Supporting information for

Twin hydrogen bonds with phosphine oxide: anticooperativity effects caused by competing proton donors

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Content

correction. r_2 dependence on $r_2^a$for selected complexes.

Table S1. Energetic and geometric parameters of 1:2 complexes formed by Me_3PO with proton donors **1**–**70** in chloroform (PCM, ε = 4.7): local electron kinetic, G^a, and potential, V^a, energy densities in kJ mol^{-1} bohr^{-3} (calculated at BCP); interatomic distance r_1^a in Å; the values of cooperativity (anticooperativity) effects on energy $\Delta\Delta E/\Delta E$ ($\Delta\Delta E = \Delta E^a - \Delta E$), geometry $\Delta r_2/r_2$ ($\Delta r_2 = r_2^a - r_2$); hydrogen bond angles for all 140 individual H-bonds α (P=O···H), β (O···H–A) (in degrees); dihedral angles γ (in degrees, defined as shown in Figure 10).

No.	Proton donor molecule	G^a	V^a	r_1^a	$\Delta\Delta E/\Delta E$	$\Delta r_2/r_2$	α		β		γ
OH proton donors											
1	Water	79.7	78.4	0.980	–0.09	0.015	128.1	129.9	179.7	179.1	175.3
2	Methanol	79.7	78.4	0.978	–0.11	0.019	128.7	126.7	179.1	179.0	179.3
3	Fluoromethanol	101.9	109.7	0.988	–0.14	0.027	128.6	124.5	177.2	177.1	178.5
4	Difluoromethanol	114.6	130.8	1.002	–0.19	0.048	128.1	128.6	175.5	175.0	176.1
5	Trifluoromethanol	132.8	161.4	1.011	–0.27	0.075	128.0	127.3	176.8	177.7	175.4
6	Chloromethanol	108.3	119.8	0.992	–0.17	0.038	127.3	128.3	177.2	176.7	171.1
7	Dichloromethanol	119.4	138.7	1.004	–0.26	0.075	129.7	127.0	171.8	174.1	177.0
8	Ethanol	75.7	73.7	0.978	–0.15	0.023	126.5	124.5	176.5	175.8	179.6
9	2,2,2-Trifluoroethanol	96.4	101.6	0.984	–0.13	0.030	129.0	129.8	175.9	174.4	161.7
10	Formic acid	116.7	135.0	1.007	–0.19	0.050	126.3	125.1	173.8	174.7	150.5
11	Acetic acid	110.9	126.1	1.002	–0.16	0.043	124.5	124.9	173.8	173.8	144.1
12	Chloroacetic acid	122.9	145.7	1.010	–0.21	0.059	125.1	125.8	174.6	174.3	150.3
13	Dichloroacetic acid	131.4	160.1	1.015	–0.23	0.067	126.0	125.5	174.4	174.9	149.2
14	Trichloroacetic acid	137.1	170.3	1.018	–0.25	0.079	126.1	126.5	174.7	174.6	152.4
15	Trifluoroacetic acid	139.6	174.6	1.020	–0.27	0.082	126.9	126.2	174.7	175.1	159.2
16	Benzoic acid	113.7	130.6	1.003	–0.16	0.046	124.4	124.5	173.6	173.8	143.7
17	Pentafluorobenzoic acid	127.7	154.0	1.013	–0.23	0.066	125.5	125.6	174.8	174.7	152.8
18	Methanesulfonic acid	144.8	184.1	1.023	–0.23	0.086	126.8	126.7	174.1	176.2	162.6
19	Benzenesulfonic acid	140.3	176.4	1.021	–0.21	0.093	125.9	125.9	174.3	176.3	162.5
20	*p*-Toluenesulfonic acid	139.0	173.8	1.020	–0.16	0.102	125.5	126.0	174.8	176.2	163.8
21	Phenylphosphonic acid	123.5	146.6	1.006	–0.16	0.055	125.2	126.6	178.5	175.3	144.9
22	Phenol	92.7	97.6	0.986	–0.20	0.039	123.7	126.3	172.9	174.1	179.4
23	2-Nitrophenol	110.0	123.4	0.994	–0.25	0.043	125.5	124.6	174.2	173.0	176.3
24	3-Nitrophenol	100.4	109.1	0.990	–0.29	0.050	125.3	131.6	175.9	175.1	150.9
25	4-Nitrophenol	106.3	117.9	0.993	–0.29	0.050	125.8	127.5	175.6	175.7	179.7
NH proton donors											
26	Ammonia	40.8	35.1	1.022	–0.07	0.007	126.9	127.4	176.1	176.3	152.1
27	Dimethylamine	40.9	35.5	1.020	–0.11	0.017	126.9	127.8	177.6	178.1	173.8
28	Aziridine	46.8	41.5	1.023	–0.16	0.016	124.0	121.5	177.4	178.3	175.0
29	Azetidine	40.4	35.1	1.020	–0.10	0.012	125.3	124.6	178.9	179.4	173.0
30	Pyrrolidine	35.3	30.5	1.021	–0.37	0.033	122.7	138.5	171.9	177.9	156.9
31	Piperidine	40.3	34.8	1.019	–0.09	0.010	129.4	126.6	178.7	178.2	179.3
32	Piperazine	36.7	31.8	1.021	–0.26	0.026	123.8	112.7	170.7	165.2	158.0
33	2-Pyrrolidone	66.4	63.3	1.026	–0.09	0.011	123.6	120.1	179.5	175.0	149.2
34	Pyrrole	68.3	64.7	1.023	–0.20	0.030	129.7	130.2	178.5	178.8	178.1
35	Imidazole	75.7	74.1	1.027	–0.24	0.036	130.9	129.8	179.3	179.1	178.7
36	Pyrazole	81.2	81.4	1.029	–0.14	0.020	129.7	122.2	179.1	173.5	170.8
37	1,4-Dihydropyrazine	58.3	53.1	1.020	–0.21	0.025	128.8	128.1	176.3	176.4	176.9
NH+ proton donors											
38	Ammonium	113.7	134.0	1.066	–1.12	0.095	127.5	124.3	177.0	179.6	179.3
39	Dimethylammonium	91.4	98.6	1.051	–1.19	0.105	126.5	124.1	178.9	176.6	177.1
40	Trimethylammonium	76.1	78.1	1.047	–1.27	0.140	123.8	124.6	177.9	175.2	179.3
41	Imidazolium	107.3	122.0	1.049	–1.00	0.079	127.0	127.8	176.8	178.0	174.5
42	Pyridinium	112.7	130.7	1.053	–1.03	0.077	125.4	129.0	176.0	176.2	173.5
43	2-Picolinium	112.1	129.1	1.051	–1.05	0.057	124.8	130.4	174.3	171.8	179.0
44	3-Picolinium	110.6	127.3	1.052	–1.02	0.074	125.1	127.7	177.9	177.1	174.4
45	4-Picolinium	105.3	118.8	1.049	–1.01	0.082	126.7	128.6	176.5	175.5	174.8

