

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

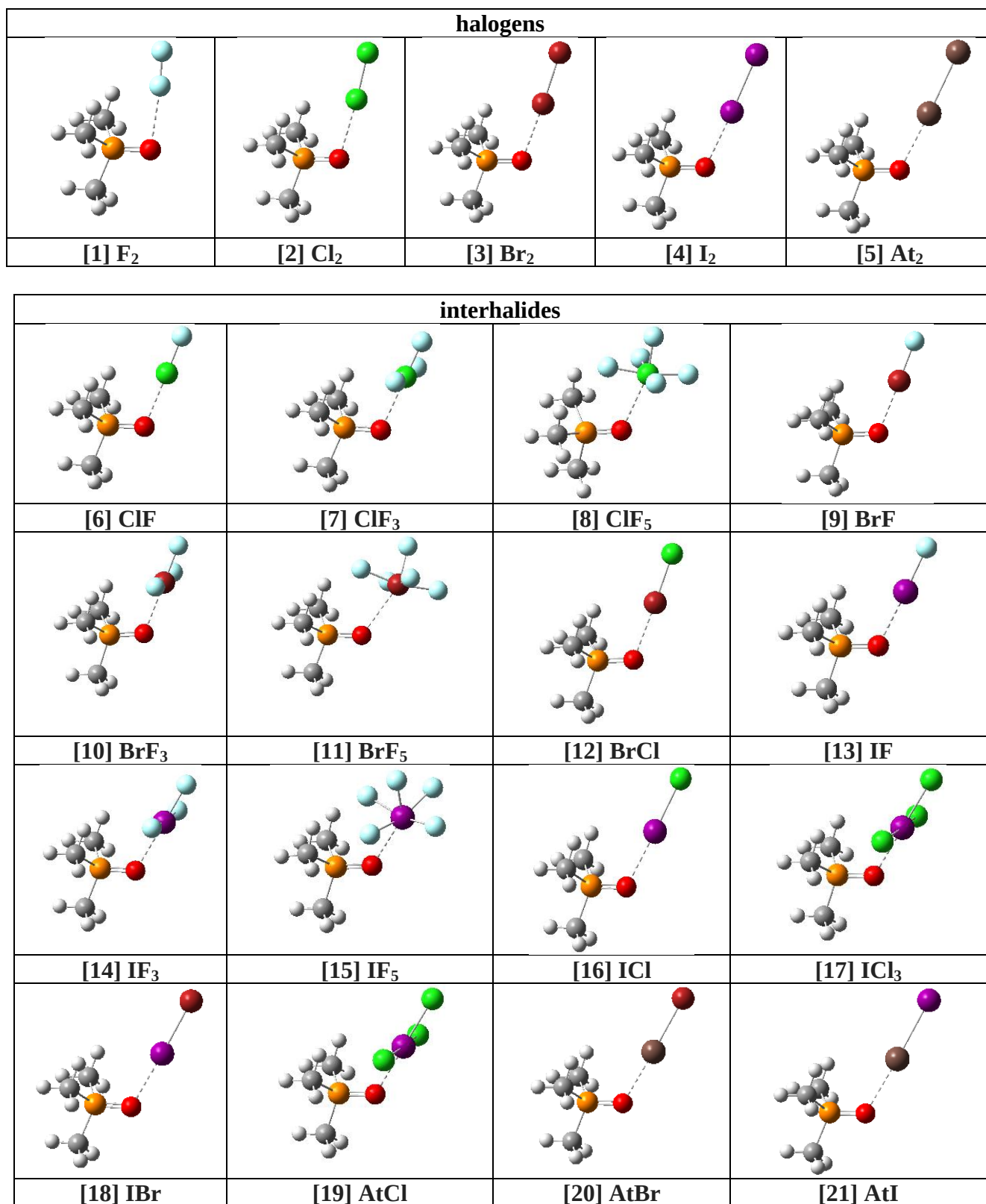
A.S. Ostras', D.M. Ivanov, A.S. Novikov, P.M. Tolstoy

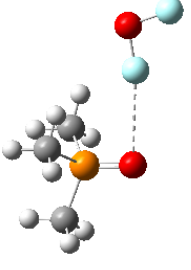
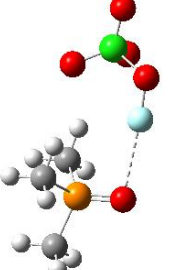
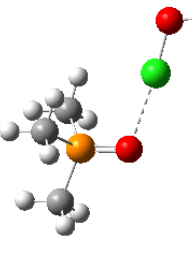
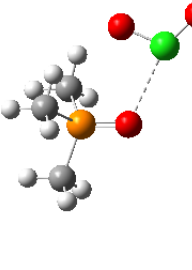
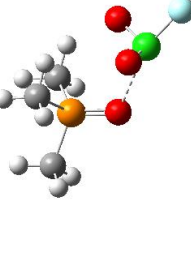
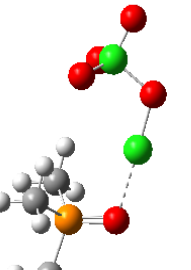
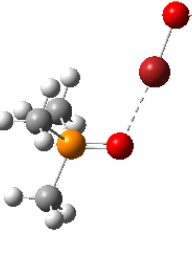
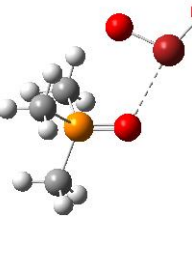
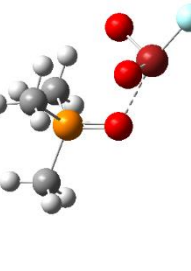
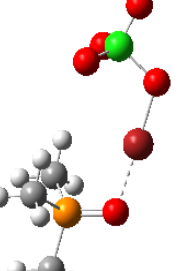
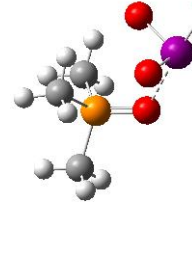
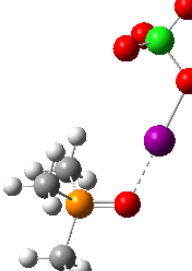
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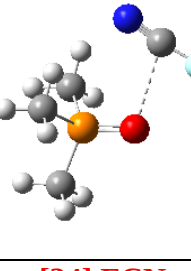
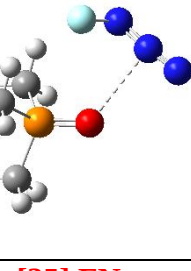
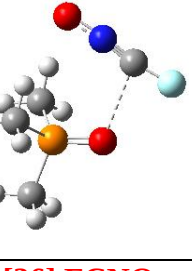
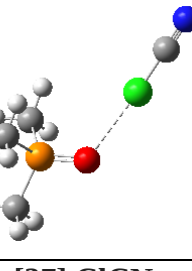
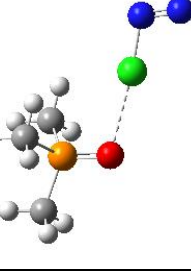
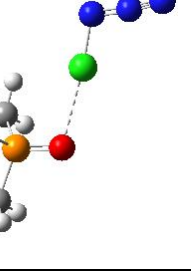
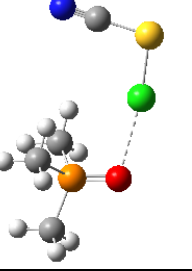
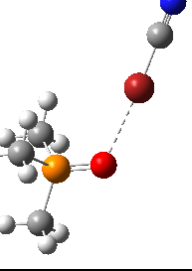
* – corresponding author, peter.tolstoy@spbu.ru

