

Supplementary Information

The Calculation of Lipophilicity of the Organophosphate Pesticides with Using Density Functional Theory

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Table S1. IUPAC names of all 22 OPs pesticides investigated in present study

Pesticide	Systematic name
Acephate	N-[Methoxy(methylsulfanyl)phosphoryl]acetamide
Aspon	O,O,O',O'-Tetrapropyl dithiopyrophosphate
Carbophenothion	S-[(4-Chlorophenyl)thio]methyl] O,O-diethyl phosphorodithioate
Chlorpyrifos	O,O-Diethyl O-3,5,6-trichloropyridin-2-yl phosphorothioate
Coumaphos	O-(3-Chloro-4-methyl-2-oxo-2H-chromen-7-yl) O,O-diethyl phosphorothioate
Crufomate	N-[(4-tert-Butyl-2-chlorophenoxy)methoxyphosphoryl]methanamine
Diazinon	O,O-Diethyl O-[2-isopropyl-6-methylpyrimidin-4-yl] phosphorothioate
Dichlorvos	2,2-Dichloroethenyl dimethyl phosphate
Dimethoate	O,O-Dimethyl S-[2-(methylamino)-2-oxoethyl] phosphorodithioate
Dioxathion	S,S'-1,4-Dioxane-2,3-diyl O,O,O',O'-tetraethyl bis(dithiophosphate)
Disulfoton	O,O-Diethyl S-[2-(ethylsulfanyl)ethyl] phosphorodithioate
Ethion	O,O,O',O'-Tetraethyl S,S'-methylene bis(phosphorodithioate)
Fenitrothion	O,O-Dimethyl O-(3-methyl-4-nitrophenyl)phosphorothioate
Fenthion	O,O-Dimethyl O-[3-methyl-4-(methylsulfanyl)phenyl] phosphorothioate
Fonofos	O-Ethyl S-phenyl ethylphosphonodithioate
Malathion	Diethyl 2-[(dimethoxyphosphorothioyl)sulfanyl]butanedioate
Methyl Parathion	O,O-Dimethyl-O-4-nitrophenylphosphorothioate
Monocrotophos	Dimethyl (E)-1-methyl-2-(methylcarbamoyl)vinyl phosphate
Parathion	O,O-Diethyl O-4-nitrophenyl phosphorothioate
Phorate	O,O-Diethyl S-[(ethylsulfanyl)methyl] phosphorodithioate
Phosalone	6-Chloro-3-[(diethoxyphosphinothioyl)sulfanyl]methyl]-1,3-benzoxazol-2-one
Temephos	O,O,O',O'-Tetramethyl O,O'-sulfanediylbis(1,4-phenylene) diphosphorothioate

Table S2. Formulas according to which the statistical processing of the results of quantum-chemical modeling was carried out. For a quantitative value n , if y_i is the estimated value and Y_i is the experimental value, the estimates are calculated as follows:

Equation	No
$ME = \frac{1}{n} \sum_{i=1}^n (y_i - Y_i)$	(S1)
$MAD = \frac{1}{n} \sum_{i=1}^n y_i - Y_i $	(S2)
$MSE = \frac{1}{n} \sum_{i=1}^n (y_i - Y_i)^2$	(S3)
$MPE = \frac{100}{n} \sum_{i=1}^n \frac{y_i - Y_i}{Y_i}$	(S4)
$MAPE = \frac{100}{n} \sum_{i=1}^n \left \frac{y_i - Y_i}{Y_i} \right $	(S5)
$SLRL = \frac{\sum_{i=1}^n (y_i - \bar{y})(Y_i - \bar{Y})}{\sum_{i=1}^n (Y_i - \bar{Y})^2}$	(S6)

$$r = \frac{\sum_{i=1}^n (y_i - \bar{y}_i)(Y_i - \bar{Y}_i)}{\sqrt{\sum_{i=1}^n (y_i - \bar{y}_i)^2 (Y_i - \bar{Y}_i)^2}} \quad (S7)$$

$$PCC = r^2 \quad (S8)$$

Table S3. Calculated solvation free energy change of transfer from the gas phase to water phase ($\Delta G_{\text{solv(water)}}$ / kcal mol⁻¹) and octanol phase ($\Delta G_{\text{solv(octanol)}}$ / kcal mol⁻¹) under standard state conditions, and corresponding log KOW values of examined OPs pesticide set at B3LYP/DEF2-SVP level of theory, with experimentally determined log P.

