Supporting information for

Phosphine oxides as spectroscopic halogen bond descriptors: IR and NMR correlations with interatomic distances and complexation energy

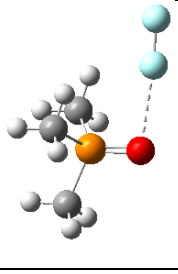
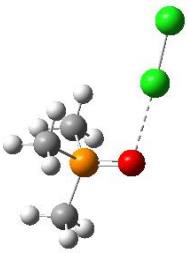
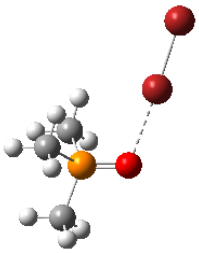
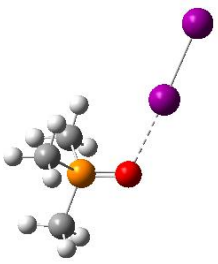
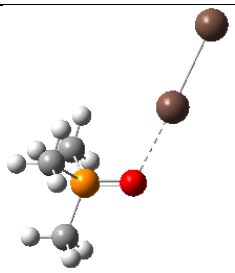
A.S. Ostras', D.M. Ivanov, A.S. Novikov, P.M. Tolstoy

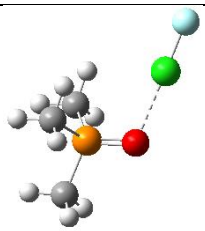
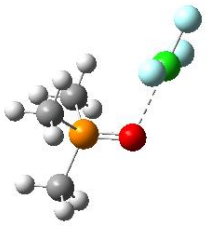
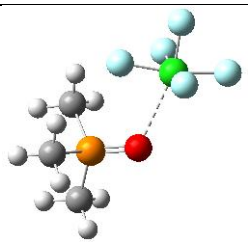
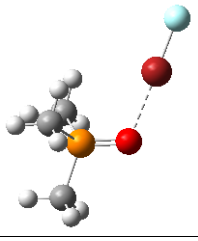
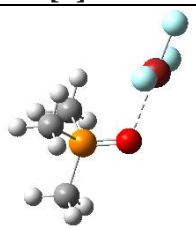
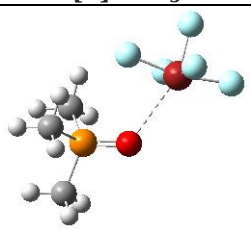
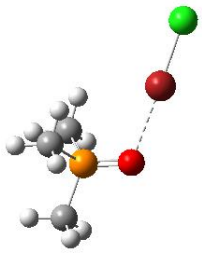
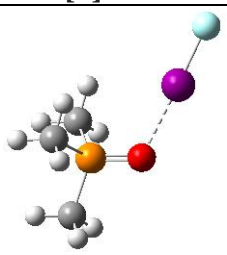
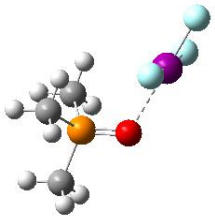
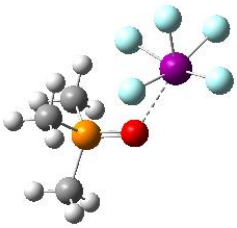
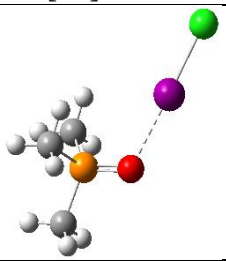
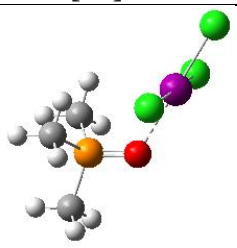
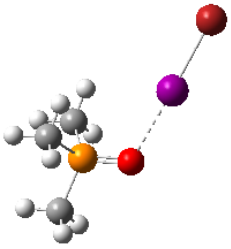
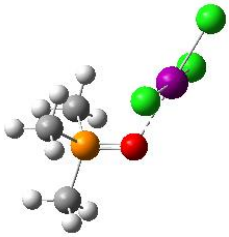
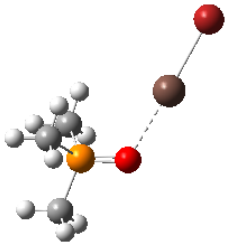
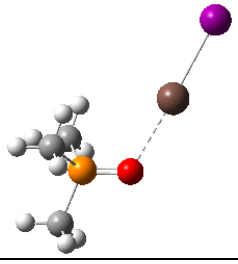
Institute of Chemistry, St. Petersburg State University, Russia

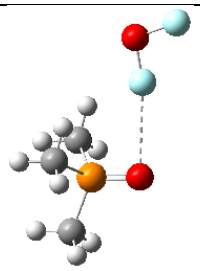
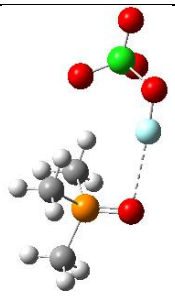
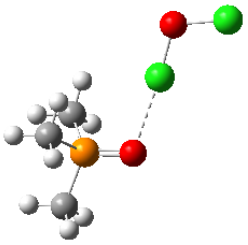
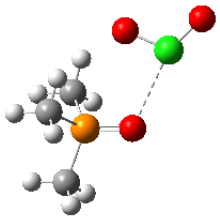
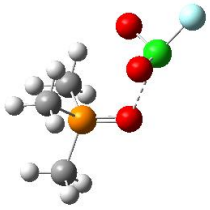
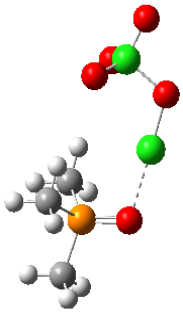
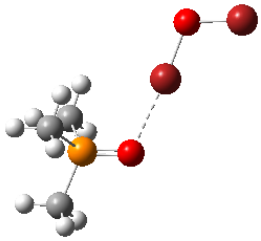
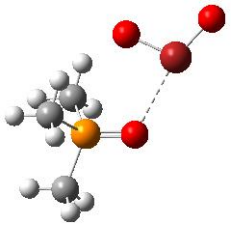
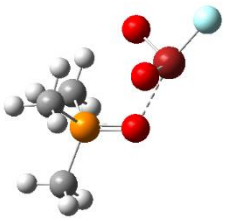
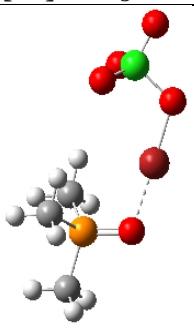
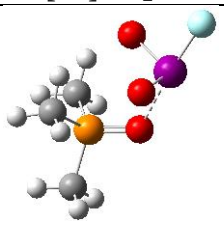
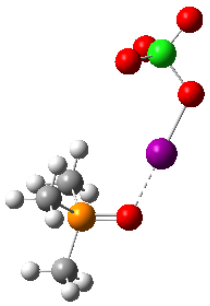
* – corresponding author, peter.tolstoy@spbu.ru

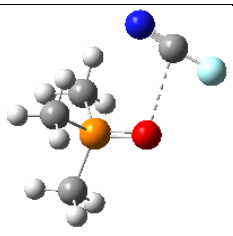
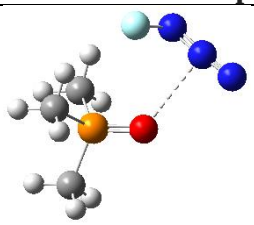
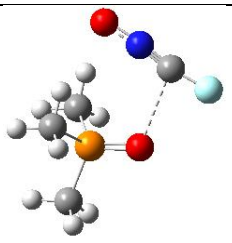
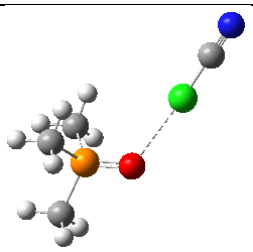
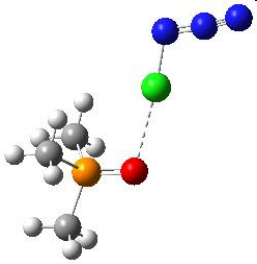
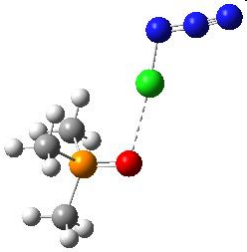
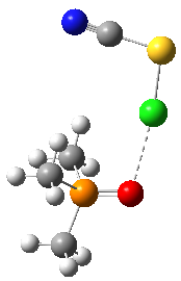
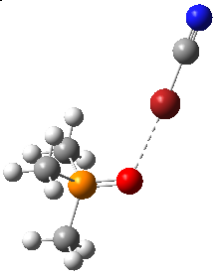
Contents **Page**