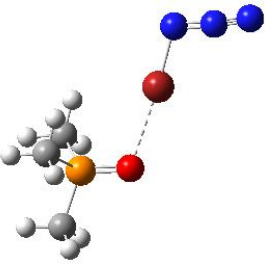
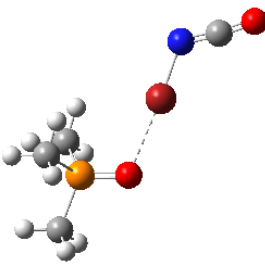
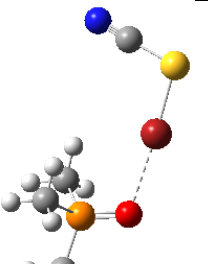
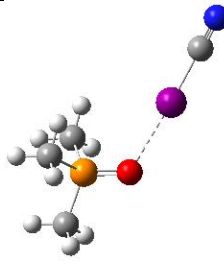
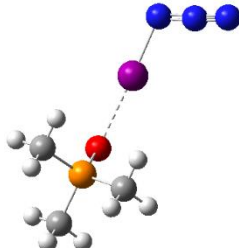
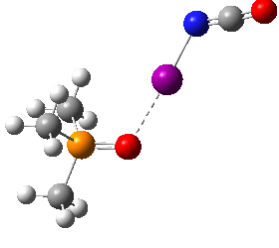
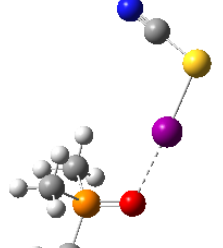
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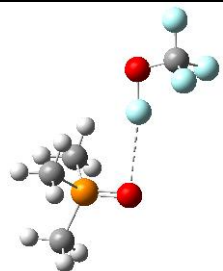
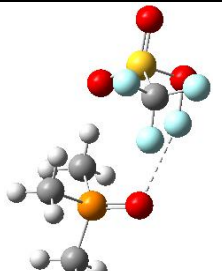
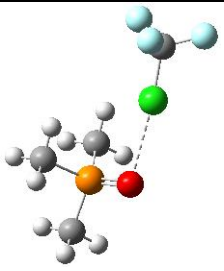
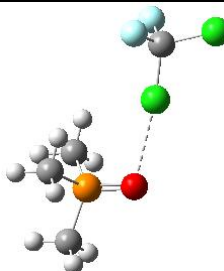
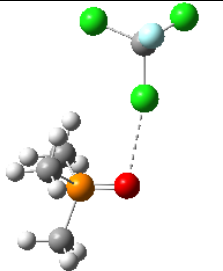
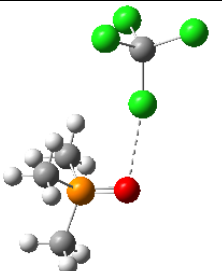
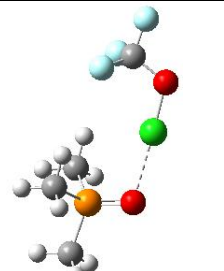
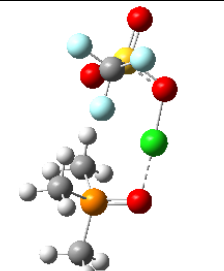
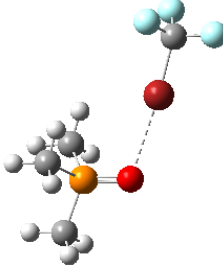
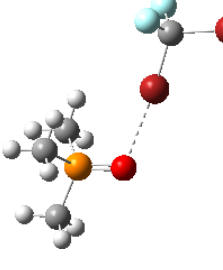
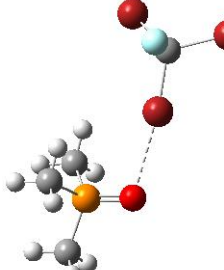
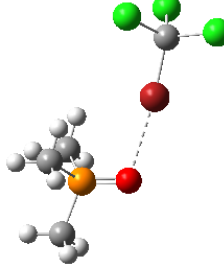
Figure S1. Calculated (M06-2x/ def2-TZVPPD) optimized structures of 128 intermolecular 1:1 complexes formed by $\text{Me}_3\text{P}=\text{O}$ with halogen-containing molecules. The complexes in which the dominant intermolecular interaction is other than the halogen bond are marked in red color.