OPs	$\Delta G_{\text{Octanol}}$	ΔG_{Water}	LogK _{OW} (PBE-def2-SVP)	LogP _{exp}	Ref.
Acephate	-63.71	-67.90	-0.73	-0.80	[1,2]
Aspon	-64.77	-22.30	7.44	6.00	[1,2]
Carbophenothion	-68.48	-38.65	5.23	5.30	[1,2]
Chlorpyrifos	-47.88	-16.78	5.45	5.00	[1,3]
Coumaphos	-75.65	-56.83	3.30	4.50	[1,4]
Crufomate	-65.48	-52.31	2.31	3.40	[1,2]
Diazinon	-51.50	-27.60	4.19	3.80	[1,2]
Dichlorvos	-34.98	-22.67	2.16	1.40	[1,2]
Dimethoate	-68.81	-66.63	0.38	0.80	[1,2]
Dioxathion	-86.57	-54.62	5.60	4.30	[1,2]
Disulfoton	-57.59	-29.23	4.97	4.00	[1,2]
Ethion	-69.85	-49.66	3.54	5.10	[1,2]
Fenitrothion	-46.26	-31.87	2.52	3.30	[1,2]
Fenthion	-47.26	-23.50	4.16	4.10	[1,5]
Fonofos	-62.34	-39.63	3.98	3.90	[1,2]
Malathion	-59.98	-49.22	1.89	2.40	[1,2]
Methyl Parathion	-43.86	-31.52	2.16	2.90	[1,2]
Monocrotophos	-66.07	-70.97	-0.86	-0.20	[1,2]
Parathion	-49.61	-31.33	3.20	3.80	[1,2]
Phorate	-50.94	-25.34	4.49	3.60	[1,2]
Phosalone	-74.83	-57.01	3.12	4.40	[1,2]
Temephos	-75.58	-41.72	5.94	6.00	[1,2]

Table S4. Calculated solvation free energy change of transfer from the gas phase to water phase ($\Delta G_{\text{solv(water)}}$ / kcal mol⁻¹) and octanol phase ($\Delta G_{\text{solv(octanol)}}$ / kcal mol⁻¹) under standard state conditions, and corresponding log KOW values of examined OPs pesticide set at PBE/DEF2-SVP level of theory, with experimentally determined log P.

OPs	$\Delta G_{\text{Octanol}}$	ΔG_{Water}	LogK _{OW} (PBE-def2-SVP)	LogP _{exp}	Ref.
Acephate	-60.27	-58.11	-0.38	-0.80	[1,2]
Aspon	-18.39	-61.15	7.49	6.00	[1,2]
Carbophenothion	-36.73	-67.08	5.32	5.30	[1,2]
Chlorpyrifos	-13.10	-42.92	5.23	5.00	[1,3]
Coumaphos	-49.89	-69.94	3.52	4.50	[1,4]
Crufomate	-44.09	-61.05	2.97	3.40	[1,2]
Diazinon	-25.48	-49.70	4.25	3.80	[1,2]
Dichlorvos	-16.70	-30.45	2.41	1.40	[1,2]
Dimethoate	-60.84	-64.91	0.71	0.80	[1,2]
Dioxathion	-47.37	-76.90	5.18	4.30	[1,2]
Disulfoton	-26.74	-56.24	5.17	4.00	[1,2]
Ethion	-45.09	-67.44	3.92	5.10	[1,2]
Fenitrothion	-25.87	-41.28	2.70	3.30	[1,2]
Fenthion	-23.46	-47.25	4.17	4.10	[1,5]
Fonofos	-37.40	-60.55	4.06	3.90	[1,2]
Malathion	-43.06	-55.25	2.14	2.40	[1,2]
Methyl Parathion	-25.70	-38.94	2.32	2.90	[1,2]