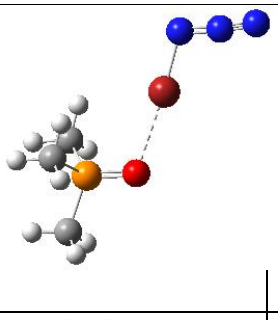
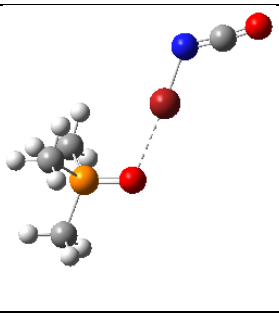
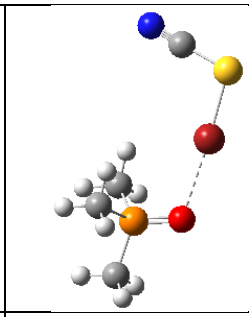
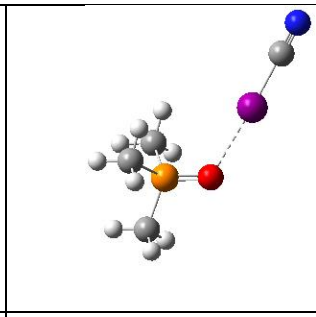
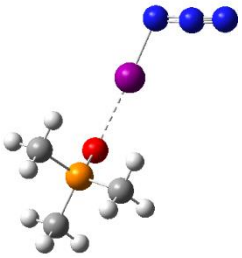
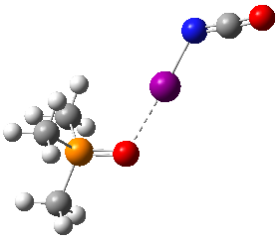
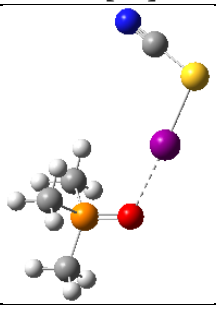
Figure S1. Calculated (M06-2x/ def2-TZVPPD) optimized structures of 128 intermolecular 1:1 complexes formed by $Me_3P{=}O$ with halogen-containing molecules. The complexes in which the dominant intermolecular interaction is other than the halogen bond are marked in red color.

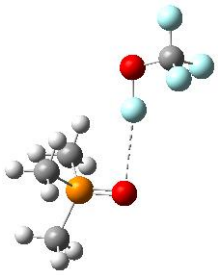
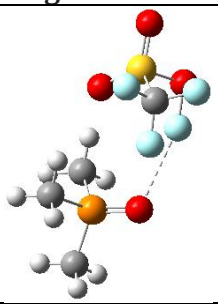
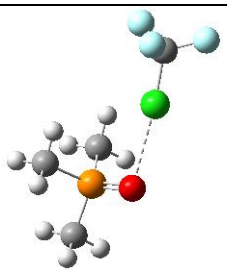
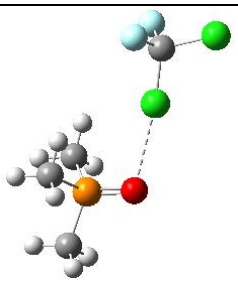
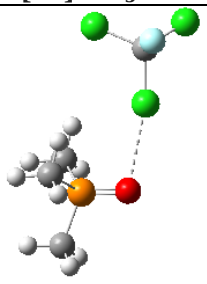
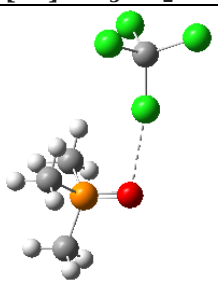
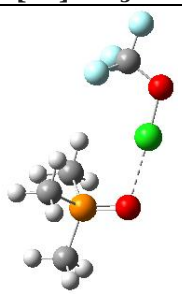
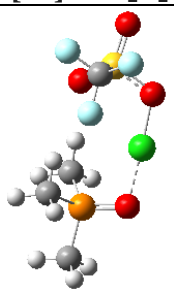
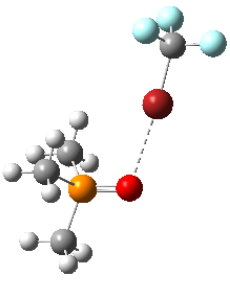
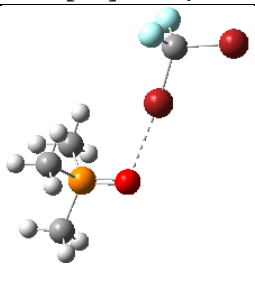
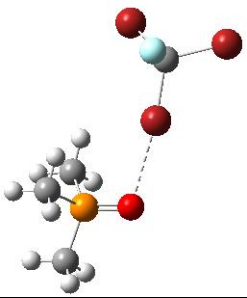
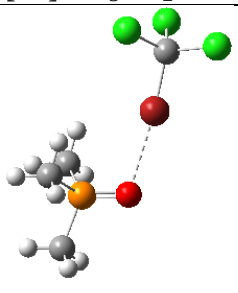
halogens				
				
[1] F_2	**[2] Cl_2**	**[3] Br_2**	**[4] I_2**	**[5] At_2**

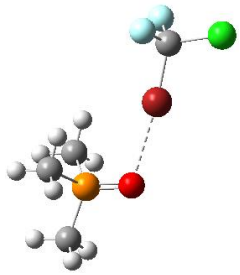
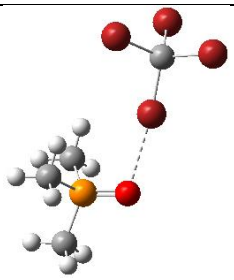
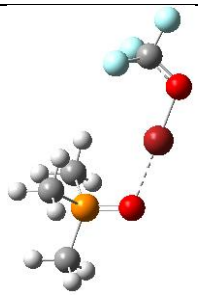
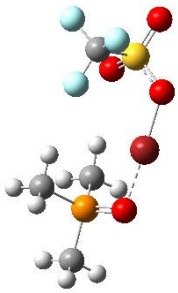
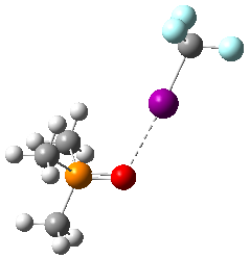
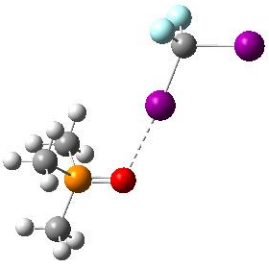
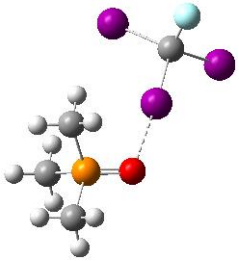
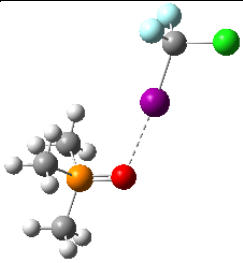
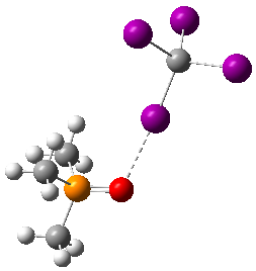
interhalides			
			
[6] ClF	**[7] ClF_3**	**[8] ClF_5**	**[9] BrF**
			
[10] BrF_3	**[11] BrF_5**	**[12] BrCl**	**[13] IF**
			
[14] IF_3	**[15] IF_5**	**[16] ICl**	**[17] ICl_3**
			
[18] IBr	**[19] AtCl**	**[20] AtBr**	**[21] AtI**

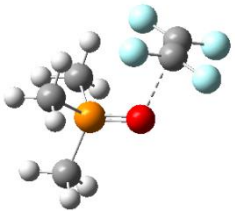
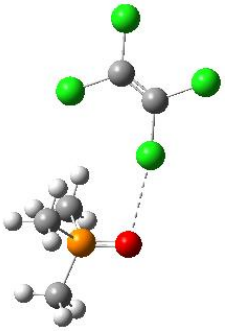
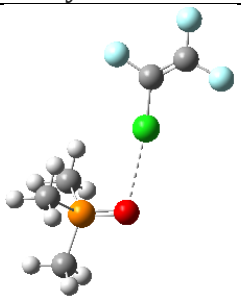
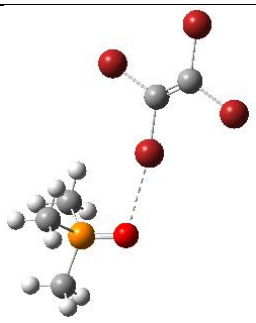
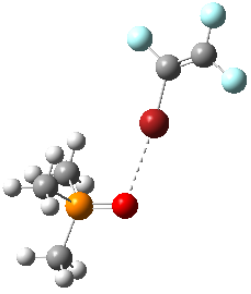
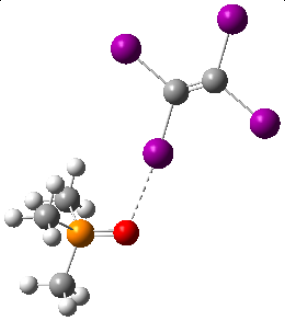
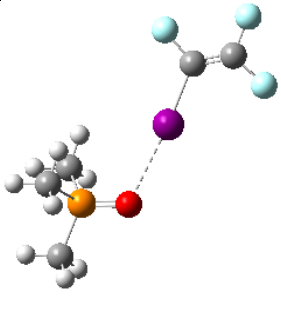
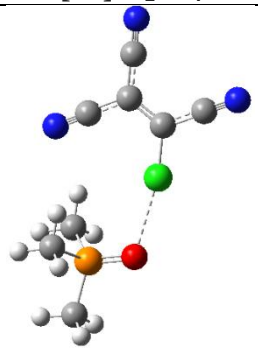
oxohalides			
			
