Electronic supplementary information (ESI)

Unusual Acid-Base Properties of Molecular P_4 in Hydrogen-, Halogen-, and Pnicogen-Bonded Complexes

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Table S1. Structures, molecular graphs, and total energies of complexes P_4:FH

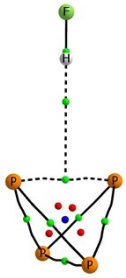
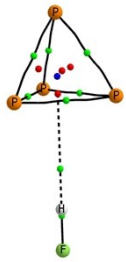
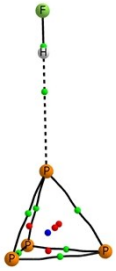
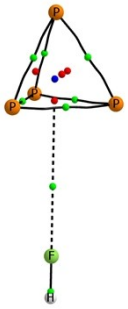
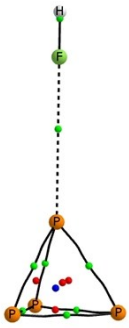
	p4_hf_bond MP2= -1463.99073187 NIMAG= 0 P,0.075200252,0.,1.4206287826 P,1.3644484116,0.,-0.4026434501 P,-0.543139563,-1.1093009246,-0.3840576681 P,-0.543139563,1.1093009246,-0.3840576681 H,2.7104969568,0.,1.9166107784 F,3.4681276008,0.,2.4523365444
	p4_hf_face MP2= -1463.98982298 NIMAG= 0 P,-0.0000000001,0.,1.1596679569 P,1.2826248216,0.0000000002,-0.6369744036 P,-0.6413124108,-1.1107856792,-0.6369744036 P,-0.641312411,1.110785679,-0.6369744036 H,-0.0000000001,0.,-3.161358354 F,-0.0000000001,0.,-4.0873716555
	p4_hf_vertex MP2= -1463.98882723 NIMAG= 0 F,0.,0.,5.2613460811 H,0.,0.,4.3363471638 P,-0.0000000929,1.2794583614,-0.072742632 P,0.,0.,1.7205993678 P,-1.1080433976,-0.6397292611,-0.072742632 P,1.1080434905,-0.6397291002,-0.072742632
	p4_fh_face MP2= -1463.98848270 NIMAG= 0 P,0.2469268164,0.0000000001,1.2645917141 P,1.5283707911,0.,-0.5403606751 P,-0.3903619038,-1.1038164428,-0.537932989 P,-0.3903619038,1.1038164428,-0.5379329891 F,-3.2874125311,0.,1.1622758463 H,-4.1573020201,0.,1.4698282245
	p4_fh_vertex MP2= -1463.98795963 NIMAG= 0 P,-1.1049411801,-0.6379380899,-1.13924506 P,0.,-0.0000000021,0.67074297 P,1.1049411801,-0.6379380899,-1.13924506 P,0.,1.2758761734,-1.13924506 F,0.,-0.0000000021,4.02821878 H,0.,-0.0000000021,4.9507851

