3(BJ)/def2TZVP.

	Theory			
	Isomer 1	Isomer 2	Isomer 3	Isomer 4
A / MHz[a]	560.7 [1.2%][c]	447.3 [-19.2%]	668.2 [20.6%]	478.3 [-13.6%]
B / MHz	302.5 [-2.5%]	427.2 [37.8%]	260.9 [-15.9%]	352.8 [13.8%]
C / MHz	239.6 [-1.7%]	292.4 [20.0%]	218.3 [-10.4%]	264.8 [8.7%]
D_J / kHz	0.074	0.094	0.048	0.090
D_{JK} / kHz	-0.37	-0.109	-0.31	-0.080
D_K / kHz	0.57	0.038	0.63	0.033
d_1 / kHz	-0.023	0.044	-0.0142	0.0172
d_2 / kHz	-0.00051	-0.0110	-0.00043	-0.039
$\|\mu_a\|$ / D	2.3	0.3	1.4	1.7
$\|\mu_b\|$ / D	4.8	6.0	5.4	5.0
$\|\mu_c\|$ / D	1.9	0.9	1.3	2.8
ΔE / kJ mol^{-1} [b]	0.0	2.8	3.6	5.1
ΔG / kJ mol^{-1}	0.0	3.6	3.2	4.8

[a] Rotational constants (A, B, C), Watson's S-reduction centrifugal distortion constants (D_J, D_{JK}, D_K, d_1, d_2) and electric dipole moments (μ_α, α = a, b, c). [b] Relative energies corrected with the zero-point energy (ZPE), Gibbs energy (ΔG, 298K, 1 atm). [c] Relative deviations with the experimental observations in square brackets.

Table S2. Theoretical prediction of the rotational parameters of cresyl saligenin phosphate (CBDP) using the calculation level MP2/def2-TZVP.

	Theory			
	Isomer 1	Isomer 2	Isomer 3	Isomer 4
A / MHz[a]	519.3 [-6.2%][c]	485.2 [-12.4%]	638.7 [15.3%]	458.5 [-17.2%]
B / MHz	353.4 [14.0%]	447.9 [44.4%]	283.7 [-8.5%]	402.5 [29.8%]
C / MHz	261.4 [7.3%]	303.3 [24.5%]	229.9 [-5.7%]	287.2 [17.8%]
D_J / kHz	0.072	0.036	0.032	0.087
D_{JK} / kHz	-0.077	-0.048	-0.178	-0.078
D_K / kHz	0.033	0.023	0.33	0.027
d_1 / kHz	0.0034	-0.0148	-0.0096	0.022
d_2 / kHz	-0.032	-0.0049	-0.00023	-0.0141
$\|\mu_a\|$ / D	2.2	4.3	1.3	3.7
$\|\mu_b\|$ / D	5.2	4.4	5.6	4.0
$\|\mu_c\|$ / D	1.6	0.0	1.3	3.0
ΔE / kJ mol^{-1} [b]	2.1	0.0	6.4	8.0
ΔG / kJ mol^{-1}	0.0	0.9	4.7	5.2

[a] Rotational constants (A, B, C), Watson's S-reduction centrifugal distortion constants (D_J, D_{JK}, D_K, d_1, d_2) and electric dipole moments (μ_α, α = a, b, c). [b] Relative energies corrected with the zero-point energy (ZPE), Gibbs energy (ΔG, 298K, 1 atm). [c] Relative deviations with the experimental observations in square brackets.

Table S3. Theoretical prediction of the rotational parameters of cresyl saligenin phosphate (CBDP) using the calculation level MP2/cc-PV(T+d)Z on the P atom and cc-PVTZ for the C, H, O atoms.

	Theory			
	Isomer 1	Isomer 2	Isomer 3	Isomer 4
A / MHz[a]	521.1 [-5.9%%][c]	483.7 [-12.7%]	644.3 [16.3%]	457.9 [-17.3%]
B / MHz	351.9 [13.5%]	447.3 [44.2%]	281.8 [-9.1%]	400.5 [29.1%]
C / MHz	260.9 [7.1%]	303.6 [24.6%]	229.0 [-6.0%]	286.4 [17.5 %]
D_J / kHz	0.072	0.038	0.031	0.084
D_{JK} / kHz	-0.077	-0.051	-0.172	-0.076
D_K / kHz	0.033	0.024	0.33	0.029
d_1 / kHz	0.0022	-0.0157	-0.0093	0.024
d_2 / kHz	-0.032	-0.0053	-0.00025	-0.0173
$\lvert\mu_a\rvert$ / D	2.2	4.3	1.3	2.6
$\lvert\mu_b\rvert$ / D	5.0	4.2	5.4	4.8
$\lvert\mu_c\rvert$ / D	1.6	0.1	1.3	2.6
ΔE / kJ mol^{-1} [b]	1.0	0.0	5.3	7.7
ΔG / kJ mol^{-1}	0.0	2.1	5.0	6.4

[a] Rotational constants (A, B, C), Watson's S-reduction centrifugal distortion constants (D_J, D_{JK}, D_K, d_1, d_2) and electric dipole moments (μ_α, α = a, b, c). [b] Relative energies corrected with the zero-point energy (ZPE), Gibbs energy (ΔG, 298K, 1 atm). [c] Relative deviations with the experimental observations in square brackets.

Table S4. Theoretical prediction of the rotational parameters of phenyl saligenin phosphate (PSP) using the calculation level B3LYP/def2-TZVP.