[22] OF_2	**[23] ClO_3OF**	**[24] Cl_2O**	**[25] ClO_2**
			
[26] ClO_2F	**[27] ClO_3OCl**	**[28] Br_2O**	**[29] BrO_2**
			
[30] BrO_2F	**[31] ClO_3OBr**	**[32] IO_2F**	**[33] ClO_3OI**

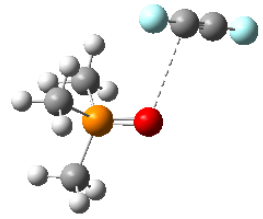
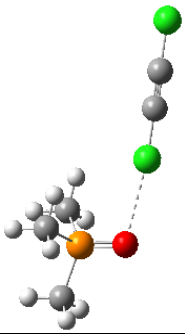
pseudohalides			
			
[34] FCN	**[35] FN_3**	**[36] FCNO**	**[37] ClCN**
			
[38] ClN_3	**[39] ClNCO**	**[40] ClSCN**	**[41] BrCN**

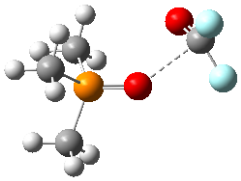
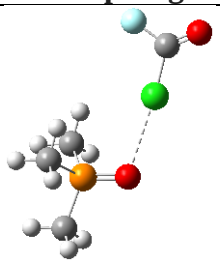
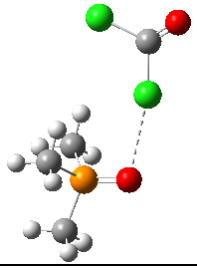
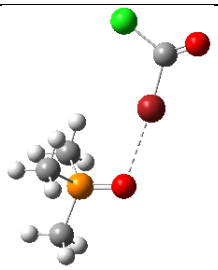
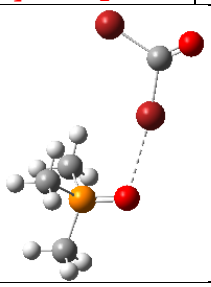
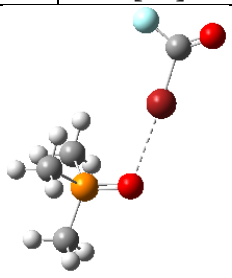
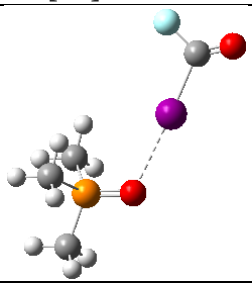
			
[42] BrN_3	**[43] BrNCO**	**[44] BrSCN**	**[45] ICN**
			
[46] IN_3	**[47] INCO**	**[48] ISCN**	

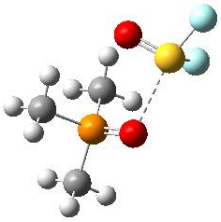
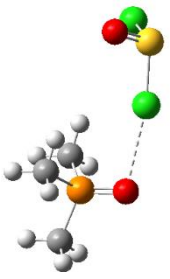
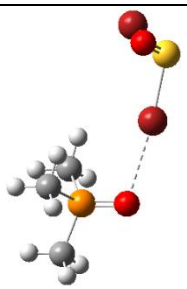
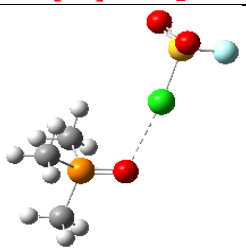
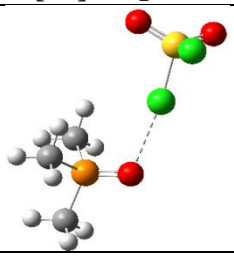
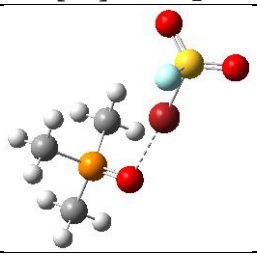
halogenated methanes and their derivatives			
			
[49] CF_3OF	**[50] CF_3SO_2OF**	**[51] CF_3Cl**	**[52] CCl_2F_2**
			
[53] CCl_3F	**[54] CCl_4**	**[55] CF_3OCl**	**[56] CF_3SO_2OCl**
			
[57] CF_3Br	**[58] CBr_2F_2**	**[59] CBr_3F**	**[60] $CBrCl_3$**

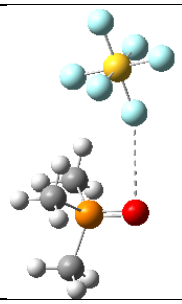
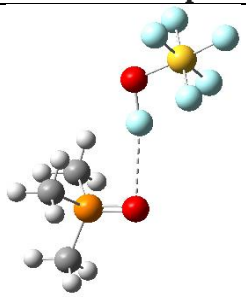
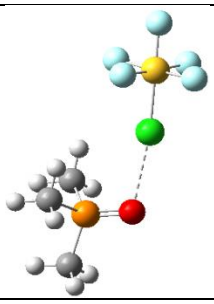
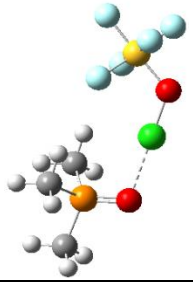
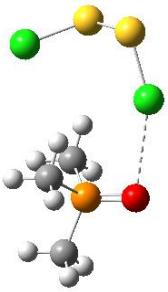
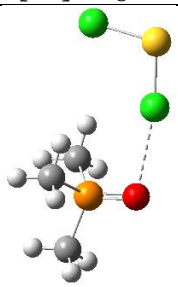
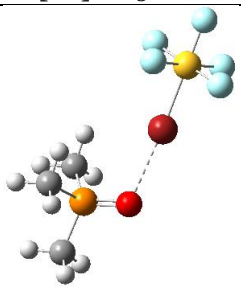
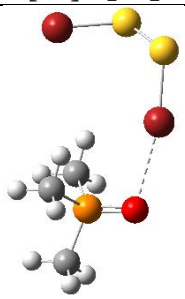
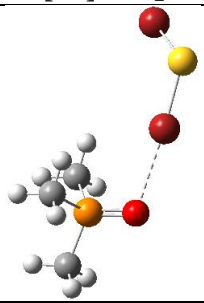
			
[61] $CBrClF_2$	**[62] CBr_4**	**[63] CF_3OBr**	**[64] CF_3SO_2OBr**
			
[65] CF_3I	**[66] CI_2F_2**	**[67] CI_3F**	**[68] $CIClF_2$**
			
[69] CI_4			

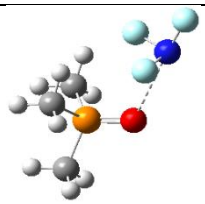
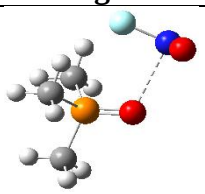
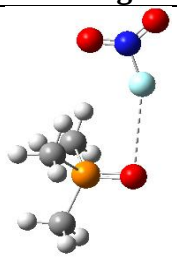
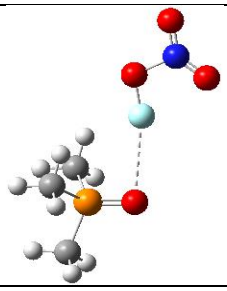
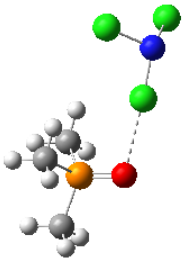
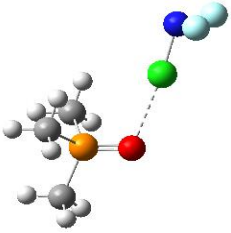
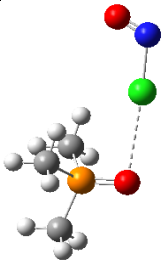
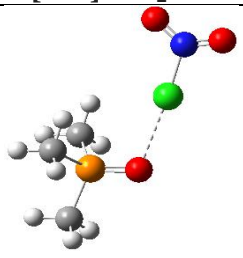
halogenated ethylene, halogenated acetylene and their derivatives			
			
[70] C_2F_4	**[71] C_2Cl_4**	**[72] C_2F_3Cl**	**[73] C_2Br_4**
			
[74] C_2F_3Br	**[75] C_2I_4**	**[76] C_2F_3I**	**[77] $C_2(CN)_3Cl$**

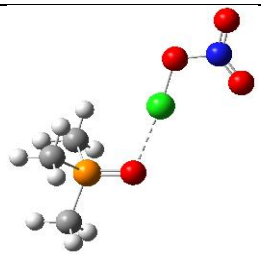
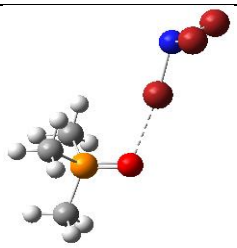
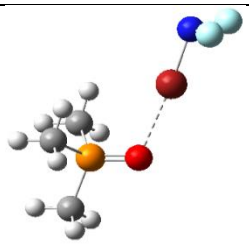
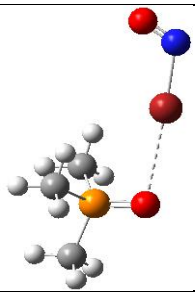
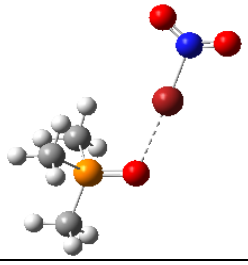
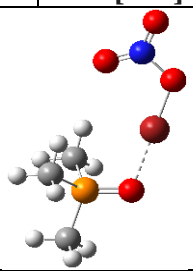
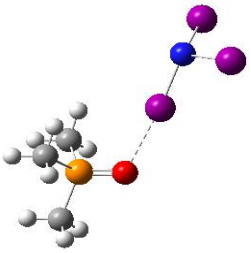
	