46	3,5-Lutidinium	109.7	125.7	1.051	–1.01	0.073	124.1	126.5	176.6	179.0	176.8
47	2,6-Lutidinium	85.3	90.3	1.044	–1.21	0.099	122.6	129.2	177.7	177.3	178.9
48	2,4,6-Collidinium	84.7	89.1	1.043	–1.16	0.096	124.9	129.6	176.4	177.1	179.2
49	2-(Dimethylamino)pyridinium	69.2	68.0	1.035	–1.21	0.112	126.0	128.0	158.8	158.0	178.4
50	3-(Dimethylamino)pyridinium	105.6	118.8	1.048	–0.98	0.071	126.3	127.1	178.8	178.6	178.8
51	4-(Dimethylamino)pyridinium	97.9	106.2	1.041	–0.97	0.063	128.1	126.7	176.2	179.1	173.6
52	3,5-(Dimethylamino)pyridinium	101.2	111.6	1.045	–0.95	0.067	128.8	126.7	177.5	178.8	176.4
53	3,4,5-(Trimethoxy)pyridinium	100.9	111.7	1.045	–1.04	0.079	126.4	127.7	178.5	177.8	175.5
54	3,4,5-Trifluoropyridinium	130.2	162.1	1.068	–1.05	0.103	122.7	125.7	177.9	176.8	169.5
55	3,4,5-Trichloropyridinium	123.9	150.8	1.063	–1.03	0.105	124.6	127.2	178.4	175.6	176.2
56	3,5-Diaminopyridinium	107.9	122.6	1.049	–0.97	0.068	123.6	129.3	179.3	176.4	166.6
CH proton donors											
57	Trifluoroethylene	40.0	33.4	1.085	–0.13	0.025	134.2	135.5	174.3	178.6	177.5
58	Trichloroethylene	42.0	35.3	1.087	–0.03	0.019	135.5	136.8	175.0	174.8	172.9
59	Acetylene	43.1	35.5	1.077	–0.14	0.023	133.0	133.0	179.6	179.6	179.2
60	Fluoroacetylene	44.9	37.3	1.076	–0.14	0.023	133.1	133.1	179.7	179.6	178.9
61	Hydrogen cyanide	68.4	64.1	1.092	–0.27	0.039	131.2	130.1	179.9	179.8	178.7
62	Trinitromethane	75.5	73.9	1.108	–0.27	0.071	132.1	127.8	176.2	176.3	166.9
63	1,1-Dinitroethane	48.1	42.4	1.097	–0.22	0.050	127.7	128.8	168.3	173.8	168.7
64	2-Nitropropane	24.3	20.9	1.090	–0.20	0.022	120.8	117.8	168.6	172.2	141.9
65	Trichloromethane	52.4	46.9	1.090	–0.13	0.037	129.0	133.1	175.3	179.3	177.4
66	Dichloromethane	41.8	35.9	1.088	–0.07	0.019	130.5	132.9	175.8	176.6	179.7
67	Chloromethane	26.0	22.2	1.088	–0.06	0.026	125.1	121.6	172.0	170.7	133.0
68	Methane	6.2	4.9	1.091	–3.94	0.081	128.4	130.5	175.5	173.9	178.2
69	Trifluoromethane	47.0	40.8	1.092	–0.21	0.030	133.8	133.0	176.0	177.7	178.0
70	Tribromomethane	49.1	43.4	1.090	–0.30	0.042	129.9	128.2	177.8	175.2	179.9

Table S2. The numeric values of the main geometric, energetic and spectroscopic parameters of hydrogen-bonded 1:1 complexes formed by Me_3PO with proton donors **1**–**70** (PCM, ε = 4.7), taken from ref. 51: hydrogen bond energy Δ*E* (in kJ mol^{-1}), local electron kinetic, *G*, and potential, *V*, energy densities at BCP (in kJ mol^{-1} bohr^{-3}), hydrogen bond distance, r_2 (in Å); angles α and β (in degrees), the changes of ^{1}H and ^{31}P NMR chemical shifts, ΔδH and ΔδP (in ppm) and the change of P=O vibrational, $\Delta\nu_{P=O}$ (in cm^{-1}).