	Theory	
	Isomer 1	Isomer 2
A / MHz [a]	627.8 [-0.1%][d]	862.7 [37.2%]
B / MHz	320.1 [-1.7%]	245.0 [-24.8%]
C / MHz	247.9 [-1.1%]	216.5 [-13.6%]
D_J / kHz	0. 157	0.043
D_{JK} / kHz	-0. 80	-0.49
D_K / kHz	1.20	1.80
d_1 / kHz	-0.060	-0.0116
d_2 / kHz	-0.0022	-0.00030
$\|\mu_a\|$ / D	2.1	1.4
$\|\mu_b\|$ / D	4.4	5.0
$\|\mu_c\|$ / D	2.2	0.7
ΔE / kJ mol^{-1} [b]	0.0	2.0
ΔG / kJ mol^{-1}	0.0	2.2

[a] Rotational constants (A, B, C), Watson's S-reduction centrifugal distortion constants (D_J, D_{JK}, D_K, d_1, d_2) and electric dipole moments (μ_α, α = a, b, c). [b] Relative energies corrected with the zero-point energy (ZPE), Gibbs energy (ΔG, 298K, 1 atm). [c] Relative deviations with the experimental observations in square brackets.

Table S5. Theoretical prediction of the rotational parameters of phenyl saligenin phosphate (PSP) using the calculation level MP2/def2-TZVP.

	Theory	
	Isomer 1	Isomer 2
A / MHz [a]	560.1 [-10.9%][d]	787.7 [25.3%]
B / MHz	401.8 [23.4%]	270.9 [-16.8%]
C / MHz	277.7 [10.8%]	230.6 [-8.0%]
D_J / kHz	0.21	0.039
D_{JK} / kHz	-0.29	-0.33
D_K / kHz	0.135	0.90
d_1 / kHz	0.048	-0.0117
d_2 / kHz	-0.093	-0.00040
$\lvert\mu_a\rvert$ / D	1.6	1.2
$\lvert\mu_b\rvert$ / D	5.2	5.3
$\lvert\mu_c\rvert$ / D	1.9	0.8
ΔE / kJ mol^{-1} [b]	0.0	5.0
ΔG / kJ mol^{-1}	0.0	5.0

[a] Rotational constants (A, B, C), Watson's S-reduction centrifugal distortion constants (D_J, D_{JK}, D_K, d_1, d_2) and electric dipole moments (μ_α, α = a, b, c). [b] Relative energies corrected with the zero-point energy (ZPE), Gibbs energy (ΔG, 298K, 1 atm). [c] Relative deviations with the experimental observations in square brackets.

Table S6. Theoretical prediction of the rotational parameters of phenyl saligenin phosphate (PSP) using the calculation level MP2/cc-PV(T+d)Z on the P atom and cc-PVTZ for the C, H, O atoms.

	Theory	
	Isomer 1	Isomer 2
A / MHz [a]	568.0 [-9.7%][d]	794.5 [26.4%]
B / MHz	392.1 [20.4%]	269.5 [-17.3%]
C / MHz	274.7 [9.6%]	230.0 [-8.3%]
D_J / kHz	0.178	0.036
D_{JK} / kHz	-0.23	-0.31
D_K / kHz	0.105	0.88
d_1 / kHz	0.033	-0.0108
d_2 / kHz	-0.085	-0.00037
$\|\mu_a\|$ / D	2.1	1.2
$\|\mu_b\|$ / D	4.8	5.2
$\|\mu_c\|$ / D	1.8	0.7
ΔE / kJ mol^{-1} [b]	0.0	4.3
ΔG / kJ mol^{-1}	0.0	4.4

[a] Rotational constants (A, B, C), Watson's S-reduction centrifugal distortion constants (D_J, D_{JK}, D_K, d_1, d_2) and electric dipole moments (μ_α, α = a, b, c). [b] Relative energies corrected with the zero-point energy (ZPE), Gibbs energy (ΔG, 298K, 1 atm). [c] Relative deviations with the experimental observations in square brackets.

Table S7. Measured rotational transition frequencies (Freq.) of cresyl saligenin phosphate (CBDP), and residuals (observed-calculated) according to fit of Table 1.

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	Freq./ MHz	Residual / MHz
8	0	8	7	1	7	4036.7639	-0.0032
8	0	8	7	0	7	4046.1467	-0.0035
8	1	8	7	0	7	4050.4046	-0.0042
7	2	6	6	1	5	4066.3784	0.0007
7	2	5	6	2	4	4090.5224	-0.0052
5	3	2	4	2	2	4096.5797	0.0157
4	4	1	3	3	0	4154.9651	0.0013
4	4	0	3	3	1	4156.3866	-0.0422
8	1	7	7	2	6	4199.0423	0.0297
5	3	3	4	2	3	4218.6733	0.0173
6	2	4	5	1	4	4236.6507	-0.0088
8	2	7	7	2	6	4299.0624	0.0115
8	1	7	7	1	6	4373.0260	-0.0195
8	3	6	7	3	5	4459.2037	0.0034
8	2	7	7	1	6	4473.1042	0.0204
8	5	4	7	5	3	4488.5477	0.0095
8	5	3	7	5	2	4490.7503	0.0013
8	4	5	7	4	4	4499.6558	-0.0071
9	0	9	8	1	8	4527.7071	0.0022
9	1	9	8	1	8	4529.5804	-0.0066
9	0	9	8	0	8	4531.9652	0.0016
9	1	9	8	0	8	4533.8506	0.0049
8	4	4	7	4	3	4535.1332	0.0120
6	3	3	5	2	3	4605.5857	0.0155
8	2	6	7	2	5	4647.8373	-0.0090
8	3	5	7	3	4	4656.1094	-0.0098
5	4	2	4	3	1	4706.9866	0.0036
5	4	1	4	3	2	4717.3040	0.0027
9	1	8	8	2	7	4747.4650	-0.0153
6	3	4	5	2	4	4833.3524	-0.0157
9	2	8	8	1	7	4901.1071	0.0394
7	3	5	6	2	4	4908.6120	-0.0407
7	2	5	6	1	5	4933.6002	-0.0179
9	3	7	8	3	6	4996.3319	0.0039
10	0	10	9	1	9	5016.6662	-0.0101
10	1	10	9	1	9	5017.4876	-0.0036
10	0	10	9	0	9	5018.5657	0.0073
10	1	10	9	0	9	5019.3731	-0.0003
9	7	3	8	7	2	5032.9178	-0.0110
9	7	2	8	7	1	5032.9178	-0.0176
9	5	5	8	5	4	5060.8141	0.0007
9	4	6	8	4	5	5066.8625	0.0413
9	5	4	8	5	3	5067.7016	-0.0066
7	3	4	6	2	4	5130.9474	0.0016
9	4	5	8	4	4	5142.6923	-0.0117
9	2	7	8	2	6	5177.1121	-0.0019
7	1	6	6	0	6	5207.4384	0.0386
10	2	8	9	3	7	5228.6126	-0.0099
6	4	3	5	3	2	5244.8736	0.0069
9	3	6	8	3	5	5269.0017	-0.0051
10	1	9	9	2	8	5270.0434	0.0068