[78] C_2F_2	[79] C_2Cl_2

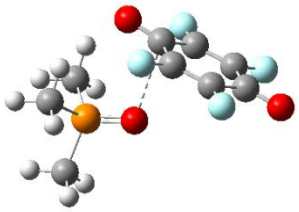
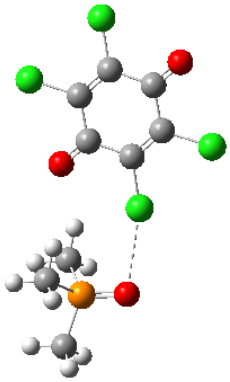
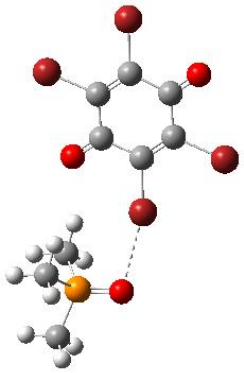
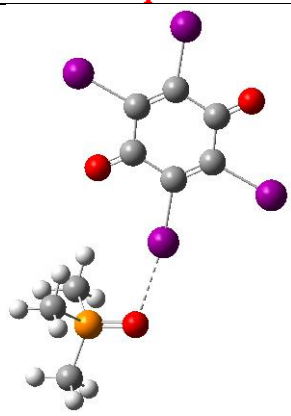
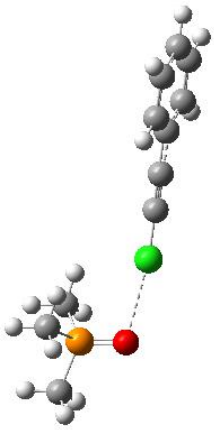
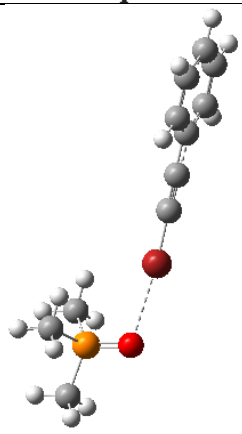
phosgene and its derivatives			
			
[80] COF_2	[81] COClF	[82] $COCl_2$	[83] COBrCl
			
[84] $COBr_2$	[85] COBrF	[86] COIF	

thionyl- and sulphurylhalides		
		
[87] SOF_2	[88] SO_2ClF	[89] $SOCl_2$
		
[90] $SOBr_2$	[91] SO_2Cl_2	[92] SO_2BrF

sulphur halides and sulphur hypohalites		
		
[93] SF_6	[94] SF_5OF	[95] SF_5Cl
		
[96] SF_5OCl	[97] S_2Cl_2	[98] SCl_2
		
[99] SF_5Br	[100] S_2Br_2	[101] SBr_2

halogenated nitrogen-containing compounds			
			
[102] NF_3	[103] NOF	[104] NO_2F	[105] NO_2OF
			
[106] NCl_3	[107] NF_2Cl	[108] NOCl	[109] NO_2Cl

			
[110] NO_2OCl	**[111] NBr_3**	**[112] NF_2Br**	**[113] NOBr**
			
[114] NO_2Br	**[115] NO_2OBr**	**[116] NI_3**	

organic compounds		
		
[117] tetrafluoro-1,4-benzoquinone	**[118] tetrachloro-1,4-benzoquinone**	**[119] tetrabromo-1,4-benzoquinone**
		
[120] tetraiodo-1,4-benzoquinone	**[121] $C_6H_5(C\equiv C)Cl$**	**[122] $C_6H_5(C\equiv C)Br$**

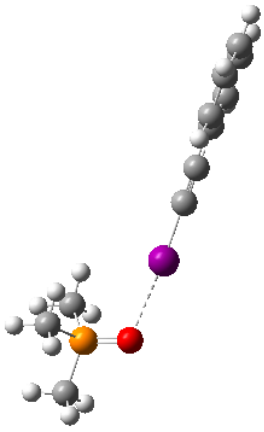
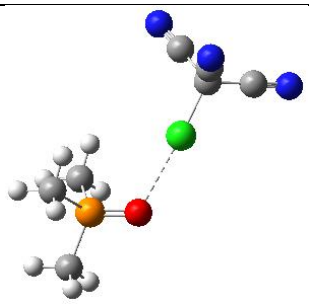
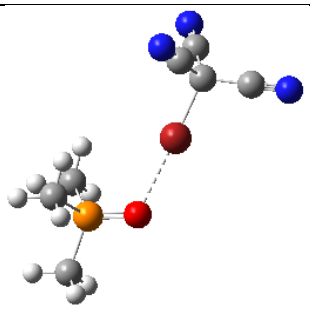
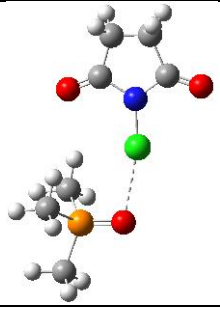
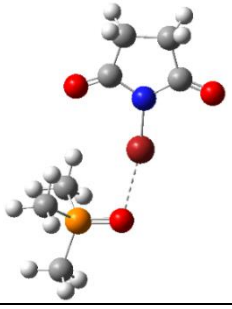
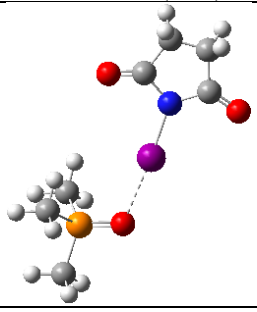
		
[123] $C_6H_5(C{\equiv}C)I$	**[124] $CCl(CN)_3$**	**[125] $CBr(CN)_3$**
		
[126] N-chlorosuccinimide	**[127] N-bromosuccinimide**	**[128] N-iodosuccinimide**

Table S1. Results of quantum-chemical calculation (M06-2x/def2-TZVPPD) of optimized geometries, complexation energies (BSSE-corrected) and spectroscopic parameters of 128 intermolecular 1:1 complexes formed by $Me_3P{=}O$ with halogen-containing molecules. The complexes in which the dominant intermolecular interaction is other than the halogen bond are marked in red color. In ambiguous cases the halogen atoms which participate in halogen bond formation are highlighted in bold font. For the definitions of the parameters listed please refer to Scheme 1 in the main text.

№	Halogen donor	ESP_{max}, kJ/mol	ΔδP, ppm	Δν, cm^{-1}	ΔE, kJ/mol	α (P=O···X), °	β (O···X–R), °	r, Å
	halogens							
1	F_2	57.49	3.51	8.15	8.60	99.4	174.6	2.56
2	Cl_2	106.58	9.22	29.58	25.76	109.2	177.0	2.61
3	Br_2	79.54	12.13	42.15	33.64	112.7	177.8	2.62
4	I_2	112.61	17.09	53.4	42.34	117.2	177.9	2.67
5	At_2	152.51	16.33	56.5	51.3	119.2	177.9	2.67
	interhalides							
6	ClF	170.89	15.5	49.45	43.45	112.4	179.3	2.38
7	ClF_3	169.84	17.01	54.59	45.12	113.7	180.0	2.43
8	ClF_5	133.88	11.38	29.3	36.86	122.2	163.4	2.69
9	BrF	205.54	21.67	71.34	59.97	115.0	179.3	2.36
10	BrF_3	207.38	24.59	79.07	60.89	115.7	179.8	2.40
11	BrF_5	179.03	14.53	41.36	53.04	124.8	155.6	2.68
12	BrCl	140.96	13.55	46.81	38.61	113.7	178.3	2.57
13	IF	250.69	25.63	77.7	79.57	119.4	178.6	2.43
14	IF_3	239.14	30.54	95.66	77.37	120.2	179.8	2.43
15	IF_5	212.36	17.91	59.42	71.43	127.1	145.4	2.68
16	ICl	139.91	20.08	69.01	59.66	119.3	178.6	2.53
17	ICl_3	173.25	36.02	119.17	88.31	122.0	179.3	2.53
18	IBr	166.16	18.08	65.22	53.57	118.6	178.5	2.58
19	AtCl	239.25	22.99	68.99	76.14	121.4	178.5	2.54
20	AtBr	215.0	21.23	69.25	69.64	120.8	178.3	2.57
21	AtI	128.63	17.88	61.41	59.33	119.3	178.0	2.63
	oxohalides							
22	OF_2	28.35	1.15	1.61	3.58	95.4	169.2	2.91
23	ClO_3OF	45.15	3.76	8.09	10.04	101.9	176.1	2.67
24	Cl_2O	132.04	11.73	35.48	31.98	111.3	175.4	2.52
25	ClO_2	139.13	9.82	26.1	36.65	117.9	159.2	2.74
26	ClO_2F	179.81	12.14	35.41	46.33	117.1	158.5	2.58
27	ClO_3OCl	173.0	24.99	80.16	50.48	109.5	178.4	2.26
28	Br_2O	153.83	16.41	50.99	44.24	114.4	175.4	2.51
29	BrO_2	174.04	14.31	42.92	54.34	119.7	165.7	2.68
30	BrO_2F	217.35	22.96	86.47	75.40	118.5	165.0	2.40
31	ClO_3OBr	211.05	39.60	121.01	76.66	112.1	178.3	2.16
32	IO_2F	254.1	36.39	139.07	124.07	121.1	173.8	2.27
33	ClO_3OI	263.29	39.96	118.46	105.28	118.56	179.6	2.28
	pseudohalides							
34	FCN	116.55	9.19	23.39	36.80	---	---	2.65
35	FN_3	122.85	6.79	14.03	26.87	---	---	2.70
36	FCNO	115.24	11.29	34.68	40.74	---	---	2.57
37	ClCN	122.06	7.63	18.22	26.35	124.7	177.0	2.70
38	ClN_3	97.65	7.53	25.61	23.46	108.7	174.8	2.67
39	ClNCO	121.0	9.18	27.09	27.41	110.3	176.0	2.61
40	ClSCN	100.0	8.79	26.96	24.44	107.8	172.0	2.71