Monocrotophos	-62.72	-60.78	-0.34	-0.20	[1,2]
Parathion	-25.55	-45.61	3.52	3.80	[1,2]
Phorate	-26.15	-49.70	4.13	3.60	[1,2]
Phosalone	-48.89	-68.13	3.37	4.40	[1,2]
Temephos	-34.90	-70.76	6.28	6.00	[1,2]

Table S5. Calculated solvation free energy change of transfer from the gas phase to water phase ($\Delta G_{\text{solv}}(\text{water})$ / kcal mol⁻¹) and octanol phase ($\Delta G_{\text{solv}}(\text{octanol})$ / kcal mol⁻¹) under standard state conditions, and corresponding log KOW values of examined OPs pesticide set at PBE/DEF2-TZVP level of theory, with experimentally determined log P.

OPs	$\Delta G_{\text{Octanol}}$	ΔG_{Water}	LogK _{OW} (PBE-def2-SVP)	LogP _{exp}	Ref.
Acephate	-68.00	-73.43	-0.95	-0.80	[1,2]
Aspon	-69.44	-26.05	7.60	6.00	[1,2]
Carbophenothion	-73.02	-44.02	5.08	5.30	[1,2]
Chlorpyrifos	-49.06	-20.33	5.04	5.00	[1,3]
Coumaphos	-81.19	-63.41	3.12	4.50	[1,4]
Crufomate	-69.99	-54.07	2.79	3.40	[1,2]
Diazinon	-55.96	-32.80	4.06	3.80	[1,2]
Dichlorvos	-33.87	-19.80	2.47	1.40	[1,2]
Dimethoate	-80.37	-78.14	0.39	0.80	[1,2]
Dioxathion	-82.11	-56.76	4.44	4.30	[1,2]
Disulfoton	-65.43	-36.77	5.02	4.00	[1,2]
Ethion	-75.83	-51.91	4.19	5.10	[1,2]
Fenitrothion	-45.41	-51.61	-1.09	3.30	[1,2]
Fenthion	-47.53	-32.55	2.63	4.10	[1,5]
Fonofos	-50.87	-27.94	4.02	3.90	[1,2]
Malathion	-68.16	-46.74	3.75	2.40	[1,2]
Methyl Parathion	-67.41	-52.98	2.53	2.90	[1,2]
Monocrotophos	-44.76	-32.25	2.19	-0.20	[1,2]
Parathion	-71.69	-76.61	-0.86	3.80	[1,2]
Phorate	-53.42	-34.13	3.38	3.60	[1,2]
Phosalone	-56.74	-34.35	3.92	4.40	[1,2]
Temephos	-76.22	-57.67	3.25	6.00	[1,2]

Table S6. Calculated solvation free energy change of transfer from the gas phase to water phase ($\Delta G_{\text{solv}}(\text{water})$ / kcal mol⁻¹) and octanol phase ($\Delta G_{\text{solv}}(\text{octanol})$ / kcal mol⁻¹) under standard state conditions, and corresponding log KOW values of examined OPs pesticide set at B3LYP/DEF2-TZVP level of theory, with experimentally determined log P.

OPs	$\Delta G_{\text{Octanol}}$	ΔG_{Water}	LogK _{OW} (PBE-def2-SVP)	LogP _{exp}	Ref.
Acephate	-72.86	-78.42	-0.97	-0.80	[1,2]
Aspon	-71.90	-30.61	7.24	6.00	[1,2]
Carbophenothion	-75.45	-47.51	4.90	5.30	[1,2]
Chlorpyrifos	-52.55	-26.25	4.61	5.00	[1,3]
Coumaphos	-87.76	-71.30	2.88	4.50	[1,4]
Crufomate	-77.01	-62.27	2.58	3.40	[1,2]
Diazinon	-57.57	-34.95	3.97	3.80	[1,2]
Dichlorvos	-37.94	-25.05	2.26	1.40	[1,2]
Dimethoate	-83.94	-83.22	0.13	0.80	[1,2]
Dioxathion	-94.67	-63.57	5.45	4.30	[1,2]
Disulfoton	-67.22	-39.84	4.80	4.00	[1,2]
Ethion	-79.44	-56.00	4.11	5.10	[1,2]
Fenitrothion	-53.35	-39.56	2.42	3.30	[1,2]
Fenthion	-51.73	-28.18	4.13	4.10	[1,5]