8	3	6	7	2	5	5277.3088	-0.0165
6	4	3	5	3	3	5280.2997	0.0011
6	4	2	5	3	3	5285.7591	0.0003
10	2	9	9	2	8	5297.2413	0.0264
10	2	9	9	1	8	5350.7715	0.0074
11	0	11	10	1	10	5504.7166	-0.0135
11	1	11	10	1	10	5505.0777	0.0003
11	0	11	10	0	10	5505.5254	-0.0197
11	1	11	10	0	10	5505.8909	-0.0014
10	3	8	9	3	7	5522.8778	-0.0043
10	8	3	9	8	2	5590.1896	0.0084
10	8	2	9	8	1	5590.1896	0.0078
10	7	4	9	7	3	5600.0645	0.0064
10	7	3	9	7	2	5600.0645	-0.0282
10	6	5	9	6	4	5615.3692	0.0077
10	6	4	9	6	3	5616.4327	-0.0011
9	3	7	8	2	6	5625.8067	-0.0002
10	4	7	9	4	6	5628.9783	-0.0092
10	5	6	9	5	5	5635.2230	-0.0099
10	5	5	9	5	4	5653.4044	-0.0011
10	2	8	9	2	7	5677.3124	-0.0030
8	2	6	7	1	6	5689.1029	-0.0168
8	3	5	7	2	5	5696.5365	-0.0008
7	4	4	6	3	3	5753.8977	0.0030
7	4	3	6	3	3	5773.2116	-0.0014
11	1	10	10	2	9	5776.1948	0.0021
11	2	10	10	2	9	5789.4569	0.0058
11	1	10	10	1	9	5803.3802	0.0090
11	2	10	10	1	9	5816.6338	0.0042
6	5	2	5	4	1	5819.9922	-0.0049
7	4	4	6	3	4	5853.1301	-0.0011
11	2	9	10	3	8	5861.0139	-0.0098
10	3	7	9	3	6	5862.4302	-0.0121
7	4	3	6	3	4	5872.4474	-0.0022
10	3	8	9	2	7	5971.5763	0.0012
12	0	12	11	1	11	5992.3598	-0.0104
12	1	12	11	1	11	5992.5096	-0.0065
12	0	12	11	0	11	5992.6971	-0.0203
12	1	12	11	0	11	5992.8507	-0.0127
8	1	7	7	0	7	6018.6933	0.0005
11	3	9	10	3	8	6039.0919	0.0076
12	3	9	11	4	8	6084.2735	0.0157
8	2	7	7	1	7	6109.3589	0.0111
8	3	6	7	2	6	6144.5649	-0.0009
11	2	9	10	2	8	6155.2836	0.0002
11	4	8	10	4	7	6183.3375	0.0075
11	6	6	10	6	5	6189.7141	0.0141
11	6	5	10	6	4	6192.9973	-0.0013
11	5	7	10	5	6	6210.1903	-0.0010
8	4	5	7	3	4	6218.1511	0.0056
11	5	6	10	5	5	6251.7827	-0.0118
12	1	11	11	2	10	6272.9887	0.0095
12	2	11	11	2	10	6279.2460	-0.0074
12	1	11	11	1	10	6286.2372	-0.0002
12	2	11	11	1	10	6292.5195	0.0078
9	3	6	8	2	6	6317.6899	-0.0079
11	3	9	10	2	8	6333.3534	0.0096
6	6	1	5	5	0	6371.1246	0.0008
6	6	0	5	5	0	6371.1246	0.0000
6	6	1	5	5	1	6371.1246	-0.0097
6	6	0	5	5	1	6371.1246	-0.0105