41	$BrCN$	175.88	8.84	27.08	33.94	121.2	176.9	2.71
42	BrN_3	126.78	11.92	38.85	34.34	113.4	175.7	2.63
43	BrNCO	153.04	13.44	43.86	40.48	114.7	176.6	2.56
44	BrSCN	129.15	12.66	41.38	34.65	113.0	176.4	2.66
45	ICN	207.38	13.61	42.04	50.70	123.8	177.7	2.68
46	IN_3	168.26	19.02	60.71	54.14	119.3	177.9	2.58
47	INCO	205.8	21.08	65.71	62.87	119.9	177.5	2.53
48	ISCN	170.63	20.02	66.95	54.38	118.8	177.8	2.59
halogenated methanes and their derivatives								
49	CF_3OF	28.09	2.00	4.75	5.25	95.2	172.1	2.77
50	CF_3SO_2OF	55.13	4.03	10.1	14.66	111.7	152.0	2.70
51	CF_3Cl	89.0	5.37	12.77	16.70	108.6	173.7	2.83
52	CCl_2F_2	85.84	5.61	14.90	16.89	108.1	173.0	2.82
53	CCl_3F	81.38	6.22	15.54	17.72	104.7	168.4	2.83
54	CCl_4	80.59	6.14	16.52	17.93	104.7	168.4	2.83
55	CF_3OCl	154.09	15.18	55.81	40.20	109.4	178.0	2.44
56	CF_3SO_2OCl	171.19	41.07	134.46	60.47	108.2	177.3	2.04
57	CF_3Br	103.43	6.75	20.68	22.74	112.2	175.9	2.83
58	CBr_2F_2	99.49	6.53	22.12	23.25	112.39	175.0	2.82
59	CBr_3F	97.13	8.56	23.93	24.13	109.7	172.6	2.81
60	$CBrCl_3$	96.86	8.20	24.88	24.32	110.3	174.2	2.79
61	$CBrClF_2$	99.75	6.91	21.52	23.04	111.6	174.2	2.82
62	CBr_4	96.34	8.41	25.99	24.97	109.7	174.0	2.78
63	CF_3OBr	191.89	23.76	88.61	86.78	113.6	179.4	2.35
64	CF_3SO_2OBr	220.0	44.03	141.39	87.13	111.3	177.1	2.11
65	CF_3I	131.78	10.07	32.29	34.79	117.9	176.6	2.81
66	CI_2F_2	121.28	11.06	35.38	34.75	117.2	175.4	2.80
67	CI_3F	119.18	13.25	40.29	35.73	116.4	176.1	2.77
68	$ClClF_2$	128.89	10.58	36.42	35.51	117.3	175.7	2.79
69	CI_4	118.91	13.50	42.88	37.37	116.7	176.3	2.74
halogenated ethylene, halogenated acetylene and their derivatives								
70	C_2F_4	86.89	4.52	11.28	19.42	---	---	2.78
71	C_2Cl_4	76.13	5.32	15.31	18.47	104.1	170.6	2.86
72	C_2F_3Cl	86.83	5.02	14.75	16.12	107.7	172.6	2.85
73	C_2Br_4	94.24	7.90	21.93	22.69	108.7	172.0	2.84
74	C_2F_3Br	105.53	7.07	21.93	22.68	111.8	174.4	2.84
75	C_2I_4	115.76	10.15	35.81	33.99	115.2	174.4	2.81
76	C_2F_3I	136.76	9.58	32.39	35.02	117.3	175.5	2.82
77	$C_2(CN)_3Cl$	148.05	8.72	24.76	26.23	119.6	168.8	2.89
78	C_2F_2	39.64	1.57	3.95	8.24	---	---	2.98
79	C_2Cl_2	96.1	5.26	13.32	17.41	108.5	173.9	2.82
phosgene and its derivatives								
80	COF_2	173.0	7.61	18.14	34.90	---	---	2.49
81	COClF	98.44	5.34	14.11	17.40	111.9	175.1	2.82
82	$COCl_2$	84.79	5.63	15.95	16.80	105.4	168.5	2.85
83	COBrCl	69.04	6.83	21.78	21.93	111.6	175.5	2.84
84	$COBr_2$	95.03	7.18	24.03	22.65	110.1	172.9	2.83
85	COBrF	119.7	6.63	20.31	23.41	114.1	176.6	2.83
86	COIF	137.29	9.90	33.3	36.08	119.3	177.7	2.81
thionyl- and sulphurylhalides								
87	SOF_2	181.92	12.27	39.3	43.35	---	---	2.61
88	SO_2ClF	123.64	8.00	23.71	24.45	116.5	173.7	2.71
89	$SOCl_2$	6.56	6.15	17.54	16.52	104.8	169.9	2.86
90	$SOBr_2$	9.19	7.90	26.43	21.99	109.0	174.2	2.85
91	SO_2Cl_2	109.46	8.92	21.01	23.50	112.9	172.1	2.72
92	SO_2BrF	139.91	10.95	35.44	36.82	117.9	175.6	2.70
sulphur halides and sulphur hypohalites								
93	SF_6	8.4	0.62	2.78	4.18	---	---	3.14
94	SF_5OF	29.14	1.91	4.42	5.46	95.3	170.6	2.76
95	SF_5Cl	94.24	8.20	22.41	21.16	107.2	172.7	2.73

96	SF_5OCl	158.81	18.13	55.55	43.54	119.3	179.8	2.37
97	S_2Cl_2	27.3	4.86	15.70	16.70	99.5	155.9	2.95
98	SCl_2	68.25	5.73	16.76	17.03	103.8	169.7	2.83
99	SF_5Br	115.24	11.35	36.17	34.15	114.02	176.8	2.68
100	S_2Br_2	96.6	8.23	27.72	22.85	106.8	168.5	2.83
101	SBr_2	87.94	9.02	27.69	24.34	110.3	176.4	2.78
halogenated nitrogen-containing inorganic compounds								
102	NF_3	71.66	2.47	4.56	10.92	---	---	2.89
103	NOF	104.48	9.39	26.59	35.23	---	---	2.58
104	NO_2F	80.33	0.80	2.42	3.95	---	---	3.06
105	NO_2OF	31.0	1.79	2.59	3.97	97.1	166.3	2.87
106	NCl_3	105.26	9.15	27.47	25.25	107.7	176.6	2.65
107	NF_2Cl	118.91	8.11	24.48	25.20	112.1	174.8	2.65
108	NOCl	25.73	2.07	9.03	6.62	99.7	176.1	3.07
109	NO_2Cl	106.84	9.75	31.75	26.93	111.7	176.1	2.61
110	NO_2OCl	154.1	13.05	39.06	35.97	114.1	174.8	2.47
111	NBr_3	120.75	11.30	39.72	33.94	113.5	173.8	2.63
113	NF_2Br	135.45	11.00	37.49	34.26	115.2	175.9	2.64
114	NOBr	17.06	2.80	11.36	9.11	103.1	176.9	3.1
115	NO_2Br	126.0	13.45	47.13	36.72	115.2	177.5	2.59
116	NO_2OBr	189.0	26.80	86.13	60.05	112.9	179.9	2.32
117	NI_3	148.58	18.28	57.86	49.21	118.50	174.6	2.61
assorted organic compounds								
117	tetrafluoro-1,4-benzoquinone	138.86	13.69	41.38	53.0	---	---	2.61
118	tetrachloro-1,4-benzoquinone	80.1	7.95	18.75	22.52	102.9	163.0	2.87
119	tetrabromo-1,4-benzoquinone	97.39	9.04	22.71	27.18	105.3	164.1	2.87
120	tetraiodo-1,4-benzoquinone	121.0	11.10	34.35	35.71	112.4	171.2	2.83
121	$C_6H_5C_2$**Cl**	80.33	5.46	12.97	15.89	106.8	173.1	2.85
122	$C_6H_5C_2$**Br**	102.64	7.27	18.70	22.65	111.0	175.1	2.84
123	$C_6H_5C_2$**I**	134.14	10.68	30.80	34.88	116.7	176.5	2.82
124	C**Cl**$(CN)_3$	147.53	9.58	28.24	29.54	119.0	176.7	2.63
125	C**Br**$(CN)_3$	172.46	13.47	47.29	41.71	119.8	178.1	2.59
126	N-chlorosuccinimide	126	13.08	41.68	38.83	109.0	169.9	2.64
127	N-bromosuccinimide	96.34	9.73	27.5	28.54	105.0	166.9	2.67
128	N-iodosuccinimide	172.73	19.99	61.63	57.52	117.4	175.9	2.58

Table S2. The results of QTAIM analysis of electron density in intermolecular bond critical point (3; –1) for 1:1 complexes formed by $Me_3P{=}O$ with halogen-containing molecules. ρ, $\nabla^2\rho$, V and G are, respectively, electron density, Laplacian of electron density, local electron potential and kinetic energies densities at BCP. The complexes in which the dominant intermolecular interaction is other than the halogen bond are marked in red color. In ambiguous cases the halogen atoms which participate in halogen bond formation are highlighted in bold font.