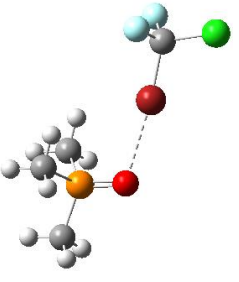
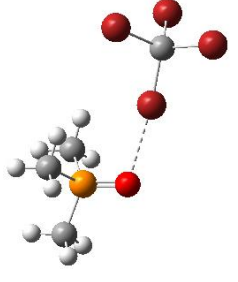
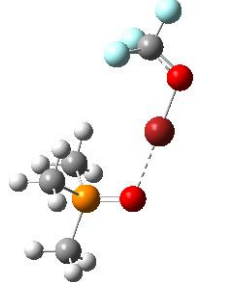
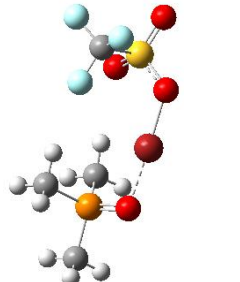
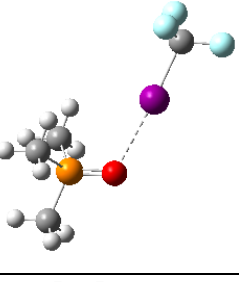
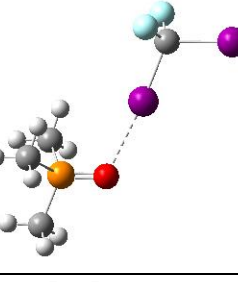
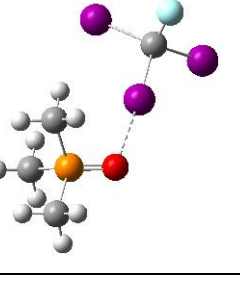
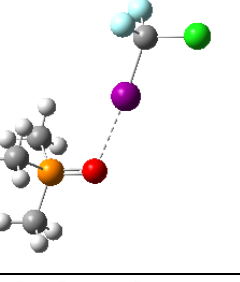
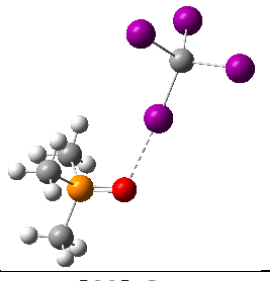


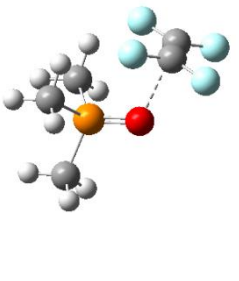
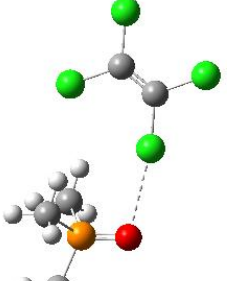
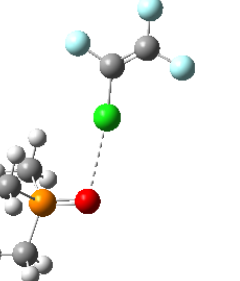
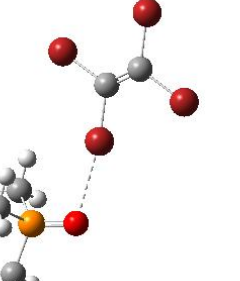
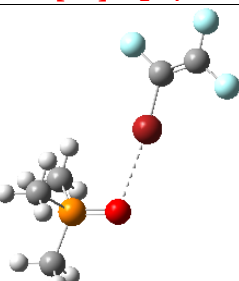
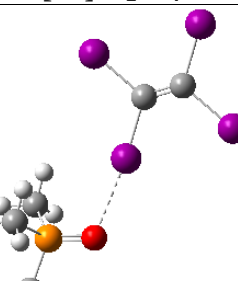
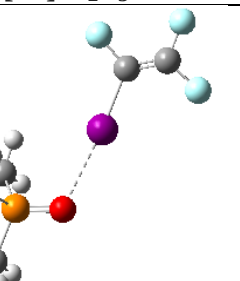
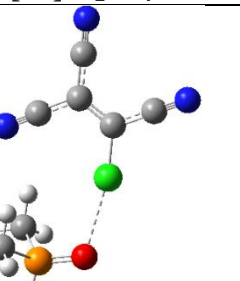
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[22] OF ₂	[23] ClO ₃ OF	[24] Cl ₂ O	[25] ClO ₂
			
[26] ClO ₂ F	[27] ClO ₃ OCl	[28] Br ₂ O	[29] BrO ₂
			
[30] BrO ₂ F	[31] ClO ₃ OBr	[32] IO ₂ F	[33] ClO ₃ OI

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 ₃ OF	[50] CF ₃ SO ₂ OF	[51] CF ₃ Cl	[52] CCl ₂ F ₂
			