7	5	3	6	4	2	6373.0258	-0.0035
7	5	2	6	4	2	6373.7371	0.0238
7	5	3	6	4	3	6378.4960	0.0065
7	5	2	6	4	3	6379.1758	0.0023
11	4	7	10	4	6	6400.3187	-0.0140
11	3	8	10	3	7	6429.2308	-0.0111
12	2	10	11	3	9	6445.4892	-0.0257
9	2	7	8	1	7	6493.1847	-0.0035
8	4	4	7	3	5	6495.2196	0.0045
12	3	10	11	3	9	6546.1277	0.0047
9	4	6	8	3	5	6628.8619	0.0145
12	3	10	11	2	9	6724.2125	0.0290
12	8	5	11	8	4	6724.9712	0.0164
12	8	4	11	8	3	6724.9712	-0.0009
12	4	9	11	4	8	6727.6747	0.0068
9	4	5	8	3	5	6759.5242	0.0173
13	1	12	12	2	11	6764.7907	0.0030
12	6	7	11	6	6	6766.9267	0.0058
13	2	12	12	2	11	6767.6883	0.0021
13	1	12	12	1	11	6771.0802	0.0182
13	2	12	12	1	11	6773.9678	0.0072
12	6	6	11	6	5	6775.7680	-0.0093
12	5	8	11	5	7	6783.2915	0.0022
13	3	10	12	4	9	6824.3532	0.0034
9	3	7	8	2	7	6841.8443	0.0014
12	5	7	11	5	6	6866.9649	-0.0126
8	5	4	7	4	3	6917.2320	0.0078
8	5	3	7	4	3	6920.1363	0.0175
8	5	4	7	4	4	6936.5500	0.0074
8	5	3	7	4	4	6939.4447	0.0074
12	3	9	11	3	8	6964.7304	-0.0011
10	4	7	9	3	6	6988.8075	-0.0206
13	2	11	12	3	10	6991.9643	0.0023
10	3	7	9	2	7	7003.0167	-0.0093
12	4	8	11	4	7	7027.1346	0.0013
13	3	11	12	3	10	7045.8315	0.0007
9	4	6	8	3	6	7048.0617	0.0023
13	2	11	12	2	10	7092.5308	-0.0393
13	3	11	12	2	10	7146.4494	0.0105
14	1	13	13	2	12	7254.1016	0.0048
14	2	13	13	2	12	7255.4310	0.0212
14	1	13	13	1	12	7256.9896	-0.0057
10	4	6	9	3	6	7257.7106	-0.0090
14	2	13	13	1	12	7258.3112	0.0029
13	4	10	12	4	9	7260.8054	0.0019
13	9	5	12	9	4	7280.8281	-0.0199
13	9	4	12	9	3	7280.8281	-0.0218
11	4	8	10	3	7	7309.6752	-0.0405
13	7	7	12	7	6	7317.8234	0.0041
13	7	6	12	7	5	7319.3539	-0.0007
10	2	8	9	1	8	7322.9935	0.0085
13	6	8	12	6	7	7346.2500	0.0114
13	5	9	12	5	8	7351.6537	0.0299
13	6	7	12	6	6	7367.4197	0.0062
9	5	5	8	4	4	7442.9152	-0.0011
9	5	4	8	4	4	7452.7188	0.0128
15	0	15	14	1	14	7454.5488	0.0065
15	1	15	14	1	14	7454.5488	-0.0037
15	0	15	14	0	14	7454.5488	-0.0185
15	1	15	14	0	14	7454.5488	-0.0287
13	3	10	12	3	9	7467.7540	-0.0058

7	7	0	6	6	0	7478.7584	-0.0005
7	7	1	6	6	0	7478.7576	-0.0011
7	7	1	6	6	1	7478.7576	-0.0020
7	7	0	6	6	1	7478.7576	-0.0020
8	6	3	7	5	2	7484.6805	-0.0055
8	6	2	7	5	3	7485.4342	-0.0109
9	5	5	8	4	5	7497.6906	-0.0024
13	5	8	12	5	7	7499.7996	-0.0139
9	5	4	8	4	5	7507.4785	-0.0040
14	3	11	13	4	10	7507.8364	-0.0003
14	2	12	13	3	11	7512.5676	0.0100
10	3	8	9	2	8	7563.6815	-0.0139
14	2	12	13	2	11	7566.4195	-0.0067
14	3	12	13	2	11	7594.1091	0.0054
13	4	9	12	4	8	7633.7405	-0.0133
15	1	14	14	2	13	7742.2071	-0.0021
15	2	14	14	1	13	7744.1137	0.0062
11	3	8	10	2	8	7754.9582	0.0055
13	4	10	12	3	9	7904.2111	-0.0024
14	5	10	13	5	9	7912.2977	0.0162
10	5	6	9	4	5	7935.4541	0.0088
16	0	16	15	1	15	7941.8622	0.0018
16	1	16	15	1	15	7941.8622	-0.0023
16	0	16	15	0	15	7941.8622	-0.0083
16	1	16	15	0	15	7941.8622	-0.0125
10	4	6	9	3	7	7949.5980	-0.0124

Table S8. Measured rotational transition frequencies (Freq.) of phenyl saligenin phosphate (parent), and residuals (observed-calculated) according to fit of Table 2.

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	Freq./ MHz	Residual / MHz
11	2	10	10	2	9	6015.3041	-0.0024
11	2	9	10	3	8	6016.4725	0.0002
11	1	10	10	1	9	6037.4015	-0.0001
11	2	10	10	1	9	6060.5249	0.0016
9	3	7	8	2	6	6062.8049	-0.0013
8	2	6	7	1	6	6064.4416	0.0035
12	3	9	11	4	8	6080.1833	0.0029
10	3	7	9	3	6	6128.3889	-0.0044
8	3	5	7	2	5	6145.7336	-0.0013
12	0	12	11	1	11	6184.8345	-0.0010
12	1	12	11	1	11	6185.1287	0.0073
12	0	12	11	0	11	6185.4838	-0.0024
12	1	12	11	0	11	6185.7785	0.0063
7	3	4	6	2	5	6186.3227	0.0022
11	3	9	10	3	8	6296.7284	0.0042
7	4	4	6	3	3	6358.9599	-0.0006
7	4	3	6	3	3	6376.0768	0.0048
14	10	5	14	9	5	6384.1840	0.0076
15	10	6	15	9	6	6367.4420	0.0179
15	10	5	15	9	6	6367.4420	0.0173
15	10	6	15	9	7	6367.4420	-0.0063
15	10	5	15	9	7	6367.4420	-0.0069
14	10	4	14	9	5	6384.1840	0.0075
14	10	5	14	9	6	6384.1840	0.0014
14	10	4	14	9	6	6384.1840	0.0013
10	3	8	9	2	7	6393.5612	-0.0006
13	10	3	13	9	4	6397.6394	-0.0009
13	10	4	13	9	4	6397.6394	-0.0009
13	10	3	13	9	5	6397.6394	-0.0023
13	10	4	13	9	5	6397.6394	-0.0023
11	9	2	10	9	1	6398.4530	-0.0066
11	9	3	10	9	2	6398.4530	-0.0066
11	8	3	10	8	2	6407.5620	0.0015
11	8	4	10	8	3	6407.5620	0.0038
12	10	2	12	9	3	6408.3029	-0.0067
12	10	3	12	9	3	6408.3029	-0.0067
12	10	2	12	9	4	6408.3029	-0.0070
12	10	3	12	9	4	6408.3029	-0.0069
11	10	1	11	9	2	6416.6146	-0.0038
11	10	2	11	9	3	6416.6146	-0.0038
11	6	6	10	6	5	6442.0499	-0.0053
11	6	5	10	6	4	6444.5339	0.0013
11	4	8	10	4	7	6446.2176	-0.0022
11	2	9	10	2	8	6454.8372	-0.0031
7	4	4	6	3	4	6455.5817	-0.0031
8	1	7	7	0	7	6465.9991	-0.0078
11	5	7	10	5	6	6466.1192	0.0030
7	4	3	6	3	4	6472.6951	-0.0011
11	5	6	10	5	5	6501.0050	0.0036