Fonofos	-70.24	-49.28	3.67	3.90	[1,2]
Malathion	-71.84	-59.18	2.22	2.40	[1,2]
Methyl Parathion	-49.24	-37.01	2.14	2.90	[1,2]
Monocrotophos	-82.31	-89.82	-1.32	-0.20	[1,2]
Parathion	-57.80	-39.68	3.18	3.80	[1,2]
Phorate	-58.02	-34.28	4.16	3.60	[1,2]
Phosalone	-83.30	-66.05	3.02	4.40	[1,2]
Temephos	-82.73	-49.20	5.88	6.00	[1,2]

Table S7. Calculated solvation free energy change of transfer from the gas phase to water phase ($\Delta G_{\text{solv}}(\text{water})$ / kcal mol⁻¹) and octanol phase ($\Delta G_{\text{solv}}(\text{octanol})$ / kcal mol⁻¹) under standard state conditions, and corresponding log KOW values of examined OPs pesticide set at PBEh-3c level of theory, with experimentally determined log P.

OPs	$\Delta G_{\text{Octanol}}$	ΔG_{Water}	LogK _{OW} (PBE-def2-SVP)	LogP _{exp}	Ref.
Acephate	-73.41	-79.67	-1.10	-0.80	[1,2]
Aspon	-71.60	-30.59	7.19	6.00	[1,2]
Carbophenothion	-76.44	-48.52	4.89	5.30	[1,2]
Chlorpyrifos	-52.30	-24.82	4.82	5.00	[1,3]
Coumaphos	-84.41	-66.65	3.11	4.50	[1,4]
Crufomate	-78.83	-65.01	2.42	3.40	[1,2]
Diazinon	-59.19	-36.83	3.92	3.80	[1,2]
Dichlorvos	-38.86	-27.04	2.07	1.40	[1,2]
Dimethoate	-84.65	-84.08	0.10	0.80	[1,2]
Dioxathion	-95.93	-65.56	5.32	4.30	[1,2]
Disulfoton	-64.60	-37.30	4.78	4.00	[1,2]
Ethion	-79.36	-59.41	3.50	5.10	[1,2]
Fenitrothion	-51.12	-36.86	2.50	3.30	[1,2]
Fenthion	-57.36	-34.84	3.95	4.10	[1,5]
Fonofos	-75.01	-54.30	3.63	3.90	[1,2]
Malathion	-69.73	-59.31	1.83	2.40	[1,2]
Methyl Parathion	-48.09	-35.83	2.15	2.90	[1,2]
Monocrotophos	-80.41	-88.16	-1.36	-0.20	[1,2]
Parathion	-55.92	-36.65	3.38	3.80	[1,2]
Phorate	-57.95	-35.29	3.97	3.60	[1,2]
Phosalone	-82.56	-65.73	2.95	4.40	[1,2]
Temephos	-90.69	-57.81	5.76	6.00	[1,2]

Table S8. Calculated solvation free energy change of transfer from the gas phase to water phase ($\Delta G_{\text{solv}}(\text{water})$ / kcal mol⁻¹) and octanol phase ($\Delta G_{\text{solv}}(\text{octanol})$ / kcal mol⁻¹) under standard state conditions, and corresponding log KOW values of examined OPs pesticide set at PBE0/DEF2-SVP level of theory, with experimentally determined log P.

OPs	$\Delta G_{\text{Octanol}}$	ΔG_{Water}	LogK _{OW} (PBE-def2-SVP)	LogP _{exp}	Ref.
Acephate	-65.93	-70.47	-0.80	-0.80	[1,2]
Aspon	-67.43	-25.96	7.27	6.00	[1,2]
Carbophenothion	-69.79	-40.98	5.05	5.30	[1,2]
Chlorpyrifos	-49.70	-19.57	5.28	5.00	[1,3]
Coumaphos	-78.40	-59.84	3.25	4.50	[1,4]
Crufomate	-69.29	-53.92	2.70	3.40	[1,2]
Diazinon	-54.66	-31.39	4.08	3.80	[1,2]
Dichlorvos	-36.34	-24.04	2.16	1.40	[1,2]
Dimethoate	-72.38	-71.27	0.20	0.80	[1,2]
Dioxathion	-90.90	-59.79	5.45	4.30	[1,2]
Disulfoton	-60.43	-32.59	4.88	4.00	[1,2]
Ethion	-71.88	-53.56	3.21	5.10	[1,2]
Fenitrothion	-47.92	-33.59	2.51	3.30	[1,2]