Table S2. Structures, molecular graphs, and total energies of complexes P_4:ClH

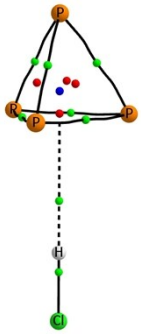
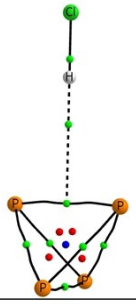
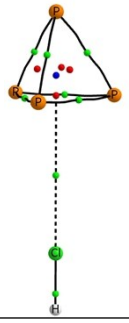
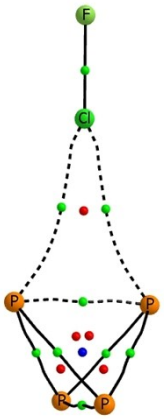
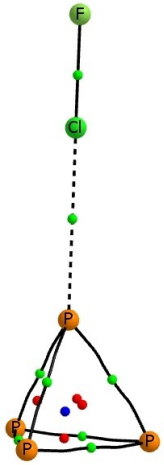
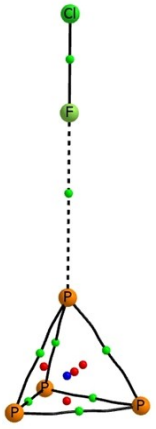
	p4_hcl_face MP2= -1823.96529060 NIMAG= 0 P,0.0586512328,0.0000000001,1.3378707913 P,1.3288243247,0.,-0.4698103454 P,-0.5818023117,-1.1092980794,-0.4736053868 P,-0.5818023118,1.1092980794,-0.4736053869 H,-2.7332727334,0.,0.966357842 Cl,-3.9408234191,0.,1.3932914811
	p4_hcl_bond MP2= -1823.96512695 NIMAG= 0 P,0.0087247546,0.,1.3692486077 P,1.293848219,0.,-0.4481904252 P,-0.6164706683,-1.1083948673,-0.4359105899 P,-0.6164706683,1.1083948673,-0.43591059 H,2.7084559633,0.,1.9151675781 Cl,3.7553964512,0.,2.6554662965
	p4_clh_face MP2= -1823.96451141 NIMAG= 0 P,-0.0000000001,0.,1.5392881722 P,1.2765399829,0.0000000002,-0.2680149289 P,-0.6382699914,-1.1055160543,-0.2680149289 P,-0.6382699918,1.1055160541,-0.2680149289 Cl,-0.0000000001,0.,-3.7293435082 H,-0.0000000001,0.,-5.0061050129

Table S3. Structures, molecular graphs, and total energies of complexes P_4:ClF

	p4_clf_bond MP2= -1923.01548249 NIMAG= 0 P,-0.1570792195,0.,1.2578359893 P,1.1335394036,0.,-0.5673743715 P,-0.7768866129,-1.1094886998,-0.5493417922 P,-0.7768866129,1.1094886998,-0.5493417922 Cl,2.8776045586,0.,2.0347736968 F,4.2331032791,0.,2.9932560339
	p4_clf_vertex MP2= -1923.01396130 NIMAG= 0 F,0.,0.,6.0976993338 Cl,0.,0.,4.4375256674 P,-0.000000093,1.2811826849,-0.1909964494 P,0.,0.,1.5987282477 P,-1.1095367055,-0.640591423,-0.1909964494 P,1.1095367985,-0.6405912619,-0.1909964494
	p4_fcl_vertex MP2= -1923.01028982 NIMAG= 0 P,-0.0000000927,1.276462852,-0.2936927833 P,0.,0.,1.5140427548 P,-1.1054492105,-0.6382315062,-0.2936927833 P,1.1054493031,-0.6382313457,-0.2936927833 F,0.,0.,4.6428577346 Cl,0.,0.,6.2850807259

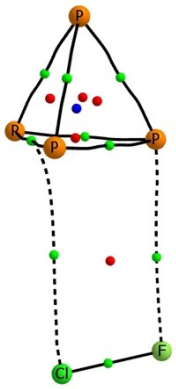
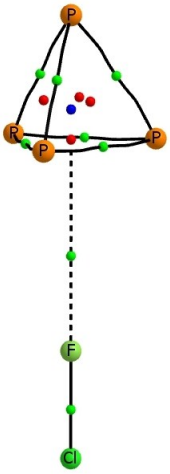
	p4_fcl_parallel (face) MP2= -1923.01215457 NIMAG= 0 P,-1.21146583,-0.6076497,0. P,0.69027168,-0.83300056,-1.10447052 P,0.69027168,-0.83300056,1.10447052 P,-0.15423164,-2.55355702,0. F,-1.07806265,2.7298742,0. Cl,0.55940035,2.8137711,0.
	p4_fcl_face MP2= -1923.01099892 NIMAG= 0 P,0.3041561954,0.0000000001,1.2457620273 P,1.5833278153,0.,-0.5597909174 P,-0.3337943552,-1.1049627666,-0.5586346147 P,-0.3337943552,1.1049627666,-0.5586346148 F,-3.0612245298,0.,1.0823063115 Cl,-4.6088826749,0.,1.6294860961

Table S4. Components of spin-spin coupling constants for complexes with molecular P_4