14	3	11	13	4	9	6508.5977	-0.0002
12	1	11	11	2	10	6509.0258	0.0010
12	2	11	11	2	10	6520.4795	-0.0040
6	5	2	5	4	1	6527.8850	-0.0092
6	5	1	5	4	1	6528.0129	0.0254
6	5	2	5	4	2	6528.8505	-0.0231
6	5	1	5	4	2	6528.9708	0.0038
12	1	11	11	1	10	6532.1401	-0.0062
12	2	11	11	1	10	6543.6057	0.0005
8	2	7	7	1	7	6602.1052	-0.0032
14	4	10	13	5	9	6613.3416	0.0014
12	2	10	11	3	9	6657.4810	0.0008
11	4	7	10	4	6	6659.7274	0.0001
8	3	6	7	2	6	6669.5967	-0.0036
13	0	13	12	1	12	6686.3628	-0.0009
13	1	13	12	1	12	6686.4735	-0.0145
13	0	13	12	0	12	6686.6496	0.0000
13	1	13	12	0	12	6686.7725	-0.0014
11	3	8	10	3	7	6732.7326	0.0017
11	3	9	10	2	8	6735.0925	0.0003
9	3	6	8	2	6	6776.0637	-0.0003
12	3	10	11	3	9	6824.7765	0.0033
8	4	5	7	3	4	6845.0261	-0.0004
8	4	4	7	3	4	6894.0187	0.0034
13	3	10	12	4	9	6905.1693	-0.0043
9	2	7	8	1	7	6920.2633	0.0026
12	2	10	11	2	9	6937.7292	-0.0028
12	9	4	11	9	3	6987.1505	-0.0052
12	9	3	11	9	2	6987.1505	-0.0054
12	8	5	11	8	4	6999.0882	0.0037
12	8	4	11	8	3	6999.0882	-0.0071
18	11	8	18	10	9	7009.5176	-0.0139
12	7	6	11	7	5	7016.9122	-0.0071
12	4	9	11	4	8	7017.1149	-0.0021
12	7	5	11	7	4	7017.2746	0.0094
13	1	12	12	2	11	7018.1380	0.0006
13	2	12	12	2	11	7023.6833	0.0054
17	11	7	17	10	7	7031.0539	0.0065
17	11	6	17	10	7	7031.0539	0.0062
17	11	7	17	10	8	7031.0539	-0.0037
17	11	6	17	10	8	7031.0539	-0.0040
13	2	12	12	1	11	7035.1390	0.0024
12	6	7	11	6	6	7043.1336	0.0014
16	11	5	16	10	6	7048.9760	0.0031
16	11	6	16	10	6	7048.9760	0.0032
16	11	5	16	10	7	7048.9760	0.0004
16	11	6	16	10	7	7048.9760	0.0005
12	6	6	11	6	5	7049.8460	0.0024
15	11	4	15	10	5	7063.7572	0.0065
15	11	5	15	10	5	7063.7572	0.0065
15	11	4	15	10	6	7063.7572	0.0058
15	11	5	15	10	6	7063.7572	0.0059
8	4	5	7	3	5	7065.0940	0.0012
12	5	8	11	5	7	7065.2894	0.0020
14	11	3	14	10	4	7075.8121	0.0096
14	11	4	14	10	4	7075.8121	0.0096
14	11	3	14	10	5	7075.8121	0.0094
14	11	4	14	10	5	7075.8121	0.0094

13	11	2	13	10	3	7085.5164	0.0123
13	11	2	13	10	4	7085.5164	0.0122
13	11	3	13	10	3	7085.5164	0.0123
13	11	3	13	10	4	7085.5164	0.0122
8	3	5	7	2	6	7093.0380	0.0018
12	11	1	12	10	2	7093.1737	-0.0195
7	5	3	6	4	2	7103.9327	-0.0044
7	5	2	6	4	2	7104.4901	0.0008
12	3	10	11	2	9	7105.0250	0.0000
7	5	3	6	4	3	7108.7372	-0.0081
7	5	2	6	4	3	7109.2965	-0.0009
8	4	4	7	3	5	7114.0812	-0.0003
12	5	7	11	5	6	7137.2311	0.0049
14	0	14	13	1	13	7187.7690	0.0198
14	1	14	13	0	13	7187.9035	-0.0234
6	6	1	5	5	0	7205.8623	0.0000
6	6	0	5	5	0	7205.8623	-0.0005
6	6	1	5	5	1	7205.8623	-0.0084
6	6	0	5	5	1	7205.8623	-0.0090
13	2	11	12	3	10	7249.4637	0.0008
9	4	6	8	3	5	7272.2369	-0.0005
12	3	9	11	3	8	7305.0824	0.0057
12	4	8	11	4	7	7323.8518	0.0011
9	1	8	8	0	8	7340.8262	-0.0055
13	3	11	12	3	10	7343.8914	0.0049
9	4	5	8	3	5	7390.8779	0.0019
9	3	7	8	2	7	7404.8984	0.0018
13	2	11	12	2	10	7416.7566	0.0007
9	2	8	8	1	8	7418.7182	0.0030
10	3	7	9	2	7	7477.1256	0.0093
13	3	11	12	2	10	7511.1800	0.0005
14	1	13	13	2	12	7523.1468	0.0000
14	2	13	13	2	12	7525.7765	0.0039
14	1	13	13	1	12	7528.6930	0.0058
14	2	13	13	1	12	7531.3154	0.0023
13	4	10	12	4	9	7576.3899	-0.0021
13	9	5	12	9	4	7577.7165	-0.0005
13	9	4	12	9	3	7577.7165	-0.0017
13	7	6	12	7	5	7616.8763	-0.0040
10	4	7	9	3	6	7639.8016	0.0009
13	6	8	12	6	7	7646.9552	0.0073
13	5	9	12	5	8	7660.8479	0.0021
13	6	7	12	6	6	7663.1973	-0.0047
8	5	4	7	4	3	7671.7485	0.0005
8	5	3	7	4	3	7674.1016	0.0083
14	3	11	13	4	10	7674.6561	-0.0089
8	5	4	7	4	4	7688.8600	0.0006
8	5	3	7	4	4	7691.2024	-0.0022
14	2	12	13	3	11	7805.0986	-0.0024
9	4	5	8	3	6	7814.3140	0.0022
10	2	8	9	1	8	7816.2076	0.0031
13	3	10	12	3	9	7842.1082	-0.0022
14	2	12	13	2	11	7899.5206	-0.0039
14	3	12	13	2	11	7950.5495	0.0045
11	4	8	10	3	7	7957.6281	0.0009
13	4	9	12	4	8	7972.7271	-0.0043