Fenthion	-51.13	-27.91	4.07	4.10	[1,5]
Fonofos	-66.56	-44.61	3.85	3.90	[1,2]
Malathion	-64.96	-52.25	2.23	2.40	[1,2]
Methyl Parathion	-45.21	-32.85	2.17	2.90	[1,2]
Monocrotophos	-68.60	-73.85	-0.92	-0.20	[1,2]
Parathion	-51.32	-32.72	3.26	3.80	[1,2]
Phorate	-53.65	-28.83	4.35	3.60	[1,2]
Phosalone	-77.18	-59.76	3.05	4.40	[1,2]
Temephos	-80.94	-47.21	5.91	6.00	[1,2]

Table S9. Calculated solvation free energy change of transfer from the gas phase to water phase ($\Delta G_{\text{solv}}(\text{water})$ / kcal mol⁻¹) and octanol phase ($\Delta G_{\text{solv}}(\text{octanol})$ / kcal mol⁻¹) under standard state conditions, and corresponding log KOW values of examined OPs pesticide set at PBE0/DEF2-TZVP level of theory, with experimentally determined log P.

OPs	$\Delta G_{\text{Octanol}}$	ΔG_{Water}	LogK _{OW} (PBE-def2-SVP)	LogP _{exp}	Ref.
Acephate	-72.59	-79.66	-1.24	-0.80	[1,2]
Aspon	-69.65	-28.02	7.30	6.00	[1,2]
Carbophenothion	-75.71	-47.75	4.90	5.30	[1,2]
Chlorpyrifos	-50.70	-23.07	4.84	5.00	[1,3]
Coumaphos	-85.30	-67.85	3.06	4.50	[1,4]
Crufomate	-77.57	-62.73	2.60	3.40	[1,2]
Diazinon	-57.61	-34.65	4.02	3.80	[1,2]
Dichlorvos	-36.04	-22.73	2.33	1.40	[1,2]
Dimethoate	-84.26	-83.56	0.12	0.80	[1,2]
Dioxathion	-92.40	-60.60	5.57	4.30	[1,2]
Disulfoton	-66.93	-38.57	4.97	4.00	[1,2]
Ethion	-78.33	-54.64	4.15	5.10	[1,2]
Fenitrothion	-50.56	-35.84	2.58	3.30	[1,2]
Fenthion	-51.53	-28.04	4.12	4.10	[1,5]
Fonofos	-71.46	-50.64	3.65	3.90	[1,2]
Malathion	-69.33	-57.23	2.12	2.40	[1,2]
Methyl Parathion	-45.82	-32.60	2.32	2.90	[1,2]
Monocrotophos	-80.67	-87.61	-1.22	-0.20	[1,2]
Parathion	-54.73	-35.60	3.35	3.80	[1,2]
Phorate	-57.67	-33.20	4.29	3.60	[1,2]
Phosalone	-80.48	-63.22	3.03	4.40	[1,2]
Temephos	-80.47	-46.74	5.91	6.00	[1,2]

Table S10. Calculated solvation free energy change of transfer from the gas phase to water phase ($\Delta G_{\text{solv}}(\text{water})$ / kcal mol⁻¹) and octanol phase ($\Delta G_{\text{solv}}(\text{octanol})$ / kcal mol⁻¹) under standard state conditions, and corresponding log KOW values of examined OPs pesticide set at B97-3c level of theory, with experimentally determined log P.