№	Halogen bond donor	G, kJ/mol	V, kJ/mol	ρ, a.u.	$\nabla^2\rho$, a.u.
		halogens			
1	F_2	42.13	-33.02	0.0147	0.0781
2	Cl_2	56.43	-50.57	0.0231	0.0949
3	Br_2	61.61	-58.58	0.0270	0.0985
4	I_2	62.57	-63.28	0.0288	0.0942
5	At_2	70.69	-70.05	0.0297	0.1090
		interhalides			
6	**Cl**F	90.94	-91.733	0.0372	0.1373
7	**Cl**F_3	88.03	-88.58	0.0375	0.1333
8	**Cl**F_5	55.01	-50.67	0.0230	0.0904
9	**Br**F	101.48	-113.47	0.0455	0.1363
10	**Br**F_3	99.88	-110.36	0.0465	0.1362
11	**Br**F_5	60.60	-57.53	0.0267	0.0970
12	**Br**Cl	68.21	-66.47	0.0297	0.1066
13	**I**F	100.35	-116.74	0.0448	0.1279
14	**I**F_3	104.48	-127.49	0.0513	0.1241
15	**I**F_5	66.58	-67.49	0.0313	0.1001
16	**I**Cl	81.27	-88.70	0.0369	0.1125
17	**I**Cl_3	120.83	-156.92	0.0610	0.1291
18	**I**Br	74.74	-79.67	0.0342	0.1064
19	**At**Cl	94.32	-98.80	0.0378	0.1377
20	**At**Br	88.46	-91.64	0.0360	0.1306
21	**At**I	76.57	-77.11	0.0318	0.1163
		oxohalides			
22	O$\mathbf{F}_2$	17.24	-11.73	0.0068	0.0346
23	$ClO_3O\mathbf{F}$	81.62	-109.19	0.0417	0.0823
24	**Cl**$_2$O	68.31	-63.84	0.0275	0.1109
25	**Cl**O_2	45.26	-39.29	0.0184	0.0780
26	**Cl**O_2F	61.23	-56.85	0.0258	0.0999
27	$ClO_3O\mathbf{Cl}$	117.66	-132.53	0.0530	0.0157
28	**Br**$_2$O	76.81	-77.49	0.0333	0.1160
29	**Br**O_2	55.88	-51.68	0.0241	0.0915
30	**Br**O_2F	93.95	-104.43	0.0461	0.1271
31	$ClO_3O\mathbf{Br}$	151.99	-210.22	0.0761	0.1428
32	**I**O_2F	136.38	-188.17	0.0690	0.1289
33	$ClO_3O\mathbf{I}$	143.28	-185.96	0.0642	0.1533
		pseudohalides			
34	**F**CN	34.37	-29.05	0.0155	0.0605
35	**F**N_3	34.21	-27.96	0.0132	0.0616
36	**F**CNO	42.31	-37.42	0.0192	0.0719
37	**Cl**CN	45.74	-38.70	0.0181	0.0804
38	**Cl**N_3	45.74	-38.70	0.0181	0.0804
39	**Cl**NCO	56.30	-50.15	0.0225	0.0951
40	**Cl**SCN	46.31	-40.02	0.0194	0.0801
41	**Br**CN	51.36	-46.00	0.0215	0.0864

42	**Br**N_3	60.07	-56.56	0.0258	0.0969
43	**Br**NCO	68.71	-66.65	0.0292	0.1078
44	**Br**SCN	57.20	-53.39	0.0251	0.0929
45	**I**CN	61.56	-60.47	0.0269	0.0954
46	**I**N_3	74.12	-78.44	0.0334	0.1064
47	**I**NCO	82.03	-89.04	0.0365	0.1143
48	**I**SCN	72.58	-76.72	0.0335	0.1042
halogenated methanes and their derivatives					
49	CF_3O**F**	24.85	-17.84	0.0093	0.0485
50	CF_3SO_2O**F**	29.29	-21.46	0.0106	0.0566
51	CF_3**Cl**	35.33	-28.77	0.0149	0.0638
52	C**Cl**$_2F_2$	35.92	-29.39	0.0152	0.0647
53	C**Cl**$_3$F	35.73	-29.31	0.0153	0.0642
54	C**Cl**$_4$	37.11	-30.69	0.0158	0.0663
55	CF_3O**Cl**	81.20	-79.65	0.0333	0.1261
56	CF_3SO_2O**Cl**	177.74	-243.73	0.0898	0.1702
57	CF_3**Br**	40.26	-34.85	0.0176	0.0696
58	C**Br**$_2F_2$	41.37	-36.03	0.0181	0.0712
59	C**Br**$_3$F	42.38	-37.17	0.0186	0.0725
60	C**Br**Cl_3	43.57	-38.40	0.0191	0.0743
61	C**Br**ClF_2	40.92	-35.58	0.0180	0.0705
62	C**Br**$_4$	44.42	-39.29	0.0194	0.0755
63	CF_3O**Br**	103.95	-118.31	0.0477	0.1364
64	CF_3SO_2O**Br**	220.31	-362.23	0.1116	0.1194
65	CF_3**I**	48.50	-45.43	0.0219	0.0786
66	C**I**$_2F_2$	49.67	-46.94	0.0225	0.0798
67	C**I**$_3$F	51.90	-11.87	0.0235	0.0825
68	C**I**ClF_2	49.88	-47.13	0.0225	0.0801
69	C**I**$_4$	54.89	-53.28	0.0248	0.0861
halogenated ethylene, halogenated acetylene and their derivatives					
70	**C**$_2F_4$	27.55	-23.40	0.0130	0.0483
71	C_2**Cl**$_4$	33.70	-27.31	0.0144	0.0611
72	C_2F_3**Cl**	33.65	-27.11	0.0142	0.0612
73	C_2**Br**$_4$	39.72	-34.29	0.0174	0.0688
74	C_2F_3**Br**	39.62	-34.06	0.0172	0.0688
75	C_2**I**$_4$	48.60	-45.59	0.0219	0.0786
76	C_2F_3**I**	47.65	-44.27	0.0213	0.0777
77	$C_2(CN)_3$**Cl**	48.94	-42.33	0.0196	0.0846
78	**C**$_2F_2$	17.61	-14.06	0.0085	0.0322
79	C_2**Cl**$_2$	36.00	-29.34	0.0149	0.0650
phosgene and its derivatives					
80	**C**OF_2	44.16	-38.36	0.0191	0.0761
81	CO**Cl**F	36.21	-29.63	0.0152	0.0652
82	CO**Cl**$_2$	34.21	-27.90	0.0147	0.0617
83	CO**Br**Cl	39.86	-34.57	0.0176	0.0688
84	CO**Br**$_2$	40.24	-35.04	0.0179	0.0693
85	CO**Br**F	40.34	-34.93	0.0176	0.0697
86	CO**I**F	48.29	-45.10	0.0217	0.0784
thionyl- and sulphurylhalides					
87	**S**OF_2	53.58	-51.00	0.0248	0.0856
88	SO_2**Cl**F	45.70	-39.11	0.0189	0.0797
89	SO**Cl**$_2$	33.35	-27.23	0.0148	0.0601
90	SO**Br**$_2$	39.34	-34.32	0.0180	0.0676
91	SO_2**Cl**$_2$	45.33	-38.91	0.0189	0.0788
92	SO_2**Br**F	53.11	-48.61	0.0231	0.0877
sulphur halides and sulphur hypohalites					
93	**S**F_6	9.89	-6.37	0.0044	0.0204
94	SF_5O**F**	25.68	-18.50	0.0096	0.0501
95	SF_5**Cl**	44.21	-37.79	0.0186	0.0771
96	SF_5O**Cl**	93.64	-96.07	0.0393	0.1390