Table S9. Atomic coordinates of isomer 1 of cresyl saligenin phosphate (B3LYP-D3(BJ)/cc-pV(T+d)Z) in the principal inertial axes system.

Atom	a / Å	b / Å	c / Å
P	-0.0011	-1.7575	0.1425
O	-1.1910	-2.1634	-0.8099
O	0.8396	-0.7997	-0.8222
O	0.7004	-2.8507	0.7874
O	-0.6760	-0.7433	1.1885
C	-1.9794	-1.1129	-1.4063
C	-2.9449	2.0997	1.2888
C	-3.6207	1.9677	0.0796
C	-3.3113	0.9158	-0.7685
C	-2.3268	-0.0130	-0.4373
C	-1.6632	0.1404	0.7782
C	-1.9656	1.1844	1.6406
H	-3.1807	2.9144	1.9587
H	-4.3870	2.6775	-0.1972
H	-3.8382	0.8087	-1.7084
H	-1.4225	1.2606	2.5712
C	3.9795	1.6376	0.3810
C	2.9254	2.1509	-0.3645
C	1.8568	1.3501	-0.7627
C	1.8963	0.0088	-0.3858
C	2.9388	-0.5306	0.3503
C	3.9852	0.2964	0.7393
H	4.7940	2.2835	0.6778
H	2.9235	3.1962	-0.6449
H	2.9154	-1.5771	0.6154
H	4.8016	-0.1130	1.3175
C	0.7087	1.8994	-1.5600
H	0.5523	1.3254	-2.4743
H	-0.2232	1.8605	-0.9945
H	0.8950	2.9359	-1.8342
H	-1.4252	-0.7134	-2.2580
H	-2.8794	-1.5991	-1.7757

Table S10. Atomic coordinates of isomer 2 of cresyl saligenin phosphate (B3LYP-D3(BJ)/cc-pV(T+d)Z) in the principal inertial axes system.

Atom	a / Å	b / Å	c / Å
P	-0.5794	1.9241	-0.0328
O	-1.3652	1.3560	1.2290
O	0.9462	1.7873	0.3969
O	-0.9138	3.2553	-0.5008
O	-0.8112	0.7792	-1.1469
C	-2.4943	0.4759	1.0079
C	-1.0564	-2.8639	-1.2500
C	-1.9255	-3.0991	-0.1910
C	-2.4098	-2.0331	0.5580
C	-2.0437	-0.7311	0.2437
C	-1.1726	-0.5213	-0.8204
C	-0.6683	-1.5683	-1.5688
H	-0.6675	-3.6920	-1.8257
H	-2.2163	-4.1096	0.0578
H	-3.0736	-2.2118	1.3940
H	0.0191	-1.3632	-2.3757
C	2.7967	-1.9099	0.7952
C	3.0005	-1.1391	-0.3427
C	2.3893	0.1033	-0.5000
C	1.5682	0.5393	0.5380
C	1.3629	-0.2024	1.6884
C	1.9800	-1.4403	1.8148
H	3.2800	-2.8727	0.8865
H	3.6439	-1.5055	-1.1320
H	0.7163	0.1885	2.4591
H	1.8209	-2.0310	2.7059
C	2.5837	0.9379	-1.7323
H	3.3281	0.4888	-2.3870
H	1.6513	1.0396	-2.2897
H	2.9062	1.9473	-1.4771
H	-2.8668	0.2145	1.9939
H	-3.2715	1.0295	0.4756

Table S11. Atomic coordinates of isomer 3 of cresyl saligenin phosphate (B3LYP-D3(BJ)/cc-pV(T+d)Z) in the principal inertial axes system.