[53] CCl ₃ F	[54] CCl ₄	[55] CF ₃ OCl	[56] CF ₃ SO ₂ OCl
			
[57] CF ₃ Br	[58] CBr ₂ F ₂	[59] CBr ₃ F	[60] CBrCl ₃

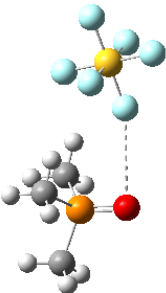
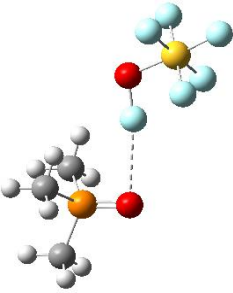
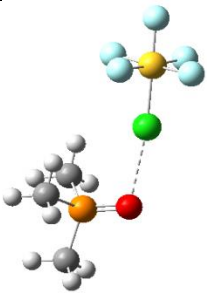
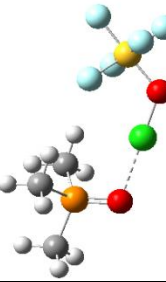
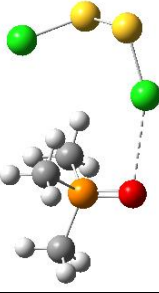
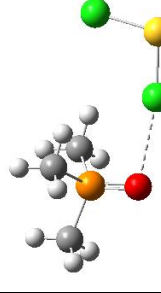
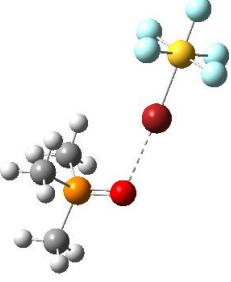
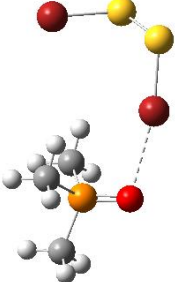
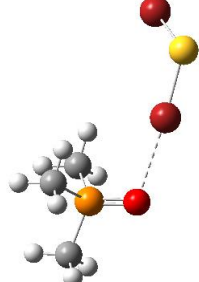
			
[61] CBrClF ₂	[62] CBr ₄	[63] CF ₃ OBr	[64] CF ₃ SO ₂ OBr
			
[65] CF ₃ I	[66] Cl ₂ F ₂	[67] Cl ₃ F	[68] ClClF ₂
			
[69] Cl ₄			

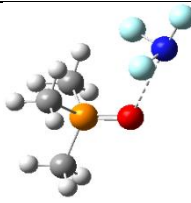
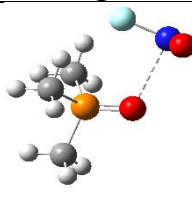
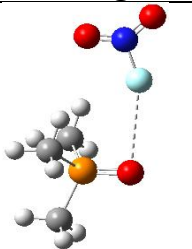
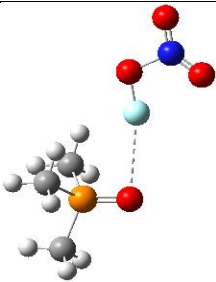
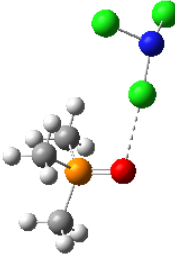
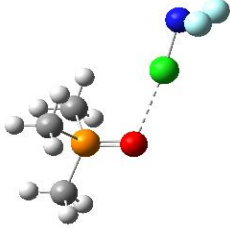
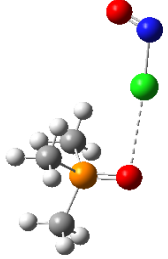
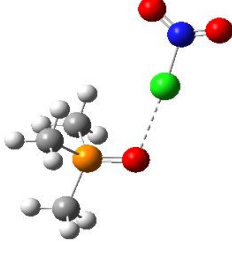
halogenated ethylene, halogenated acetylene and their derivatives			
			
[70] C ₂ F ₄	[71] C ₂ Cl ₄	[72] C ₂ F ₃ Cl	[73] C ₂ Br ₄
			
[74] C ₂ F ₃ Br	[75] C ₂ I ₄	[76] C ₂ F ₃ I	[77] C ₂ (CN) ₃ Cl

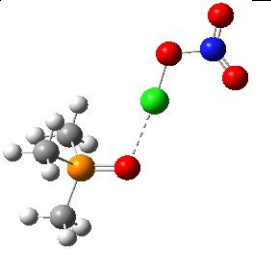
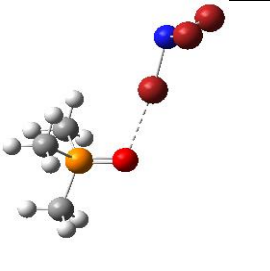
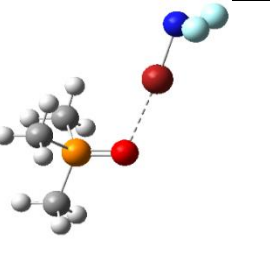
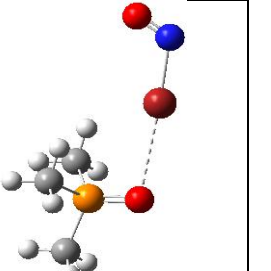
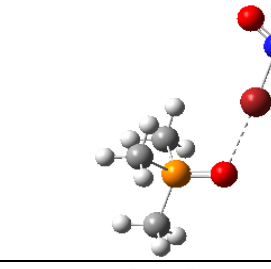
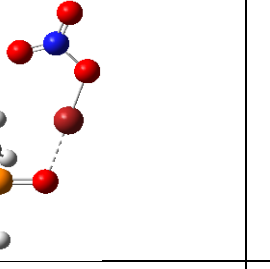
[78] C ₂ F ₂	[79] C ₂ Cl ₂

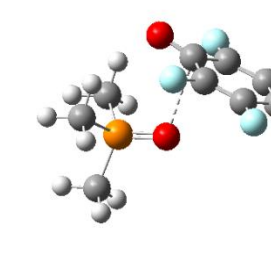
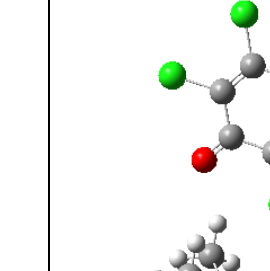
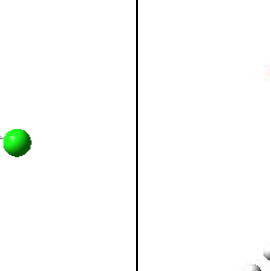
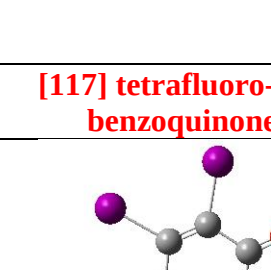
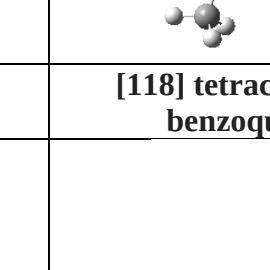
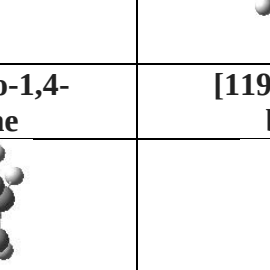
phosgene and its derivatives			
[80] COF ₂	[81] COClF	[82] COCl ₂	[83] COBrCl
[84] COBr ₂	[85] COBrF	[86] COIF	