No.	Proton donor molecule	Δ*E*	*G*	*V*	r_2	α	β	ΔδH	ΔδP	$\Delta\nu_{P=O}$
OH proton donors										
1	Water	30.08	84.29	84.18	1.764	132.2	179.1	4.9	5.7	–18.1
2	Methanol	29.68	85.97	86.19	1.760	134.3	178.7	5.3	5.9	–16.5
3	Fluoromethanol	42.27	112.79	125.71	1.651	133.9	176.6	6.5	8.9	–27.8
4	Difluoromethanol	49.20	136.54	166.97	1.563	133.9	176.0	8.3	11.0	–37.7
5	Trifluoromethanol	62.80	170.43	231.10	1.467	136.0	176.8	9.7	13.5	–50.1
6	Chloromethanol	46.24	124.88	145.04	1.609	134.4	176.8	7.8	10.0	–35.4
7	Dichloromethanol	53.58	155.97	201.21	1.508	137.0	174.4	9.8	12.1	–47.1
8	Ethanol	28.06	83.32	82.54	1.772	135.8	178.2	5.4	5.1	–16.0
9	2,2,2-Trifluoroethanol	40.35	108.13	118.25	1.668	134.9	176.9	6.2	8.3	–18.8
10	Formic acid	49.41	140.12	175.02	1.552	128.3	175.8	8.1	12.9	–47.2
11	Acetic acid	45.26	130.12	157.47	1.583	127.4	175.2	7.6	12.1	–42.6
12	Chloroacetic acid	53.22	151.70	196.19	1.517	129.2	175.2	8.8	13.5	–51.7
13	Dichloroacetic acid	59.39	164.86	222.64	1.480	129.4	176.1	9.3	15.5	–63.3
14	Trichloroacetic acid	63.16	176.97	248.87	1.447	130.0	176.1	10.0	16.4	–69.3
15	Trifluoroacetic acid	64.79	181.39	259.15	1.434	130.4	176.3	10.1	16.7	–74.1
16	Benzoic acid	46.79	134.86	165.78	1.569	127.4	175.0	8.1	12.6	–46.7
17	Pentafluorobenzoic acid	56.36	160.31	213.33	1.493	129.6	175.5	9.1	14.7	–58.1
18	Methanesulfonic acid	65.10	187.50	276.06	1.417	128.5	177.0	8.7	18.4	–35.1
19	Benzenesulfonic acid	64.42	186.23	273.13	1.419	128.5	176.3	10.4	17.7	–27.0
20	*p*-Toluenesulfonic acid	61.34	188.26	279.14	1.411	130.6	175.6	10.8	17.1	–54.5
21	Phenylphosphonic acid	54.06	149.00	191.91	1.525	129.2	178.8	8.9	14.5	–51.0
22	Phenol	40.42	107.85	118.34	1.666	136.8	177.7	6.5	7.1	–27.1
23	2-Nitrophenol	52.55	129.06	153.17	1.592	134.1	178.0	7.7	10.3	–40.8
24	3-Nitrophenol	48.99	121.78	139.32	1.617	142.7	177.9	7.1	8.5	–27.0
25	4-Nitrophenol	52.03	128.37	150.93	1.594	139.1	179.5	7.4	9.5	–39.9
NH proton donors										
26	Ammonia	12.00	41.64	35.30	2.049	130.6	177.0	2.9	2.2	–8.6
27	Dimethylamine	11.90	43.84	37.27	2.032	137.9	179.0	3.0	1.9	–7.9
28	Aziridine	15.62	50.30	44.06	1.981	133.2	175.9	3.2	3.2	–9.4
29	Azetidine	11.70	42.41	36.26	2.046	132.4	177.7	2.8	2.1	–7.4
30	Pyrrolidine	12.00	41.31	35.41	2.058	130.4	177.2	2.7	2.0	–8.0
31	Piperidine	11.55	42.00	35.80	2.049	133.1	179.0	2.9	2.0	–7.7
32	Piperazine	11.83	41.31	35.15	2.056	134.0	176.5	3.0	1.7	–7.8
33	2-Pyrrolidone	26.94	69.32	66.78	1.846	121.8	174.1	4.7	8.0	–25.7
34	Pyrrole	28.06	77.45	74.03	1.800	142.3	179.7	4.3	4.9	–14.5
35	Imidazole	33.68	88.12	87.70	1.749	147.2	178.9	4.7	5.7	–16.0
36	Pyrazole	33.35	87.87	89.42	1.750	139.0	177.2	4.5	6.1	–19.3
37	1,4-Dihydropyrazine	20.18	64.69	58.51	1.875	142.2	179.8	4.5	3.6	–11.5
NH+ proton donors										
38	Ammonium	77.43	157.15	210.79	1.496	151.2	175.5	9.8	14.1	–47.6
39	Dimethylammonium	69.12	137.33	166.42	1.570	159.6	174.6	7.6	12.6	–33.8
40	Trimethylammonium	67.45	134.39	159.89	1.584	160.7	175.7	7.2	12.7	–34.1
41	Imidazolium	66.29	142.22	178.05	1.544	150.1	176.0	7.6	12.5	–33.3
42	Pyridinium	70.04	148.19	186.87	1.533	154.4	175.9	7.3	13.5	–39.3
43	2-Picolinium	66.30	136.95	165.52	1.569	157.9	177.3	6.9	11.8	–36.7
44	3-Picolinium	68.16	144.79	180.06	1.544	155.5	174.9	7.1	12.8	–37.3
45	4-Picolinium	67.11	142.46	176.39	1.551	153.8	176.8	7.2	12.7	–40.0
46	3,5-Lutidinium	66.80	142.76	176.62	1.551	153.5	177.0	7.0	12.5	–39.4

47	2,6-Lutidinium	61.13	126.52	147.81	1.602	158.1	175.7	6.7	10.7	–34.7
48	2,4,6-Collidinium	58.65	124.70	144.13	1.609	160.1	175.3	6.6	10.3	–27.1
49	2-(Dimethylamino)pyridinium	55.79	109.71	120.29	1.662	158.8	164.0	5.8	10.6	–34.2
50	3-(Dimethylamino)pyridinium	64.44	137.12	166.46	1.568	153.2	174.2	6.8	12.1	–35.2
51	4-(Dimethylamino)pyridinium	57.36	123.90	144.06	1.608	152.5	177.2	6.6	10.8	–28.8
52	3,5-(Dimethylamino)pyridinium	60.35	130.32	154.27	1.589	153.8	177.4	6.5	11.4	–36.1
53	3,4,5-(Trimethoxy)pyridinium	63.57	136.19	162.33	1.571	164.6	176.3	6.9	11.1	–28.3
54	3,4,5-Trifluoropyridinium	85.05	183.05	257.61	1.439	153.4	175.5	8.9	16.8	–58.7
55	3,4,5-Trichloropyridinium	81.76	177.11	244.30	1.455	151.1	176.2	8.7	16.3	–72.4
56	3,5-Diaminopyridinium	63.92	137.72	167.75	1.566	153.3	176.9	6.8	12.0	–37.3
CH proton donors										
57	Trifluoroethylene	14.86	44.54	36.38	2.022	148.7	176.1	2.7	2.0	–7.3
58	Trichloroethylene	14.78	45.53	37.63	2.014	145.5	172.4	2.6	2.1	–8.4
59	Acetylene	14.84	47.83	39.08	1.984	149.2	179.9	3.2	1.6	–7.7
60	Fluoroacetylene	15.87	49.54	40.27	1.965	150.2	179.5	3.5	1.6	–7.6
61	Hydrogen cyanide	30.77	81.55	77.71	1.776	149.5	179.4	4.8	4.9	–18.2
62	Trinitromethane	41.71	102.36	108.31	1.702	144.9	179.3	5.3	8.6	–31.8
63	1,1-Dinitroethane	25.38	61.08	54.30	1.914	141.4	165.5	3.3	4.7	–19.5
64	2-Nitropropane	9.82	27.02	23.03	2.243	120.9	173.8	1.8	2.8	–7.8
65	Trichloromethane	22.11	61.64	54.65	1.907	147.8	179.3	2.8	4.1	–11.6
66	Dichloromethane	14.94	45.22	38.10	2.026	141.7	178.4	2.6	2.5	–9.0
67	Chloromethane	7.34	28.67	23.42	2.204	142.2	178.1	2.0	1.0	–4.3
68	Methane	0.19	8.62	7.13	2.741	153.2	178.7	0.8	0.5	–0.2
69	Trifluoromethane	18.89	53.51	45.21	1.962	156.1	177.2	2.4	2.8	–7.8
70	Tribromomethane	19.29	59.47	52.31	1.917	147.1	179.3	2.6	4.2	–11.4