Atom	a / Å	b / Å	c / Å
P	-0.0422	1.6047	-0.1166
O	-0.2041	1.1821	1.4026
O	0.7274	0.3826	-0.8045
O	0.4975	2.9362	-0.3133
O	-1.4946	1.3744	-0.7364
C	-0.7809	-0.1075	1.6871
C	-4.2360	-1.0202	-0.7117
C	-3.9599	-1.7595	0.4339
C	-2.8486	-1.4467	1.2015
C	-1.9928	-0.4070	0.8432
C	-2.2872	0.3143	-0.3118
C	-3.3997	0.0198	-1.0857
H	-5.1031	-1.2517	-1.3141
H	-4.6107	-2.5694	0.7305
H	-2.6368	-2.0139	2.0993
H	-3.5876	0.6121	-1.9693
C	4.3913	-1.1872	0.3460
C	3.3848	-2.0037	-0.1562
C	2.1505	-1.4844	-0.5389
C	1.9682	-0.1082	-0.3995
C	2.9588	0.7293	0.0883
C	4.1774	0.1788	0.4672
H	5.3394	-1.6173	0.6369
H	3.5540	-3.0680	-0.2547
H	2.7753	1.7916	0.1598
H	4.9558	0.8233	0.8507
C	1.0534	-2.3506	-1.0884
H	1.3657	-3.3926	-1.1192
H	0.1452	-2.2816	-0.4873
H	0.7776	-2.0424	-2.0979
H	-0.0097	-0.8689	1.5484
H	-1.0457	-0.0815	2.7417

Table S12. Atomic coordinates of isomer 4 of cresyl saligenin phosphate (B3LYP-D3(BJ)/cc-pV(T+d)Z) in the principal inertial axes system.

Atom	a / Å	b / Å	c / Å
P	0.1313	1.8375	-0.4421
O	-0.0752	1.5162	1.1025
O	1.5145	1.1310	-0.7634
O	0.1006	3.2226	-0.8721
O	-1.0029	0.9363	-1.1515
C	-1.4216	1.2948	1.5823
C	-3.1055	-1.9892	-0.5915
C	-3.3620	-1.8821	0.7706
C	-2.8168	-0.8296	1.4949
C	-2.0267	0.1258	0.8674
C	-1.7755	-0.0069	-0.4949
C	-2.3040	-1.0528	-1.2316
H	-3.5234	-2.8086	-1.1593
H	-3.9780	-2.6179	1.2673
H	-3.0058	-0.7452	2.5573
H	-2.0871	-1.1186	-2.2875
C	2.3844	-2.8456	0.0637
C	2.8496	-1.8379	0.8996
C	2.5636	-0.4954	0.6560
C	1.7883	-0.2108	-0.4664
C	1.3306	-1.1954	-1.3250
C	1.6262	-2.5249	-1.0540
H	2.6216	-3.8776	0.2815
H	3.4509	-2.0914	1.7629
H	0.7516	-0.9120	-2.1909
H	1.2677	-3.3007	-1.7157
C	3.0682	0.6000	1.5492
H	3.7502	0.2008	2.2974
H	3.5912	1.3644	0.9740
H	2.2442	1.0979	2.0606
H	-1.3331	1.1113	2.6492
H	-2.0022	2.2086	1.4322

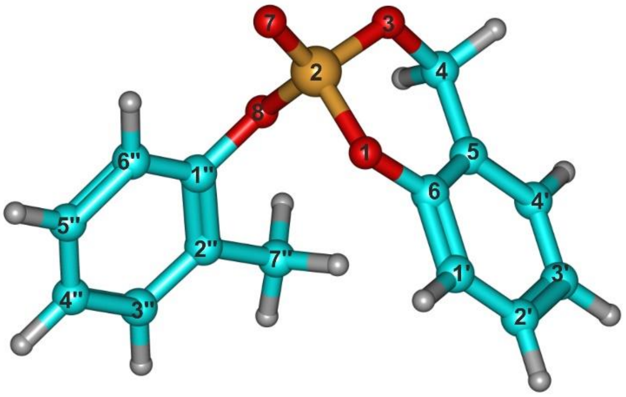
Table S13. Atomic coordinates of isomer 1 of phenyl saligenin phosphate (B3LYP-D3(BJ)/cc-pV(T+d)Z) in the principal inertial axes system..

Atom	a	b	c
P	-0.0872	1.6275	0.2585
O	1.1044	2.1865	-0.6096
O	-0.8331	2.6036	1.0291
O	-0.8871	0.7869	-0.8439
O	0.5958	0.4971	1.1700
C	-3.9504	-1.8837	0.0313
C	-2.8106	-2.3094	-0.6409
C	-1.7851	-1.4133	-0.9156
C	-1.9210	-0.0940	-0.5154
C	-3.0498	0.3531	0.1543
C	-4.0647	-0.5562	0.4277
H	-4.7460	-2.5834	0.2455
H	-2.7146	-3.3411	-0.9498
H	-0.8863	-1.7222	-1.4295
H	-3.1151	1.3863	0.4610
H	-4.9485	-0.2210	0.9523
C	3.6680	-1.9359	-0.2080
C	2.9814	-2.2432	0.9626
C	1.9565	-1.4211	1.4028
C	1.6202	-0.2933	0.6677
C	2.2942	0.0364	-0.5064
C	3.3238	-0.8027	-0.9284
H	4.4705	-2.5722	-0.5528
H	3.2450	-3.1217	1.5344
H	1.4055	-1.6320	2.3076
H	3.8617	-0.5570	-1.8356
C	1.9242	1.2423	-1.3306
H	2.8136	1.7953	-1.6236
H	1.3860	0.9448	-2.2327

Table S14. Atomic coordinates of isomer 2 of phenyl saligenin phosphate (B3LYP-D3(BJ)/cc-pV(T+d)Z) in the principal inertial axes system.