97	S_2**Cl**$_2$	27.92	-22.20	0.0128	0.0513
98	**S**Cl_2	35.62	-29.25	0.0154	0.0640
99	SF_5**Br**	55.19	-51.06	0.0241	0.0904
100	S_2**Br**$_2$	40.78	-35.74	0.0185	0.0698
101	**S**Br_2	44.26	-39.17	0.0196	0.0752
halogenated nitrogen-containing inorganic compounds					
102	**N**F_3	21.45	-16.87	0.0089	0.0397
103	**N**OF	41.62	-35.72	0.0175	0.0724
104	NO_2**F**	12.02	-7.96	0.0053	0.0245
105	NO_2O**F**	19.00	-13.03	0.0074	0.0380
106	N****Cl**$_3$	52.89	-46.91	0.0217	0.0897
107	NF_2**Cl**	51.92	-45.71	0.0211	0.0886
108	NO**Cl**	20.70	-15.73	0.0101	0.0391
109	NO_2**Cl**	56.38	-50.92	0.0233	0.0942
110	NO_2O**Cl**	75.82	-72.58	0.0306	0.1204
111	N**Br**$_3$	60.73	-57.38	0.0262	0.0976
112	NF_2**Br**	59.02	-55.42	0.0255	0.0954
113	NO**Br**	22.99	-18.58	0.0115	0.0417
114	NO_2**Br**	65.01	-62.86	0.0286	0.1023
115	NO_2O**Br**	109.93	-128.72	0.0515	0.1389
116	N**I**$_3$	70.60	-73.71	0.0318	0.1028
assorted organic compounds					
117	tetrafluoro-1,4-benzoquinone	41.03	-35.03	0.0177	0.0717
118	tetrachloro-1,4-benzoquinone	33.55	-27.27	0.0145	0.0607
119	tetrabromo-1,4-benzoquinone	38.20	-32.94	0.0171	0.0662
120	tetraiodo-1,4-benzoquinone	102.57	-76.79	0.0614	0.1155
121	$C_6H_5C_2$**Cl**	33.53	-26.99	0.0140	0.0610
122	$C_6H_5C_2$**Br**	39.51	-33.82	0.0170	0.0688
123	$C_6H_5C_2$**I**	47.84	-44.31	0.0211	0.0783
124	C**Cl**$(CN)_3$	54.42	-48.16	0.0220	0.0924
125	C**Br**$(CN)_3$	65.88	-63.24	0.0284	0.1044
126	N-chlorosuccinimide	59.88	-56.40	0.0257	0.0965
127	N-bromosuccinimide	50.44	-44.25	0.0206	0.0863
128	N-iodosuccinimide	75.57	-80.12	0.0337	0.1082

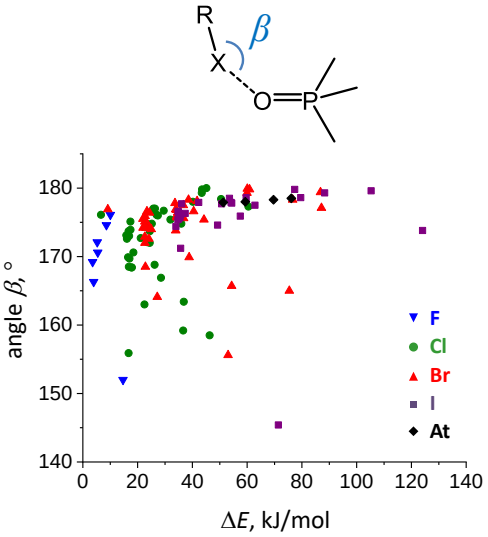


Figure S2. The correlation between angles β (angle O···X–R) and the complexation energy for 128 complexes studied in this work (X = F, Cl, Br, I, At). Stronger complexes seem to be characterized by generally smaller range of β angles closer to 180°.

Table S3. Geometric parameters of the R–X···O=P halogen bonds found in CCDC 2020 database for X = Cl, Br. *r* – X...O distance; *R* – normalized distance parameter $R = r/(R_O + R_X)$, where R_O and R_X are van-der-Waals radii of oxygen and halogen atoms, respectively, α and β – X···O=P and R–X···O angles, respectively. Search criteria: NM~X···O~P(~NM)$_3$ fragment, where (i) ~ is any bond; (ii) X = Cl, Br, I; (iii) NM is any nonmetal; (iv) d(X···O) ≡ r is less than the Bondi's vdW sums; (v) ∠(NM~X···O) ≡ β, 150° ≤ β ≤ 180°; (vi) number of bonded atoms for X is 1; (vii) number of bonded atoms for P is 4; (viii) structures are non-disordered; (ix) Final R_1 index [I≥2σ (I)] is less or equal 10%.

CCDC code	*r*, Å	*R*	α, °	*β*, °	CCDC code	*r*, Å	*R*	α, °	*β*, °
X = Cl									
AYEQOK	3.084	0.94	149.2	165.8	MAQPOJ	3.215	0.98	110.1	162.7
CAZLAT	3.037	0.93	138.1	159.9	MYPOCL	3.198	0.98	147.6	159.8
CEPSIA	2.896	0.89	120.2	170.4	NEKMUM	3.190	0.98	101.8	173.9
	2.923	0.89	128.4	165.1	NIMBUG	3.260	1.00	115.6	161.3
DAVKUG	3.180	0.97	131.8	161.5	NIYYIG	3.046	0.93	132.3	169.2
DUYXUQ	3.203	0.98	121.1	168.8	OBUCAQ	3.236	0.99	173.2	171.9
EHENIO	2.817	0.86	107.9	180.0	OCETEX	3.044	0.93	132.2	167.3
FIJROH	3.194	0.98	153.1	161.6	ROBROP	3.269	1.00	119.4	170.0
HOHNOH	2.929	0.90	144.9	171.3	RONOXN	3.245	0.99	125.7	171.0
HOHREB	3.062	0.94	140.7	173.2	RUNZAD	3.018	0.92	137.7	151.1
IKENIV	3.140	0.96	117.8	164.0	SERXAO	3.240	0.99	125.1	165.1
JANNAO	3.218	0.98	104.3	168.6	TUQZUA	2.890	0.88	120.6	168.2
KANSUO	3.183	0.97	156.8	153.5	WIXVII	2.988	0.91	120.8	171.2
KOSYIA	3.237	0.99	109.9	176.2	XUCSEU	3.232	0.99	129.8	158.1
LOGZUF	3.257	1.00	116.6	170.0	YIVPAV	2.996	0.92	132.2	175.1
MANNOH	3.091	0.95	127.0	172.1	VEPJEI	3.120	0.95	111.4	171.4
X = Br									
NEBXOK	3.035	0.90	115.2	176.3	PUVGUJ	2.975	0.88	110.9	166.7
BCMOPH	3.106	0.92	155.6	165.5		2.805	0.83	116.9	171.6
BILBUV	3.196	0.95	99.7	173.6	SIJSOU	3.034	0.90	102.1	171.5
CAKXIW	3.294	0.98	111.7	159.6	TANXAH	3.255	0.97	114.8	177.2
COJXAB	2.948	0.87	121.9	163.2	TOTNOH	3.239	0.96	126.5	162.0
CORFIZ	2.951	0.88	113.2	168.5		3.274	0.97	126.3	162.0
FEFBOI	2.875	0.85	128.8	174.8	UGISEI	3.348	0.99	104.3	157.2
FUGCAN	3.027	0.90	146.7	169.2	UXOBUG	2.802	0.83	151.9	170.6
ISIHAT	3.021	0.90	163.8	166.1		2.788	0.83	149.5	168.7
JOTVIX	2.970	0.88	160.0	166.7	VIZGUG	3.200	0.95	149.8	161.2
MUMKOV	3.046	0.90	117.8	176.8	VUJKOA	3.042	0.90	124.4	175.0
NUCYAL	3.093	0.92	105.3	167.9	XEGSUZ	3.215	0.95	131.7	169.6
OBULAZ	2.983	0.89	134.0	176.6	YEFWIQ	2.967	0.88	126.8	165.6
PASDIX	2.742	0.81	153.6	166.1	ZUFPEX	2.798	0.83	145.0	175.3
PASLAY	2.862	0.85	129.6	173.2		2.811	0.83	117.2	175.1
	2.893	0.86	127.8	169.7	VEPJEI	3.345	0.99	109.4	168.2

Table S3 continued. Geometric parameters of the R–X···O=P halogen bonds found in CCDC 2020 database for X = I. r – X...O distance; R – normalized distance parameter $R = r/(R_O + R_X)$, where R_O and R_X are van-der-Waals radii of oxygen and halogen atoms, respectively, α and β – X···O=P and R–X···O angles, respectively. Search criteria: NM~X···O~P(~NM)$_3$ fragment, where (i) ~ is any bond; (ii) X = Cl, Br, I; (iii) NM is any nonmetal; (iv) d(X···O) ≡ r is less than the Bondi's vdW sums; (v) ∠(NM~X···O) ≡ β, 150° ≤ β ≤ 180°; (vi) number of bonded atoms for X is 1; (vii) number of bonded atoms for P is 4; (viii) structures are non-disordered; (ix) Final R_1 index [I≥2σ (I)] is less or equal 10%.