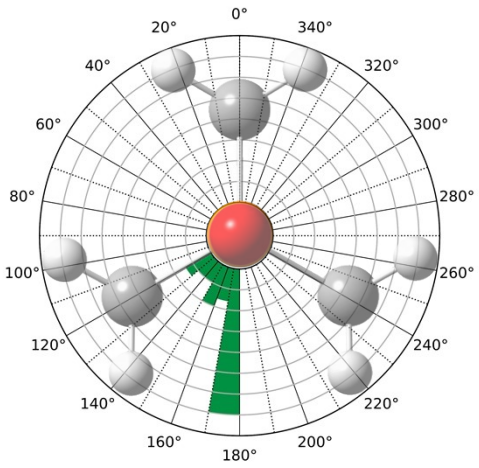

Fig. S1. Distribution diagram of AH proton donor positions in 1:1 complexes relative to Me_3PO. Each radial grid mark corresponds to five occurrences of a certain AH position.

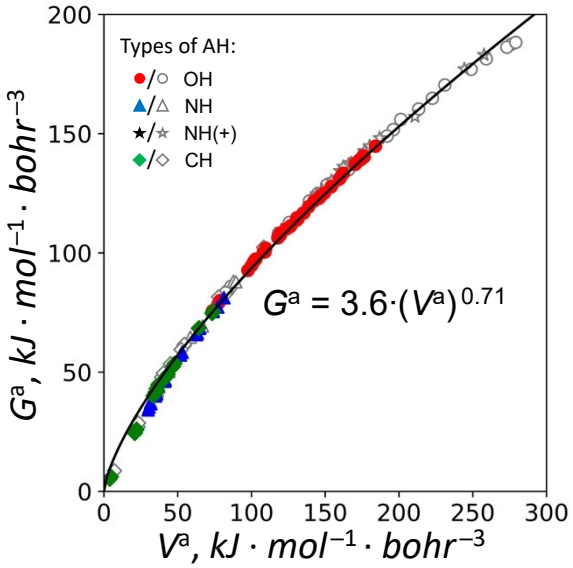

Fig. S2. Correlation between local electron kinetic G^a and potential V^a energy densities. Open gray symbols correspond to 1:1 complexes, filled red, blue and green symbols correspond to 1:2 complexes. Solid curve corresponds to correlational equation given next to the curve (V^a in kJ·mol^{-1}·bohr^{-3}, G^a in kJ·mol^{-1}·bohr^{-3}).

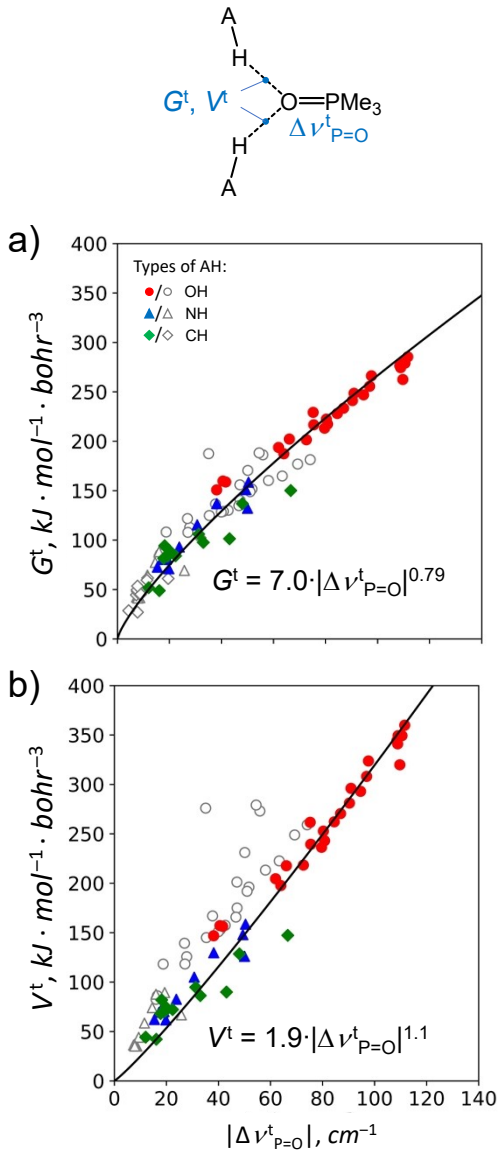

Fig. S3. Correlations between (a) total local electron kinetic energy density $G^t = G + G^a$ and $|\Delta\nu^t_{P=O}|$, (b) total local electron potential energy density $V^t = V + V^a$ and $|\Delta\nu^t_{P=O}|$. Open gray symbols correspond to 1:1 complexes; filled red, blue and green symbols correspond to 1:2 complexes. As the correlation $\Delta E^a(G^a)$ is linear (Figure 11) and the correlation $\Delta E^t(|\Delta\nu^t_{P=O}|)$ is a power function (Figure 13a), the $G^t(|\Delta\nu^t_{P=O}|)$ and $V^t(|\Delta\nu^t_{P=O}|)$ could also be described by a power function. Solid curves correspond to correlation power functions fitted for both 1:1 and 1:2 complexes by keeping the power values fixed at 0.79 for $G^t(|\Delta\nu^t_{P=O}|)$ and 1.1 for $V^t(|\Delta\nu^t_{P=O}|)$. For the fitting equations to be valid, the following units should be used: G^t and V^t in $kJ\cdot mol^{-1}\cdot bohr^{-3}$, $|\Delta\nu^t_{P=O}|$ in cm^{-1}.