thionyl- and sulphurylhalides		
[87] SOF ₂	[88] SO ₂ ClF	[89] SOCl ₂
[90] SOBr ₂	[91] SO ₂ Cl ₂	[92] SO ₂ BrF

sulphur halides and sulphur hypohalites		
		
[93] SF ₆	[94] SF ₅ OF	[95] SF ₅ Cl
		
[96] SF ₅ OCl	[97] S ₂ Cl ₂	[98] SCl ₂
		
[99] SF ₅ Br	[100] S ₂ Br ₂	[101] SBr ₂

halogenated nitrogen-containing compounds			
			
[102] NF ₃	[103] NOF	[104] NO ₂ F	[105] NO ₂ OF
			
[106] NCl ₃	[107] NF ₂ Cl	[108] NOCl	[109] NO ₂ Cl

			
[110] NO ₂ OCl	[111] NBr ₃	[112] NF ₂ Br	[113] NOBr
			
[114] NO ₂ Br	[115] NO ₂ OBr	[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 ₆ H ₅ (C≡C)Cl	[122] C ₆ H ₅ (C≡C)Br

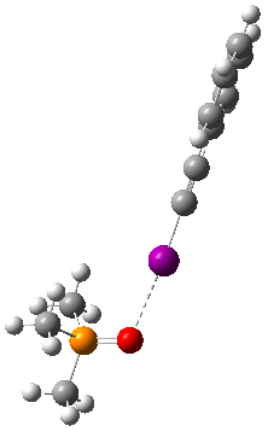
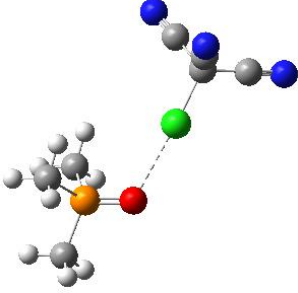
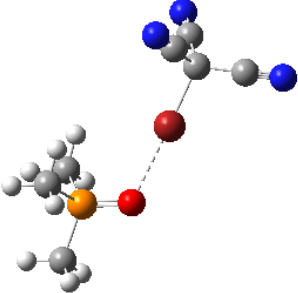
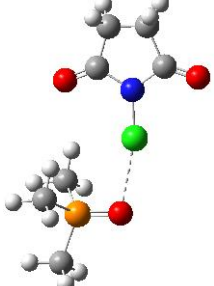
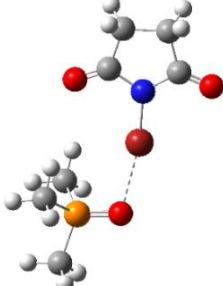
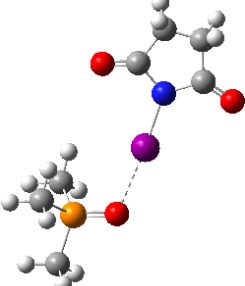
		
[123] $\text{C}_6\text{H}_5(\text{C}\equiv\text{C})\text{I}$	[124] $\text{CCl}(\text{CN})_3$	[125] $\text{CBr}(\text{CN})_3$
		
[126] N-chlorosuccinimide	[127] N-bromosuccinimide	[128] N-iodosuccinimide

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 Me₃P=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	$\Delta\delta P$, ppm	$\Delta\nu$, cm ⁻¹	ΔE , kJ/mol	α (P=O $\cdots$ X), °	β (O $\cdots$ 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 ₃ OF	45.15	3.76	8.09	10.04	101.9	176.1	2.67
24	Cl ₂ O	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 ₂ F	179.81	12.14	35.41	46.33	117.1	158.5	2.58
27	ClO ₃ OCl	173.0	24.99	80.16	50.48	109.5	178.4	2.26
28	Br ₂ O	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 ₂ F	217.35	22.96	86.47	75.40	118.5	165.0	2.40
31	ClO ₃ OBr	211.05	39.60	121.01	76.66	112.1	178.3	2.16
32	IO ₂ F	254.1	36.39	139.07	124.07	121.1	173.8	2.27
33	ClO ₃ OI	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	CICN	122.06	7.63	18.22	26.35	124.7	177.0	2.70
38	CIN ₃	97.65	7.53	25.61	23.46	108.7	174.8	2.67
39	CINCO	121.0	9.18	27.09	27.41	110.3	176.0	2.61
40	CISCN	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 ₃ OF	28.09	2.00	4.75	5.25	95.2	172.1	2.77
50	CF ₃ SO ₂ OF	55.13	4.03	10.1	14.66	111.7	152.0	2.70
51	CF ₃ Cl	89.0	5.37	12.77	16.70	108.6	173.7	2.83
52	CCl ₂ F ₂	85.84	5.61	14.90	16.89	108.1	173.0	2.82
53	CCl ₃ F	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 ₃ OCl	154.09	15.18	55.81	40.20	109.4	178.0	2.44
56	CF ₃ SO ₂ OCl	171.19	41.07	134.46	60.47	108.2	177.3	2.04
57	CF ₃ Br	103.43	6.75	20.68	22.74	112.2	175.9	2.83
58	CBr ₂ F ₂	99.49	6.53	22.12	23.25	112.39	175.0	2.82
59	CBr ₃ F	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 ₃ OBr	191.89	23.76	88.61	86.78	113.6	179.4	2.35
64	CF ₃ SO ₂ OBr	220.0	44.03	141.39	87.13	111.3	177.1	2.11
65	CF ₃ I	131.78	10.07	32.29	34.79	117.9	176.6	2.81
66	Cl ₂ F ₂	121.28	11.06	35.38	34.75	117.2	175.4	2.80
67	Cl ₃ F	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	Cl ₄	118.91	13.50	42.88	37.37	116.7	176.3	2.74
halogenated ethylene, halogenated acetylene and their derivatives								
70	C ₂ F ₄	86.89	4.52	11.28	19.42	---	---	2.78
71	C ₂ Cl ₄	76.13	5.32	15.31	18.47	104.1	170.6	2.86
72	C ₂ F ₃ Cl	86.83	5.02	14.75	16.12	107.7	172.6	2.85
73	C ₂ Br ₄	94.24	7.90	21.93	22.69	108.7	172.0	2.84
74	C ₂ F ₃ Br	105.53	7.07	21.93	22.68	111.8	174.4	2.84
75	C ₂ I ₄	115.76	10.15	35.81	33.99	115.2	174.4	2.81
76	C ₂ F ₃ I	136.76	9.58	32.39	35.02	117.3	175.5	2.82
77	C ₂ (CN) ₃ Cl	148.05	8.72	24.76	26.23	119.6	168.8	2.89
78	C ₂ F ₂	39.64	1.57	3.95	8.24	---	---	2.98
79	C ₂ Cl 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 ₂ ClF	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 ₂ Cl ₂	109.46	8.92	21.01	23.50	112.9	172.1	2.72
92	SO ₂ BrF	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 ₅ OF	29.14	1.91	4.42	5.46	95.3	170.6	2.76
95	SF ₅ Cl	94.24	8.20	22.41	21.16	107.2	172.7	2.73