OPs	$\Delta G_{\text{Octanol}}$	ΔG_{Water}	LogK _{OW} (PBE-def2-SVP)	LogP _{exp}	Ref.
Acephate	-71,71	-77,98	-1,10	-0.80	[1,2]
Aspon	-71,53	-28,94	7,47	6.00	[1,2]
Carbophenothion	-75,92	-48,07	4,88	5.30	[1,2]
Chlorpyrifos	-52,27	-24,44	4,88	5.00	[1,3]
Coumaphos	-85,91	-69,60	2,86	4.50	[1,4]
Crufomate	-76,47	-61,88	2,56	3.40	[1,2]
Diazinon	-58,11	-35,89	3,90	3.80	[1,2]
Dichlorvos	-36,49	-23,36	2,30	1.40	[1,2]
Dimethoate	-84,13	-83,37	0,13	0.80	[1,2]
Dioxathion	-96,20	-64,97	5,47	4.30	[1,2]
Disulfoton	-68,09	-40,43	4,85	4.00	[1,2]
Ethion	-79,53	-56,35	4,06	5.10	[1,2]

Fenitrothion	-51,06	-36,77	2,51	3.30	[1,2]
Fenthion	-53,90	-31,63	3,90	4.10	[1,5]
Fonofos	-71,67	-51,27	3,58	3.90	[1,2]
Malathion	-72,93	-59,51	2,35	2.40	[1,2]
Methyl Parathion	-47,69	-35,71	2,10	2.90	[1,2]
Monocrotophos	-79,05	-85,64	-1,16	-0.20	[1,2]
Parathion	-56,69	-38,86	3,13	3.80	[1,2]
Phorate	-59,63	-36,63	4,03	3.60	[1,2]
Phosalone	-81,61	-64,94	2,92	4.40	[1,2]
Temephos	-81,82	-49,06	5,74	6.00	[1,2]

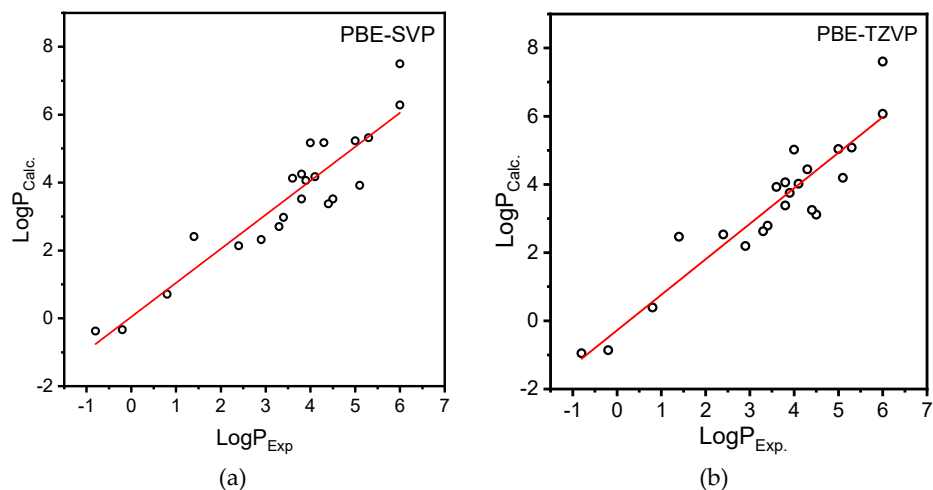


Figure S1. Relation between experimental determined log P and $\text{LogP}_{\text{Calc}}$ calculated using PBE with two different basis - a) SVP and b) TZVP.