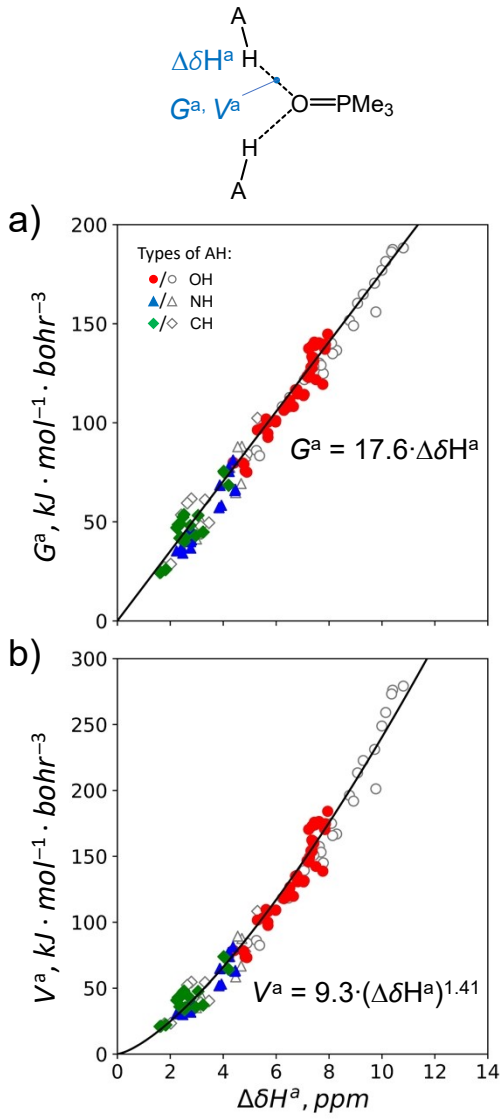

Fig. S4. Correlations between (a) local electron kinetic energy density G^a and $\Delta\delta H^a$, (b) local electron potential energy density V^a and $\Delta\delta H^a$. Open gray symbols correspond to 1:1 complexes; filled red, blue and green symbols correspond to 1:2 complexes. As the correlations $\Delta E^a(G^a)$ and $\Delta E^a(\Delta\delta H^a)$ are linear (Figure 11, Figure 13b), and the correlation $G^a(V^a)$ is described by the power function (Figure S2), the $G^a(\Delta\delta H^a)$ could be described by a linear function and $V^a(\Delta\delta H^a)$ could be described by a power function. Solid curves correspond to correlation functions fitted for both 1:1 and 1:2 complexes (the power value fixed at 1.41 for $V^a(\Delta\delta H^a)$). For the fitting equations to be valid, the following units should be used: G^a and V^a in kJ·mol^{-1}·bohr^{-3}, $\Delta\delta H^a$ in ppm.

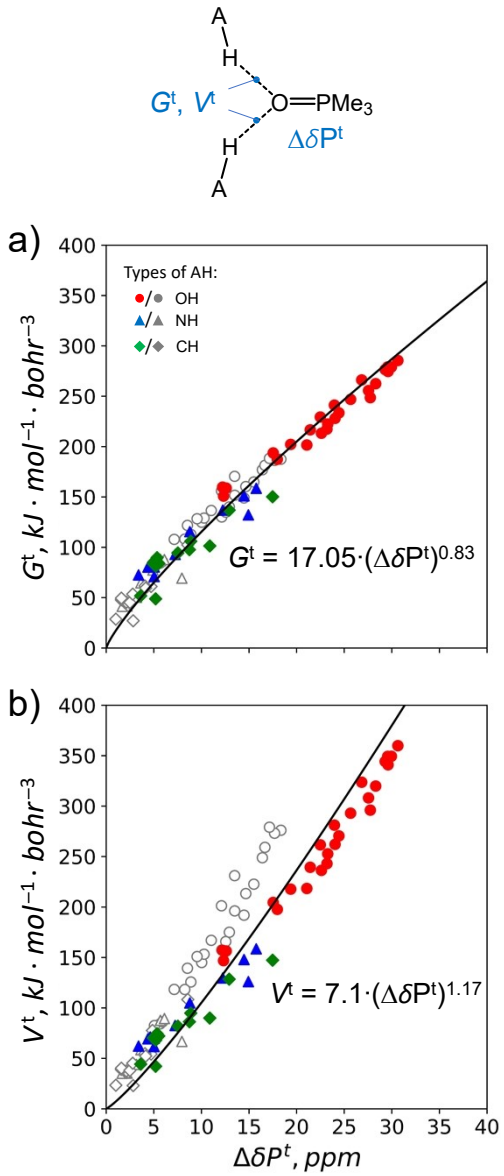

Fig. S5. Correlations between (a) total local electron kinetic energy density G^t and $\Delta\delta P^t$, (b) total local electron potential energy density V^t and $\Delta\delta P^t$. Open gray symbols correspond to 1:1 complexes; filled red, blue and green symbols correspond to 1:2 complexes. Solid curves correspond to correlation functions fitted for both 1:1 and 1:2 complexes. The power values were fixed at 0.83 for $G^t(\Delta\delta P^t)$ and 1.17 for $V^t(\Delta\delta P^t)$ because correlation $\Delta E^a(G^a)$ is linear (Figure 11) and the correlations $G^a(V^a)$ and $\Delta E^t(\Delta\delta P^t)$ are power functions (Figure S2, Figure 13c). For the fitting equations to be valid, the following units should be used: G^a and V^a in kJ·mol^{-1}·bohr^{-3}, $\Delta\delta P^t$ in ppm.

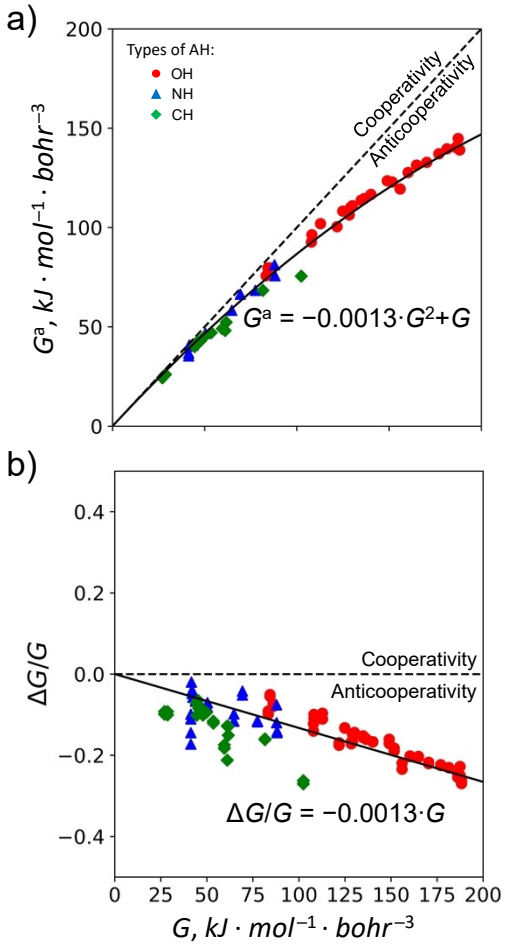

Fig. S6. (a) The correlation between G^a and G. (b) The correlation of relative hydrogen bond cooperativity on local electron kinetic energy density $\Delta G/G$ ($\Delta G = G^a - G$) and G. Solid curves correspond to correlational equations given next to the curves. The correlation $\Delta G/G(G)$ seems to be close to linear with the coefficient –0.0013 kJ^{-1} mol $bohr^3$ obtained by least squares fitting. The correlation function for $G^a(G)$ was derived from the fitting function for $\Delta G/G(G)$. Dashed lines indicate the boundaries between regions of cooperativity and anticooperativity effects. For the fitting equations to be valid G, G^a and ΔG should be in $kJ \cdot mol^{-1} \cdot bohr^{-3}$.