96	SF ₅ OCl	158.81	18.13	55.55	43.54	119.3	179.8	2.37
97	S ₂ Cl 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 ₅ Br	115.24	11.35	36.17	34.15	114.02	176.8	2.68
100	S ₂ Br 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 ₂ F	80.33	0.80	2.42	3.95	---	---	3.06
105	NO ₂ OF	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 ₂ Cl	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 ₂ Cl	106.84	9.75	31.75	26.93	111.7	176.1	2.61
110	NO ₂ OCl	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 ₂ Br	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 ₂ Br	126.0	13.45	47.13	36.72	115.2	177.5	2.59
116	NO ₂ OBr	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 ₆ H ₅ C ₂ Cl	80.33	5.46	12.97	15.89	106.8	173.1	2.85
122	C ₆ H ₅ C ₂ Br	102.64	7.27	18.70	22.65	111.0	175.1	2.84
123	C ₆ H ₅ C ₂ I	134.14	10.68	30.80	34.88	116.7	176.5	2.82
124	CCl(CN) ₃	147.53	9.58	28.24	29.54	119.0	176.7	2.63
125	CBr(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 Me₃P=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	ClF	90.94	-91.733	0.0372	0.1373
7	ClF₃	88.03	-88.58	0.0375	0.1333
8	ClF₅	55.01	-50.67	0.0230	0.0904
9	BrF	101.48	-113.47	0.0455	0.1363
10	BrF₃	99.88	-110.36	0.0465	0.1362
11	BrF₅	60.60	-57.53	0.0267	0.0970
12	BrCl	68.21	-66.47	0.0297	0.1066
13	IF	100.35	-116.74	0.0448	0.1279
14	IF₃	104.48	-127.49	0.0513	0.1241
15	IF₅	66.58	-67.49	0.0313	0.1001
16	ICl	81.27	-88.70	0.0369	0.1125
17	ICl₃	120.83	-156.92	0.0610	0.1291
18	IBr	74.74	-79.67	0.0342	0.1064
19	AtCl	94.32	-98.80	0.0378	0.1377
20	AtBr	88.46	-91.64	0.0360	0.1306
21	AtI	76.57	-77.11	0.0318	0.1163
oxohalides					
22	OF₂	17.24	-11.73	0.0068	0.0346
23	ClO₃OF	81.62	-109.19	0.0417	0.0823
24	Cl₂O	68.31	-63.84	0.0275	0.1109
25	ClO₂	45.26	-39.29	0.0184	0.0780
26	ClO₂F	61.23	-56.85	0.0258	0.0999
27	ClO₃OCl	117.66	-132.53	0.0530	0.0157
28	Br₂O	76.81	-77.49	0.0333	0.1160
29	BrO₂	55.88	-51.68	0.0241	0.0915
30	BrO₂F	93.95	-104.43	0.0461	0.1271
31	ClO₃OBr	151.99	-210.22	0.0761	0.1428
32	IO₂F	136.38	-188.17	0.0690	0.1289
33	ClO₃OI	143.28	-185.96	0.0642	0.1533
pseudohalides					
34	FCN	34.37	-29.05	0.0155	0.0605
35	FN₃	34.21	-27.96	0.0132	0.0616
36	FCNO	42.31	-37.42	0.0192	0.0719
37	CICN	45.74	-38.70	0.0181	0.0804
38	CIN₃	45.74	-38.70	0.0181	0.0804
39	CINCO	56.30	-50.15	0.0225	0.0951
40	CISCN	46.31	-40.02	0.0194	0.0801
41	BrCN	51.36	-46.00	0.0215	0.0864