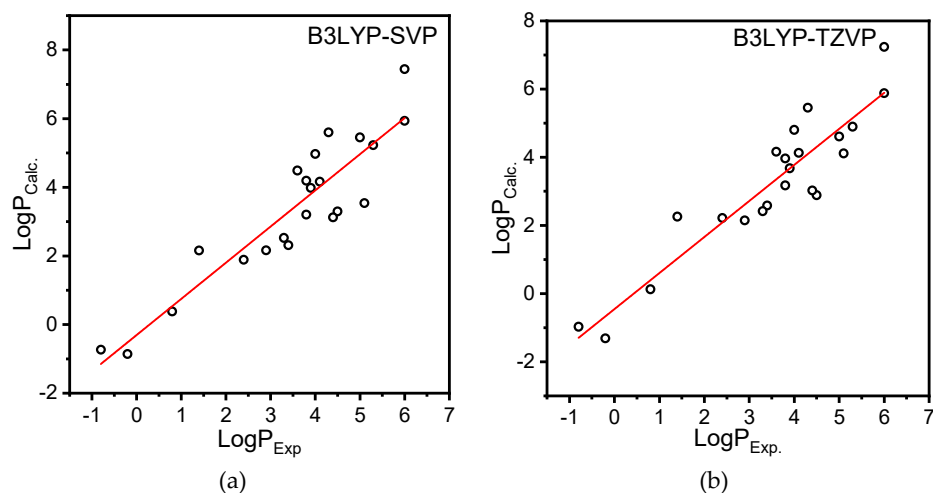


Figure S2. Relation between experimental determined log P and $\text{LogP}_{\text{Calc}}$ calculated using B3LYP with two different basis - a) SVP and b) TZVP.

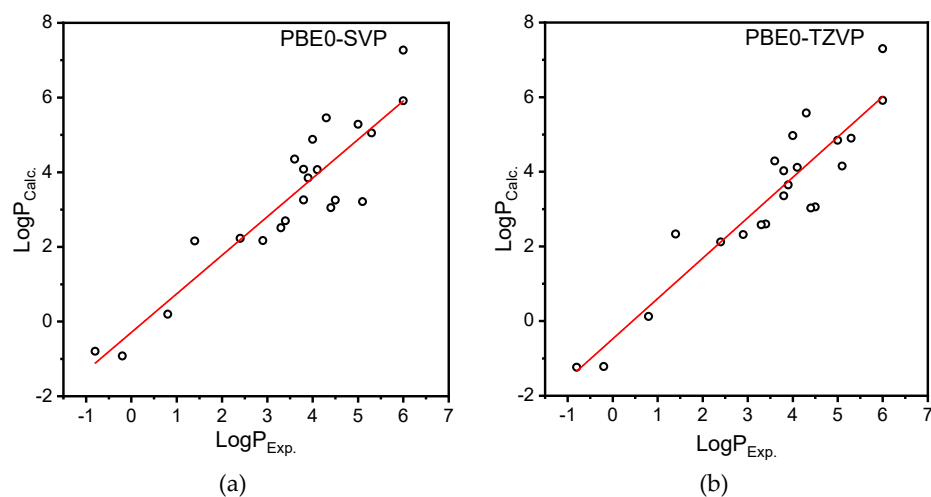


Figure S3. Relation between experimental determined log P and $\text{LogP}_{\text{Calc}}$ calculated using PBE0 with two different basis - a) SVP and b) TZVP.

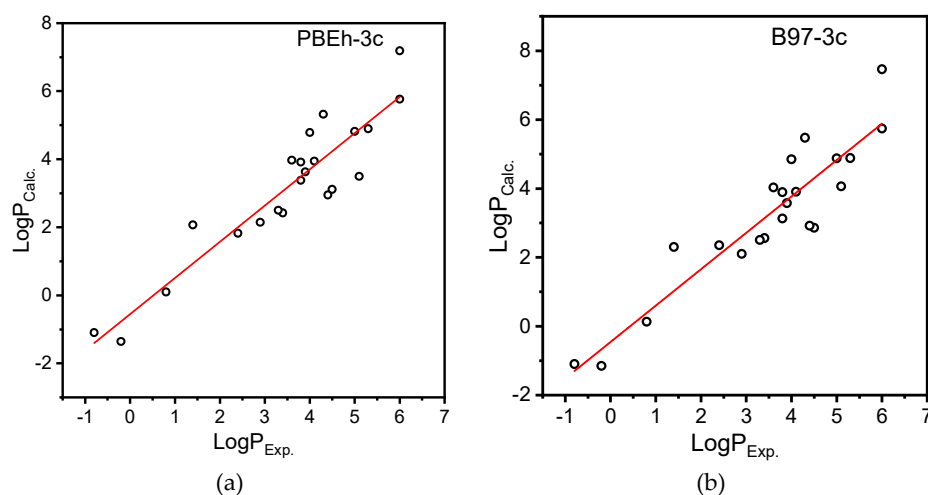


Figure S4. Relation between experimental determined log P and $\text{LogP}_{\text{Calc}}$ calculated using Grimms methods - a) PBEh-3c and b) B97-3c.

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