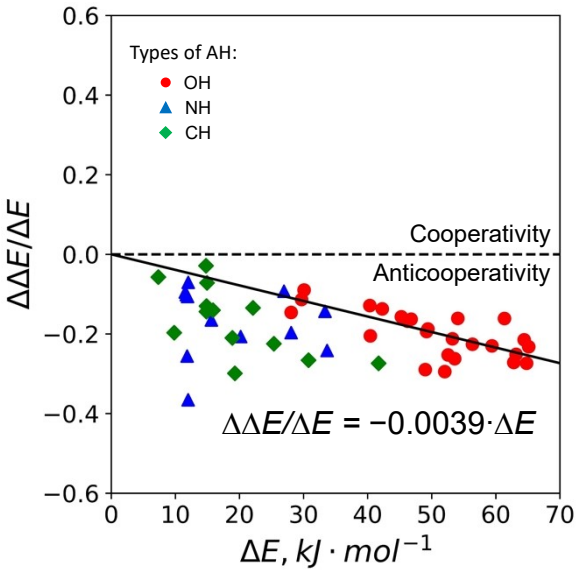

Fig. S7. The correlation of relative hydrogen bond cooperativity $\Delta\Delta E/\Delta E$ ($\Delta\Delta E = \Delta E^{a} - \Delta E$) and ΔE. Solid curve corresponds to correlational equation given next to the curve. Dashed line indicates the boundary between regions of cooperativity and anticooperativity effects. For the fitting equation to be valid ΔE and $\Delta\Delta E$ should be in kJ·mol^{-1}.

Table S3. Explicit equations of some correlation functions mentioned in the text: $\Delta\Delta\nu_{P=O}(\Delta E)$, $\Delta\Delta\delta H(\Delta E)$, $\Delta\Delta\delta P(\Delta E)$, $r_2^a(r_2)$, $\Delta^{r_2}(r_2)$, $\Delta\Delta\nu_{P=O}(r_2)$, $\Delta\Delta\delta H(r_2)$, $\Delta\Delta\delta P(r_2)$. For the equations to be valid with the given numerical coefficients, the variables should be taken in the following units: ΔE in kJ mol^{-1}; r_2^a, r_2 and Δ^{r_2} in Å; $\Delta\Delta\nu_{P=O}$ in cm^{-1}; $\Delta\Delta\delta P$ and $\Delta\Delta\delta H$ in ppm).

Correlation function	Figure	Explicit fitting function
$\Delta\Delta\nu_{P=O}(\Delta E)$	Fig. 15a	$\lvert\Delta\Delta\nu_{P=O}\rvert = 0.284\cdot(2\cdot\Delta E - 0.0039\cdot\Delta E^2)^{1.266} - 0.284\cdot\Delta E^{1.266}$
$\Delta\Delta\delta H(\Delta E)$	Fig. 15b	$\Delta\Delta\delta H = -0.00065\cdot\Delta E^2$
$\Delta\Delta\delta P(\Delta E)$	Fig. 15c	$\Delta\Delta\delta P = 0.152\cdot(2\cdot\Delta E - 0.0039\cdot\Delta E^2)^{1.205} - 0.152\cdot\Delta E^{1.205}$
$r_2^a(r_2)$	Fig. 17	$r_2^a = 0.96 - 0.426\cdot ln\left(-0.769\cdot\exp\left(-2\cdot\frac{r_2-0.96}{0.426}\right)+\exp\left(-\frac{r_2-0.96}{0.426}\right)\right)$
$\Delta^{r_2}(r_2)$	Fig. S10	$\Delta r_2/r_2 = r_2^{-1}\cdot\left(0.96 - 0.426\cdot ln\left(-0.769\cdot\exp\left(-2\cdot\frac{r_2-0.96}{0.426}\right)+\exp\left(-\frac{r_2-0.96}{0.426}\right)\right) - r\right.$
$\Delta\Delta\nu_{P=O}(r_2)$	Fig. S11a	$\lvert\Delta\Delta\nu_{P=O}(r_2)\rvert = 761\cdot\exp\left(-\frac{r_2^a(r_2)-0.96}{0.307}\right) - 284\cdot\exp\left(-\frac{r_2-0.96}{0.307}\right)$
$\Delta\Delta\delta H(r_2)$	Fig. S11b	$\Delta\Delta\delta H(r_2) = 32.85\cdot\exp\left(-\frac{r_2^a(r_2)-0.96}{0.426}\right) - 32.85\cdot\exp\left(-\frac{r_2-0.96}{0.426}\right)$

$\Delta\Delta\delta P(r_2)$	Fig. S11c	$\Delta\Delta\delta P(r_2) = 188.3 \cdot \exp\left(-\frac{r_2^a(r_2) - 0.96}{0.322}\right) - 73.8 \cdot \exp\left(-\frac{r_2 - 0.96}{0.322}\right)$