42	BrN ₃	60.07	-56.56	0.0258	0.0969
43	BrNCO	68.71	-66.65	0.0292	0.1078
44	BrSCN	57.20	-53.39	0.0251	0.0929
45	ICN	61.56	-60.47	0.0269	0.0954
46	IN ₃	74.12	-78.44	0.0334	0.1064
47	INCO	82.03	-89.04	0.0365	0.1143
48	ISCN	72.58	-76.72	0.0335	0.1042
halogenated methanes and their derivatives					
49	CF ₃ OF	24.85	-17.84	0.0093	0.0485
50	CF ₃ SO ₂ OF	29.29	-21.46	0.0106	0.0566
51	CF ₃ Cl	35.33	-28.77	0.0149	0.0638
52	CCl ₂ F ₂	35.92	-29.39	0.0152	0.0647
53	CCl ₃ F	35.73	-29.31	0.0153	0.0642
54	CCl ₄	37.11	-30.69	0.0158	0.0663
55	CF ₃ OCl	81.20	-79.65	0.0333	0.1261
56	CF ₃ SO ₂ OCl	177.74	-243.73	0.0898	0.1702
57	CF ₃ Br	40.26	-34.85	0.0176	0.0696
58	CBr ₂ F ₂	41.37	-36.03	0.0181	0.0712
59	CBr ₃ F	42.38	-37.17	0.0186	0.0725
60	CBrCl ₃	43.57	-38.40	0.0191	0.0743
61	CBrClF ₂	40.92	-35.58	0.0180	0.0705
62	CBr ₄	44.42	-39.29	0.0194	0.0755
63	CF ₃ OBr	103.95	-118.31	0.0477	0.1364
64	CF ₃ SO ₂ OBr	220.31	-362.23	0.1116	0.1194
65	CF ₃ I	48.50	-45.43	0.0219	0.0786
66	Cl ₂ F ₂	49.67	-46.94	0.0225	0.0798
67	Cl ₃ F	51.90	-11.87	0.0235	0.0825
68	ClClF ₂	49.88	-47.13	0.0225	0.0801
69	Cl ₄	54.89	-53.28	0.0248	0.0861
halogenated ethylene, halogenated acetylene and their derivatives					
70	C ₂ F ₄	27.55	-23.40	0.0130	0.0483
71	C ₂ Cl ₄	33.70	-27.31	0.0144	0.0611
72	C ₂ F 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 ₂ F 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 ₂ F 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 ₂ F 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	COF ₂	44.16	-38.36	0.0191	0.0761
81	COCIF	36.21	-29.63	0.0152	0.0652
82	COCl ₂	34.21	-27.90	0.0147	0.0617
83	COBrCl	39.86	-34.57	0.0176	0.0688
84	COBr ₂	40.24	-35.04	0.0179	0.0693
85	COBrF	40.34	-34.93	0.0176	0.0697
86	COIF	48.29	-45.10	0.0217	0.0784
thionyl- and sulphurylhalides					
87	SOF ₂	53.58	-51.00	0.0248	0.0856
88	SO ₂ ClF	45.70	-39.11	0.0189	0.0797
89	SOCl ₂	33.35	-27.23	0.0148	0.0601
90	SOBr 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 BrF	53.11	-48.61	0.0231	0.0877
sulphur halides and sulphur hypohalites					
93	SF ₆	9.89	-6.37	0.0044	0.0204
94	SF ₅ OF	25.68	-18.50	0.0096	0.0501
95	SF ₅ Cl	44.21	-37.79	0.0186	0.0771
96	SF ₅ OCl	93.64	-96.07	0.0393	0.1390

97	S ₂ Cl ₂	27.92	-22.20	0.0128	0.0513
98	SCl 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	SBr ₂	44.26	-39.17	0.0196	0.0752
halogenated nitrogen-containing inorganic compounds					
102	NF ₃	21.45	-16.87	0.0089	0.0397
103	NOF	41.62	-35.72	0.0175	0.0724
104	NO ₂ F	12.02	-7.96	0.0053	0.0245
105	NO ₂ OF	19.00	-13.03	0.0074	0.0380
106	NCl ₃	52.89	-46.91	0.0217	0.0897
107	NF ₂ Cl	51.92	-45.71	0.0211	0.0886
108	NOCl	20.70	-15.73	0.0101	0.0391
109	NO ₂ Cl	56.38	-50.92	0.0233	0.0942
110	NO ₂ OCl	75.82	-72.58	0.0306	0.1204
111	NBr ₃	60.73	-57.38	0.0262	0.0976
112	NF ₂ Br	59.02	-55.42	0.0255	0.0954
113	NOBr	22.99	-18.58	0.0115	0.0417
114	NO ₂ Br	65.01	-62.86	0.0286	0.1023
115	NO ₂ OBr	109.93	-128.72	0.0515	0.1389
116	NI 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 ₆ H ₅ C ₂ Cl	33.53	-26.99	0.0140	0.0610
122	C ₆ H ₅ C ₂ Br	39.51	-33.82	0.0170	0.0688
123	C ₆ H ₅ C ₂ I	47.84	-44.31	0.0211	0.0783
124	CCl(CN) ₃	54.42	-48.16	0.0220	0.0924
125	CBr(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

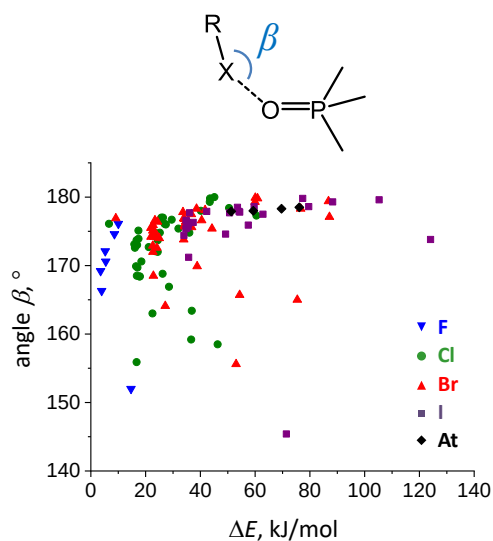


Figure S2. The correlation between angles β (angle $\text{O}\cdots\text{X}-\text{R}$) and the complexation energy for 128 complexes studied in this work ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{At}$). Stronger complexes seem to be characterized by generally smaller range of β angles 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) $d(X\cdots O) \equiv r$ is less than the Bondi's vdW sums; (v) $\angle(NM\cdots X\cdots O) \equiv \beta$, $150^\circ \leq \beta \leq 180^\circ$; (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 [$\geq 2\sigma$ (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) $d(X\cdots O) \equiv r$ is less than the Bondi's vdW sums; (v) $\angle(NM\sim X\cdots O) \equiv \beta$, $150^\circ \leq \beta \leq 180^\circ$; (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 [$I \geq 2\sigma(I)$] 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