CCDC code	r, Å	R	α, °	β, °	CCDC code	r, Å	R	α, °	β, °
X = I									
ANUQAC	2.752	0.79	158.6	174.6	MELCEM	2.894	0.83	161.0	178.1
COLCOY	2.904	0.83	133.3	166.9	QECCUW	3.018	0.86	124.6	174.9
COLCUE	2.965	0.85	135.5	169.6	ROHCEW	3.009	0.86	129.3	176.6
ECUQUO	2.835	0.81	139.0	170.6	SAXJUZ	2.683	0.77	172.2	176.8
	2.864	0.82	125.0	177.0	SIJSUA	3.098	0.89	106.7	169.9
GIDRES	2.809	0.80	114.1	173.1	SOKKUB	2.936	0.84	163.0	165.4
GULYOB	2.760	0.79	136.3	174.0		3.204	0.92	112.6	161.3
	2.862	0.82	126.8	168.1	SOKLAI	2.992	0.85	126.3	165.3
HARREA	3.217	0.92	116.4	169.2	SOKLEM	3.004	0.86	117.7	173.2
HERMAS	2.954	0.84	131.4	166.0	SOKLOW	3.006	0.86	121.2	174.4
JUZRIH	2.826	0.81	123.9	176.1		3.008	0.86	119.4	177.0
	2.915	0.83	118.2	171.0		3.040	0.87	117.7	175.5
JUZRON	2.979	0.85	116.4	163.8	SOKWUN	2.967	0.85	116.8	176.5
	2.920	0.83	127.0	174.5	SOKXAU	3.003	0.86	120.1	176.2
JUZRON01	2.776	0.79	148.0	174.2	SOKXEY	3.025	0.86	117.6	177.4
JUZRUT	2.727	0.78	152.1	175.7	ULOKIP	2.823	0.81	118.5	176.9
JUZSAA	2.847	0.81	130.4	175.7		2.809	0.80	146.2	175.7
KAQSUS	2.602	0.74	131.3	177.8	ULOKIP01	2.814	0.80	118.4	177.0
LEJBUA	2.766	0.79	136.5	172.4		2.801	0.80	146.0	175.5
	3.304	0.94	140.4	160.3	VOJNAM	2.581	0.74	122.5	171.4
	2.856	0.82	142.3	175.6	WAMBOE	3.324	0.95	110.9	166.8
	2.759	0.79	132.8	176.6	WAPBOH	2.707	0.77	143.5	172.8
LICBEG	2.768	0.79	122.2	171.9	WAPBUN	2.716	0.78	128.1	172.8
LIFTOM	2.736	0.78	154.6	177.5	WAPCAU	2.720	0.78	144.6	171.5

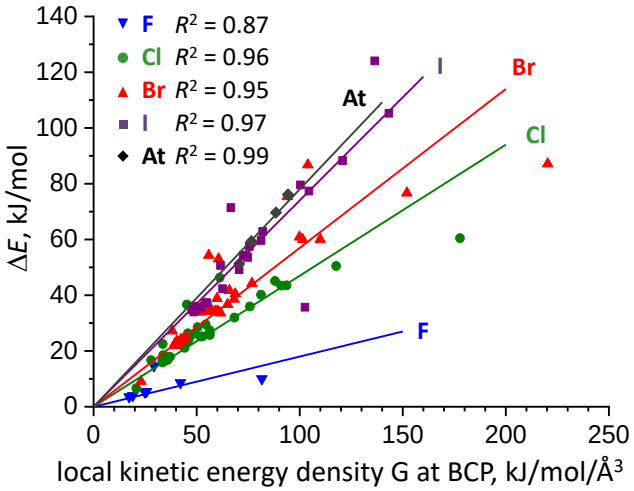


Figure S3. Correlation between calculated complexation energy ΔE and the value of local kinetic energy density G at halogen bond critical point (3;–1) for $Me_3P{=}O\cdots X{-}R$ halogen-bonded complexes studied in this work (X = F, Cl, Br, I, At). The solid lines correspond to one of Eqs. (9) in the main text.

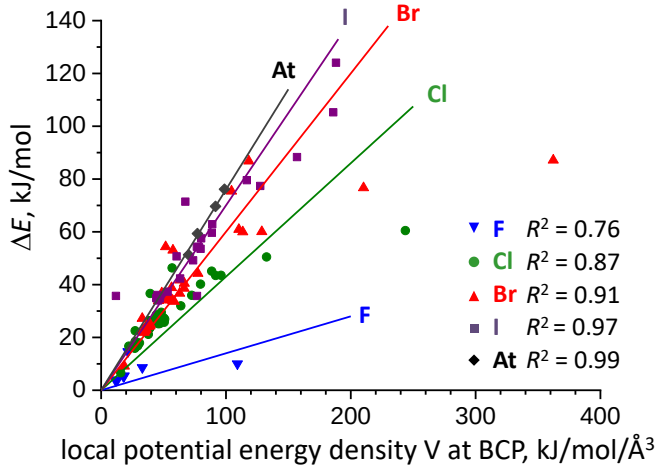


Figure S4. Correlation between calculated complexation energy ΔE and the value of local potential energy density V at halogen bond critical point (3;–1) for $Me_3P{=}O\cdots X{-}R$ complexes studied in this work (X = F, Cl, Br, I, At). The solid lines correspond to one of Eqs. (9) in the main text.

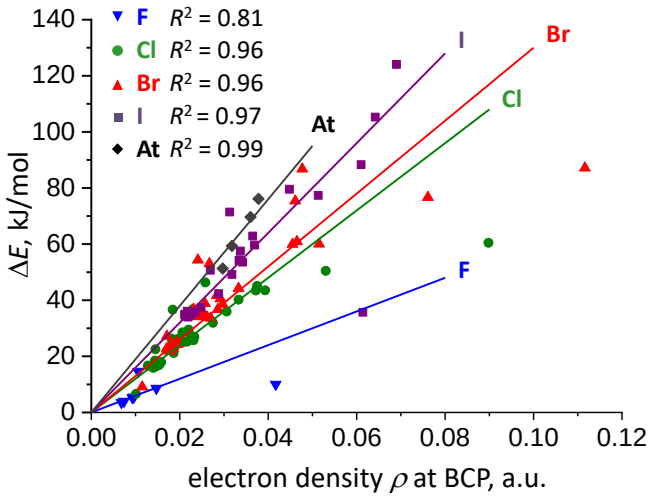


Figure S5. Correlation between calculated complexation energy ΔE and the value of electron density ρ at halogen bond critical point (3;–1) for $Me_3P{=}O\cdots X{-}R$ complexes studied in this work (X = F, Cl, Br, I, At). The solid lines correspond to one of Eqs. (9) in the main text.

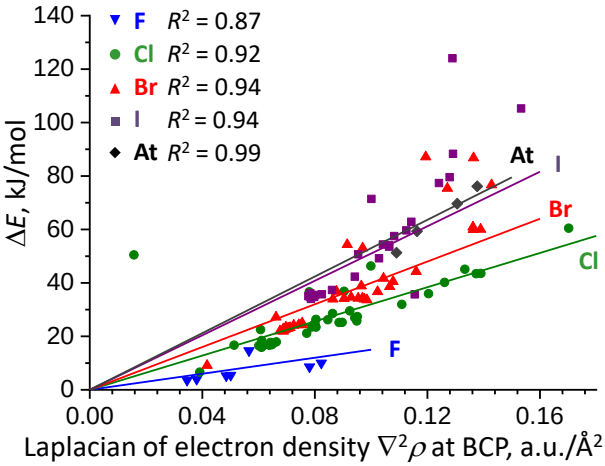


Figure S6. Correlation between calculated complexation energy ΔE and the value of the Laplacian of electron density $\nabla^2\rho$ at halogen bond critical point (3;–1) for $Me_3P{=}O\cdots X{-}R$ complexes studied in this work (X = F, Cl, Br, I, At). The solid lines correspond to one of Eqs. (9) in the main text.

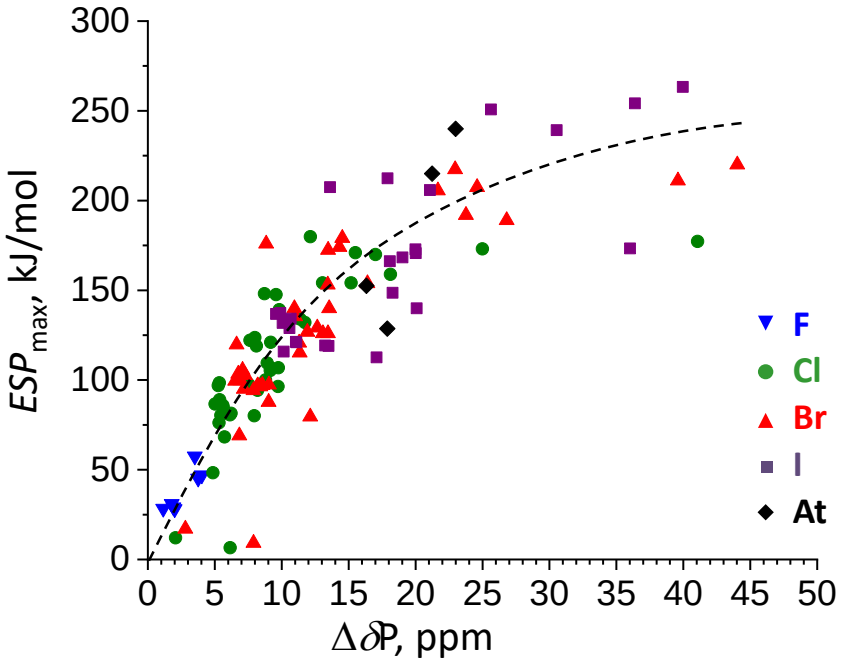


Figure S7. Correlation between the extremal value of electrostatic potential ESP_{max} (measured in the region of σ-hole of X atom on the surface of equal electron density taken at 0.001 electron/Bohr^3 level) and change of the ^{31}P NMR chemical shift upon complexation, ΔδP, for R–X···O=PMe$_3$ halogen-bonded complexes studied in this work (X = F, Cl, Br, I, At). The dashed line is drawn to guide the eye.