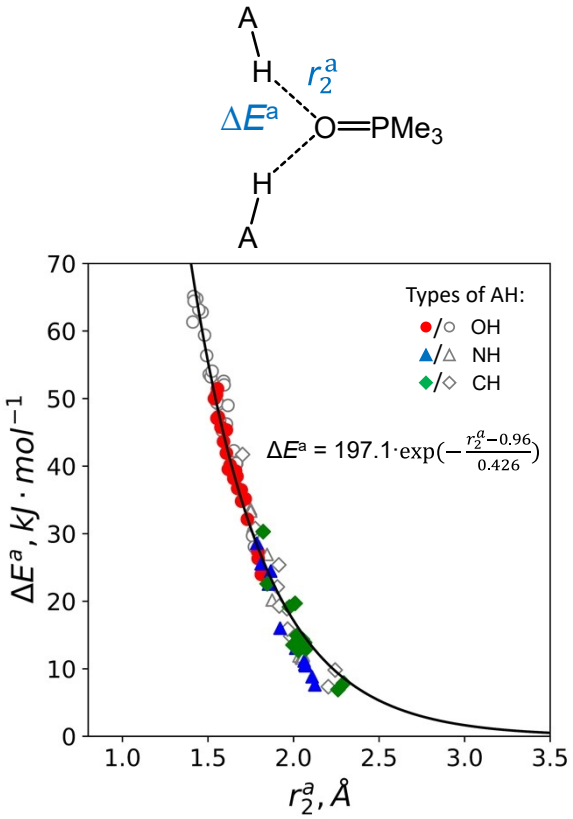

Fig. S8. Correlation between hydrogen bond energy ΔE^a and hydrogen bond length r_2^a. Open gray symbols correspond to 1:1 complexes; filled red, blue and green symbols correspond to 1:2 complexes. The solid line is drawn according to the correlation function given next to the curve. For the fitting equations to be valid, the following units should be used: ΔE^a in kJ·mol^{-1}, r_2^a in Å.

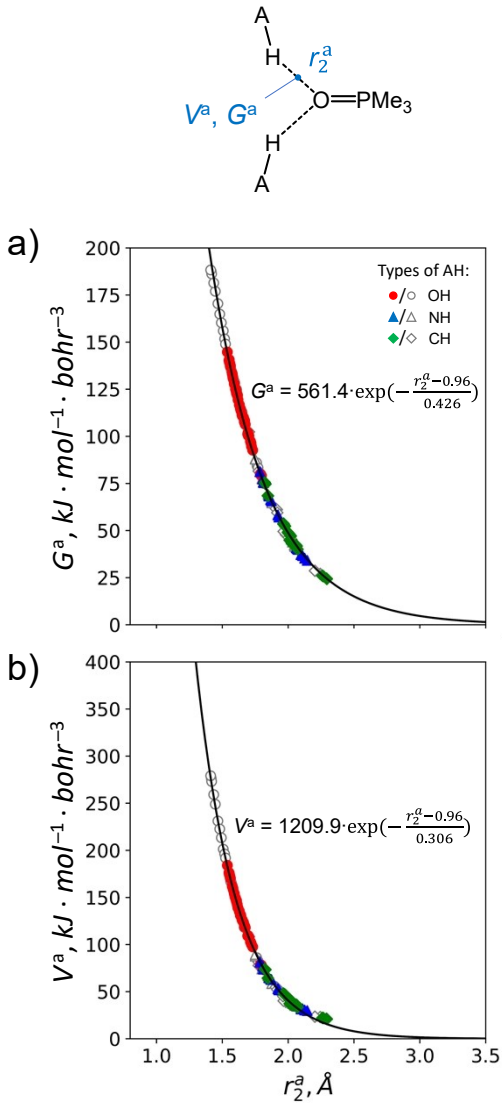

Fig. S9. Correlations between (a) G^a and hydrogen bond length r_2^a, (b) V^a and r_2^a. Open gray symbols correspond to 1:1 complexes; filled red, blue and green symbols correspond to 1:2 complexes. The solid lines correspond to correlation functions $g \cdot \exp(-(r_2^a - r_2^0)/h)$, where coefficients g and h were obtained for $G^a(r_2^a)$ and $V^a(r_2^a)$ by the least squares fitting. For the fitting equations to be valid, the following units should be used: V^a and G^a in kJ·mol^{-1}·bohr^{-3}, r_2^a in Å.

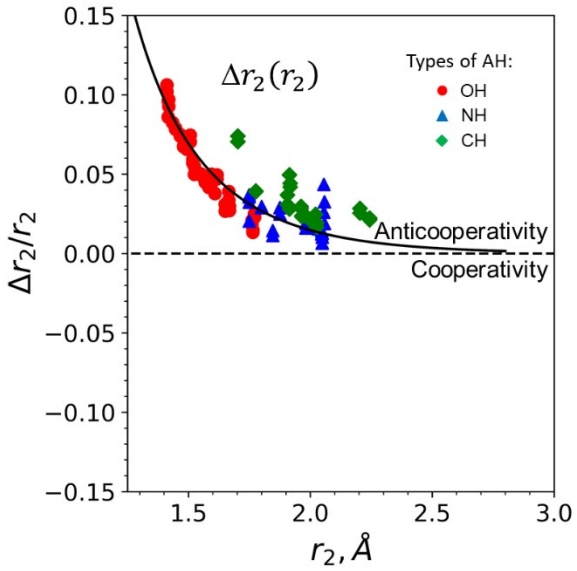

Fig. S10. The correlation of relative geometric cooperativity $\Delta^{r_2}/_{r_2}(\Delta^{r_2} = r_2^a - r_2)$ and r_2 distance for 1:2 and 1:1 complexes formed by Me_3PO with the same AH proton donors. Solid curve corresponds to correlation function, which is given in Table S3. Dashed line indicates the boundary between regions of cooperativity and anticooperativity effects.