Atom	a / Å	b / Å	c / Å
P	0.0584	-1.3773	-0.0500
O	-0.1776	-0.7406	-1.4820
O	0.6508	-2.7012	-0.0741
O	0.8219	-0.2427	0.7830
O	-1.3704	-1.2967	0.6524
C	4.5918	1.3114	-0.0308
C	4.3331	-0.0233	-0.3169
C	3.0842	-0.5773	-0.0592
C	2.0963	0.2337	0.4818
C	2.3364	1.5679	0.7773
C	3.5912	2.1038	0.5203
H	5.5675	1.7307	-0.2317
H	5.1082	-0.6471	-0.7400
H	2.8770	-1.6169	-0.2648
H	1.5440	2.1630	1.2082
H	3.7843	3.1423	0.7511
C	-4.1800	1.6570	-0.1502
C	-4.3665	0.7546	0.8917
C	-3.4154	-0.2218	1.1449
C	-2.2773	-0.2863	0.3556
C	-2.0690	0.6036	-0.6957
C	-3.0407	1.5724	-0.9360
H	-4.9217	2.4159	-0.3537
H	-5.2542	0.8073	1.5061
H	-3.5344	-0.9390	1.9437
H	-2.8978	2.2660	-1.7551
C	-0.8267	0.5465	-1.5443
H	-1.0693	0.7003	-2.5929
H	-0.1087	1.3123	-1.2417

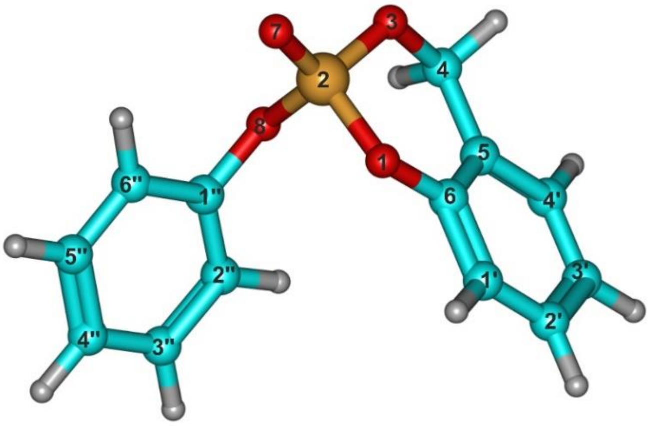
Table S15. Natural bond analysis (NBO) of cresyl saligenin phosphate (B3LYP-D3(BJ)/def2-TZVP). List of most relevant donor-acceptor interactions according to second-order perturbation theory analysis of the Fock matrix in the NBO basis.



Donor NBO (i) [a]	Acceptor NBO (j)	E_2 / kcal mol^{-1}
73. LP(3) O1	63. LP*(1) P2	338.43
69. LP(2) O7	63. LP*(1) P2	45.72
70. LP(3) O7	63. LP*(1) P2	34.3
71. LP(1) O1	63. LP*(1) P2	26.5
67. LP(2) O8	63. LP*(1) P2	23.18
72. LP(2) O1	654. BD*(2) C5-C6	22.05
12. BD(2) C2´-C1´	654. BD*(2) C5-C6	21.88
28. BD(2) C3´´-C2´´	667. BD*(2) C1´´-C6´´	21.5
69. LP(2) O7	636. BD*(1) P2-O8	20.72
70. LP(3) O7	635. BD*(1) P2-O2	20.61

[a] The first digit indicates the NBO number. LP = Lone pair, BD = Bond.

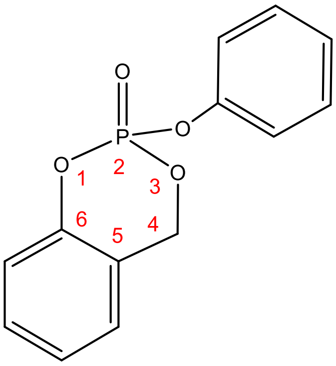
Table S16. Natural bond analysis (NBO) of phenyl saligenin phosphate (B3LYP-D3(BJ)/def2-TZVP). List of most relevant donor-acceptor interactions according to second-order perturbation theory analysis of the Fock matrix in the NBO basis.



Donor NBO (i) [a]	Acceptor NBO (j)	E_2 / kcal mol^{-1}
69. LP(3) O1	59. LP*(1) P2	339.86
63. LP(2) O7	59. LP*(1) P2	48.5
64. LP(3) O7	59. LP*(1) P2	31.54
67. LP(1) O1	59. LP*(1) P2	26.61
11. BD (2)C5´´-C6´´	610. BD*(2) C1´´-C2´´	22.82
66. LP(2) O8	59. LP*(1) P2	22.72
68. LP(2) O1	625. BD*(2) C6-C5	21.9
26. BD(2) C2´-C1´	625. BD*(2) C6-C5	21.82
64. LP(3) O7	595. BD*(1) P2-O3	21.09
8. BD(2) C4´´-C3´´	605. BD*(2) C5´´-C6´´	21.06

[a] The first digit indicates the NBO number. LP = Lone pair, BD = Bond.

Table S17. Comparison of the crystal and equilibrium structures of PSP.



Structural parameters	Equilibrium[a]	Crystal[b]
r(P=O) / Å	1.450	1.448
r(P-O1) / Å	1.605	1.575
r(P-O3) / Å	1.577	1.549
r(P-OPh) / Å	1.601	1.572
∠(O=P-O1) / deg	113.03	112.58
∠(O=P-O3) / deg	116.27	114.54
∠(O=P-OPh) / deg	117.54	116.68
∠(O1-P-O3) / deg	103.94	105.02
∠(P-O3-C4) / deg	118.19	117.72
∠(O3-C4-C5) / deg	112.94	111.21
∠(C4-C5-C6) / deg	122.11	122.70
∠(C5-C6-O1) / deg	121.82	121.89
∠(C6-O1-P) / deg	120.65	120.35
∠(P-OPh-Cα) / deg	122.61	124.00
∠(O1-P-OPh) / deg	103.53	105.28
τ(P-O1-C6-C5) / deg	14.38	11.00
τ(O1-C6-C5-C4) / deg	-2.18	-2.28
τ(C6-C5-C4-O3) / deg	16.48	19.34
τ(C5-C4-O3-P) / deg	-44.04	-46.93
τ(C4-O3-P-O1) / deg	51.50	52.36
τ(O3-P-O1-C6) / deg	-35.72	-33.19
τ(O=P-OPh-Cα) / deg	-63.75	-59.76
τ(P-OPh-Cα-Cβ) / deg	-122.53	-117.13

[a] B3LYP-D3(BJ)/cc-pV(T+d)Z. [b] Ref. 34.