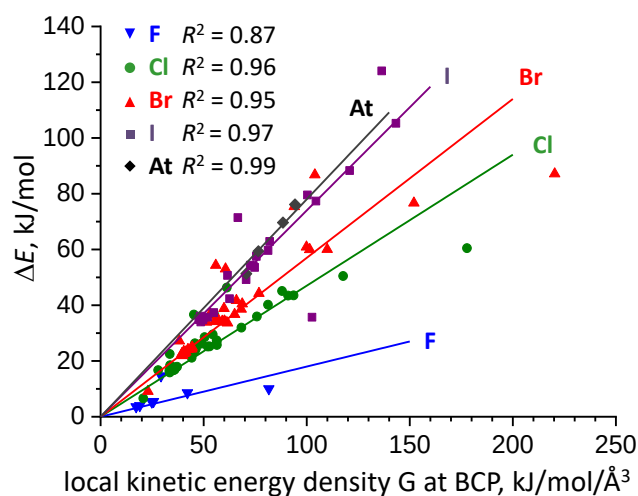


Figure S3. Correlation between calculated complexation energy ΔE and the value of local kinetic energy density G at halogen bond critical point (3;−1) for $\text{Me}_3\text{P}=\text{O}\cdots\text{X}-\text{R}$ halogen-bonded complexes studied in this work ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{At}$). The solid lines correspond to one of Eqs. (9) in the main text.

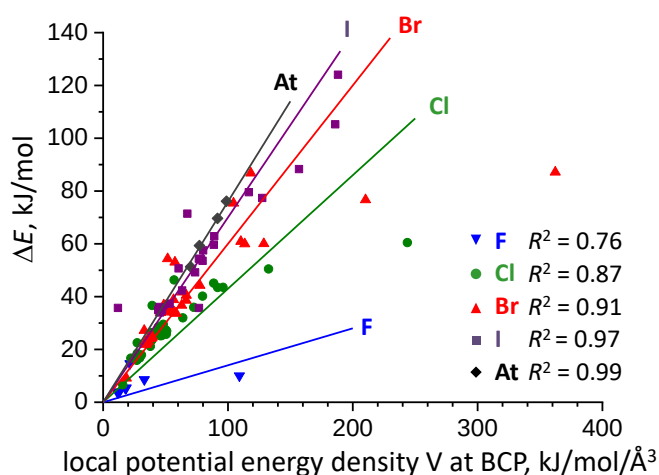


Figure S4. Correlation between calculated complexation energy ΔE and the value of local potential energy density V at halogen bond critical point (3;−1) for $\text{Me}_3\text{P}=\text{O}\cdots\text{X}-\text{R}$ complexes studied in this work ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{At}$). The solid lines correspond to one of Eqs. (9) in the main text.

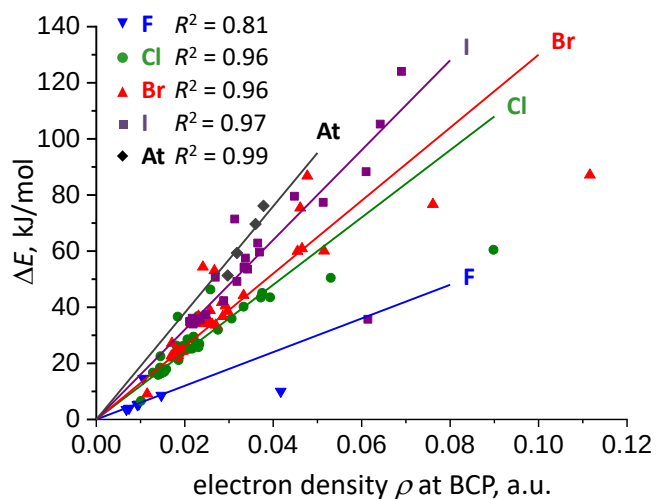


Figure S5. Correlation between calculated complexation energy ΔE and the value of electron density ρ at halogen bond critical point (3; -1) for $\text{Me}_3\text{P}=\text{O}\cdots\text{X}-\text{R}$ complexes studied in this work ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{At}$). The solid lines correspond to one of Eqs. (9) in the main text.

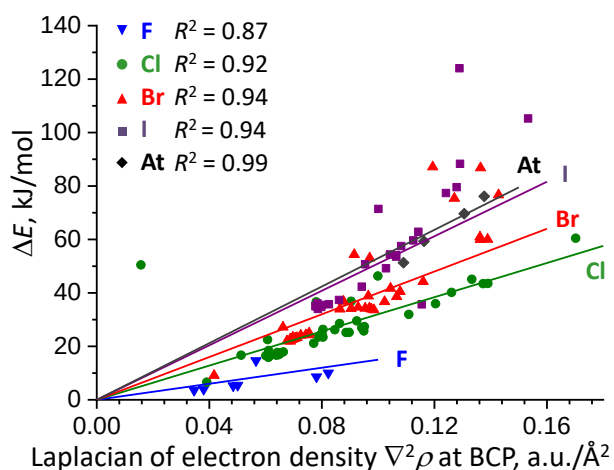


Figure S6. Correlation between calculated complexation energy ΔE and the value of the Laplacian of electron density $\nabla^2\rho$ at halogen bond critical point (3; -1) for $\text{Me}_3\text{P}=\text{O}\cdots\text{X}-\text{R}$ complexes studied in this work ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{At}$). The solid lines correspond to one of Eqs. (9) in the main text.