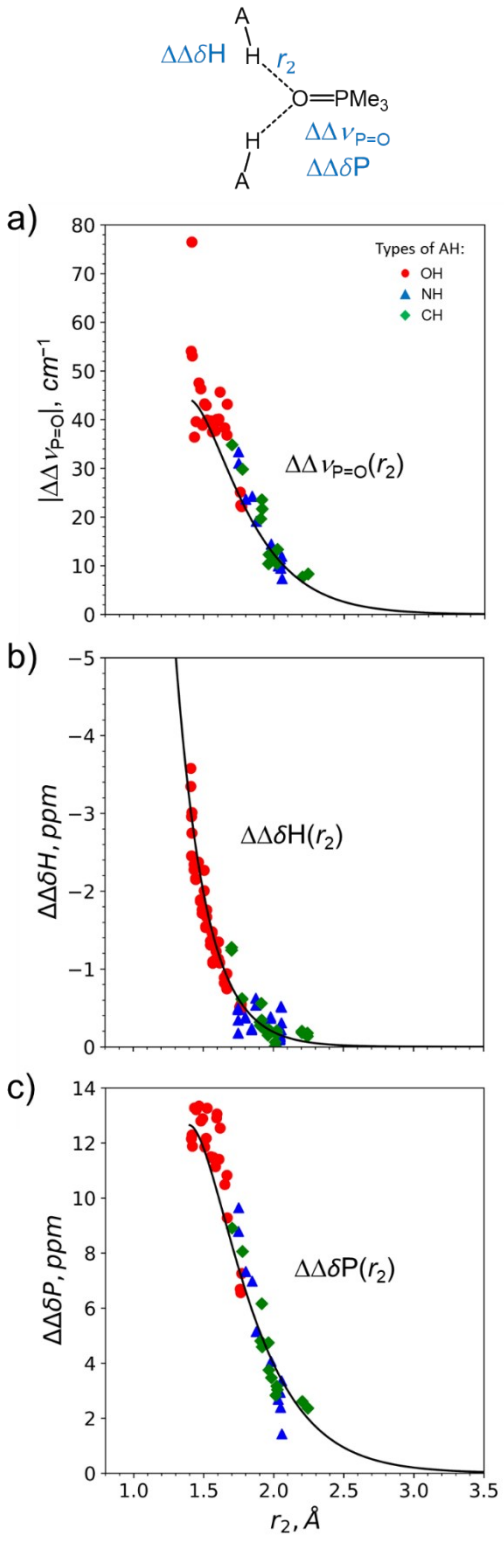

Fig. S11. The correlations of hydrogen bond length r_2 and spectral cooperativity parameters: (a) $|\Delta\Delta\nu_{P=O}| = |\Delta\nu^{t}_{P=O} - \Delta\nu_{P=O}|$, (b) $\Delta\Delta\delta H = \Delta\delta H^{a} - \Delta\delta H$, (c) $\Delta\Delta\delta P = \Delta\delta P^{t} - \Delta\delta P$. Solid curves correspond to correlation functions $\Delta\Delta\nu_{P=O}(r_2)$, $\Delta\Delta\delta H(r_2)$ and $\Delta\Delta\delta P(r_2)$ derived from correlations given in Figure 16, Figure 17 and explicitly given in Table S3.

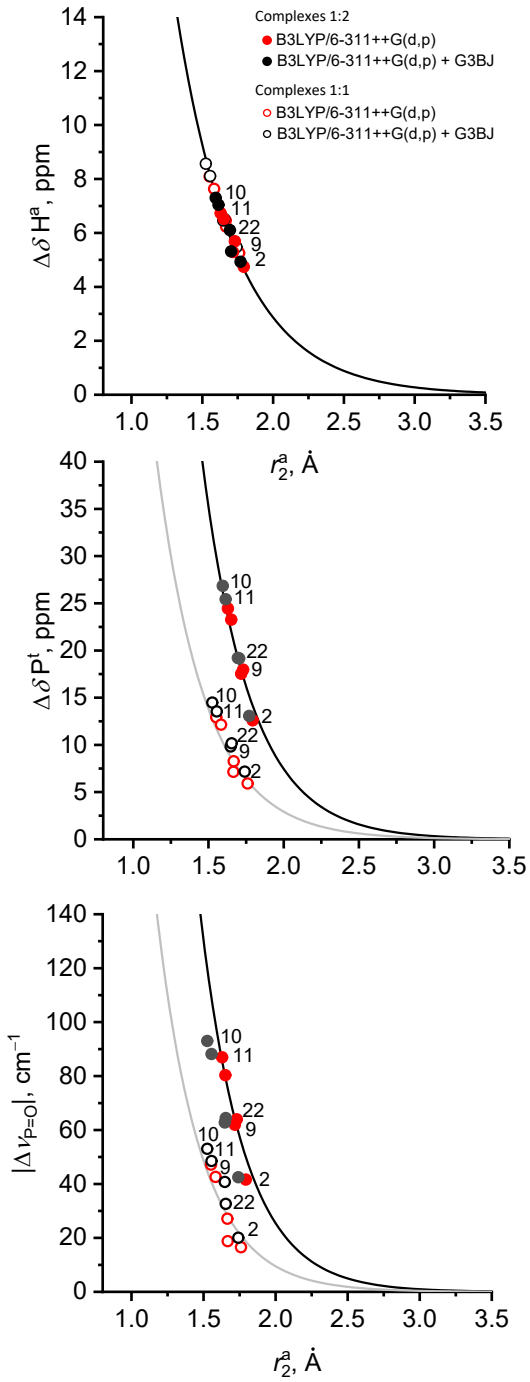

Fig. S12. Comparison of the results obtained with/without taking the dispersion correction into account. Red data points – B3LYP/6-311++G(d,p); black data points – B3LYP/6-311++G(d,p)+D3BJ. Correlations between interatomic distance r_2^a and IR, NMR spectroscopy parameters for complexes of $Me_3P{=}O$ with proton donors **2**, **9**, **10**, **11** and **22** are shown: (a) stretching frequency $|\Delta\nu^t_{P=O}|$, (b) ^1H NMR chemical shift $\Delta\delta H^a$ and (c) ^{31}P NMR chemical shift $\Delta\delta P^t$. Solid lines correspond to fitting curves (see text) obtained for 1:1 complexes (gray lines) and 1:2 complexes (black lines).

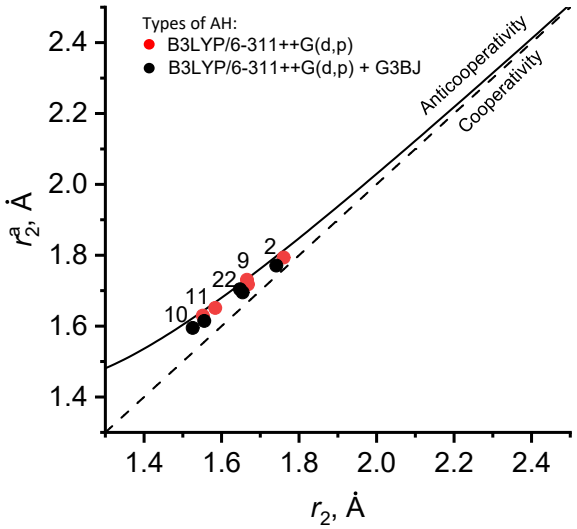

Fig. S13. Comparison of the results obtained with/without taking the dispersion correction into account. Red data points – B3LYP/6-311++G(d,p); black data points – B3LYP/6-311++G(d,p)+D3BJ. Correlation between hydrogen bond distances r_2^a and r_2 for complexes of $Me_3P{=}O$ with proton donors **2**, **9**, **10**, **11** and **22** are shown. Solid line corresponds to correlation function $r_2^a(r_2)$ given explicitly in Table S3 in ESI and derived from fitting functions shown in Figure 14 and Figure S8. Dashed line indicates the boundary between regions of cooperativity and anticooperativity effects.