Hydrogen-bonded complexes with FH

Site	PSO	DSO	FC	SD	J	
bond	-3.1	0.1	16.6	0.4	14.1	^{2h}J(F-P2)
	-0.9	1.2	-4.5	-0.1	-4.3	^{1h}J(H-P_2)
	-4.5	-0.2	-1.9	0.7	-5.9	J(F-P1)
	0.1	0.1	0.1	-0.2	0.1	J(H-P1)
	169.1	1.3	328.0	1.1	499.5	1J(F-H)
face	-2.2	0.1	1.4	0.0	-0.6	^{2h}J(F-P2)
	-0.1	1.1	-1.4	-0.4	-0.8	^{1h}J(H-P_2)
	-12.7	-0.4	-9.0	0.6	-21.4	J(F-P1)
	0.6	-0.1	1.7	-0.5	1.7	J(H-P1)
	176.5	1.5	322.4	1.8	502.2	1J(F-H)
vertex	-0.5	0.2	64.6	0.6	64.9	^{2h}J(F-P1)
	-2.0	1.3	-14.2	0.6	-14.3	^{1h}J(H-P_1)
	-0.4	-0.2	1.1	0.6	1.1	J(F-P2)
	-0.2	0.1	-0.3	0.5	0.1	J(H-P2)
	174.9	1.0	329.9	1.7	507.5	1J(F-H)

Hydrogen-bonded complexes with ClH

Site	PSO	DSO	FC	SD	J	
face	-0.4	0.0	0.2	0.0	-0.2	^{2h}J(Cl-P_2)
	0.0	1.0	-2.2	-0.4	-1.6	^{1h}J(H-P_2)
	-2.6	0.0	-1.4	0.1	-3.9	J(Cl-P1)
	0.4	-0.2	3.2	-0.6	2.9	J(H-P1)
	14.0	0.1	23.0	0.3	37.4	1J(Cl-H)
bond	-0.4	0.0	1.8	0.1	1.5	^{2h}J(Cl-P_2)
	-0.8	1.1	-6.4	-0.1	-6.2	^{1h}J(H-P_2)
	-0.7	0.0	-0.2	0.1	-0.9	J(Cl-P1)
	0.1	0.0	0.2	-0.3	0.1	J(H-P1)
	13.5	0.1	24.2	0.2	38.0	1J(Cl-H)

Halogen-bonded complexes with ClF

Site	PSO	DSO	FC	SD	J
bond	3.0	0.0	60.9	0.6	64.5	J(Cl-P1)
	3.5	0.0	-1.8	0.9	2.6	^{1x}J(Cl-P_2)
vertex						
(P…Cl)	-0.4	0.1	351.4	-1.1	350.0	^{1x}J(Cl-P_1)
	0.9	0.0	6.8	-0.1	7.6	J(Cl-P2)
vertex	0.9	0.6	383.1	-0.3	384.3	^{1p}J(P-F1)
(P…F)	0.1	0.0	7.1	0.0	7.2	J(F-P2)

Pnicogen-bonded complexes with FH

Site	PSO	DSO	FC	SD	J	
face	-0.3	0.3	15.2	-0.2	15.1	^{1p}J(F-P2)
	-1.1	-0.3	-22.6	0.1	-23.9	J(F-P1)
vertex	-0.4	0.4	168.2	0.2	168.3	^{1p}J(P-F1)
	-0.1	-0.1	3.0	0.2	3.0	J(F-P2)

Pnicogen-bonded complex with ClH

Site	PSO	DSO	FC	SD	J	
face	0.0	0.0	6.3	0.0	6.3	^{1p}J(Cl-P_2)
	0.1	0.0	-7.6	0.2	-7.3	J(Cl-P1)

Pnicogen-bonded complexes with FCl

Site	PSO	DSO	FC	SD	J	
face	0.9	0.5	25.2	-0.2	26.4	^{1p}J(F-P2)
	5.7	-0.2	-40.1	1.2	-33.5	J(F-P1)
parallel	-1.3	0.4	67.2	-0.4	66.0	^{1p}J(F-P4)
(face)	0.4	0.1	-0.1	-0.3	0.0	J(F-P2)
	-0.1	0.0	3.4	0.0	3.4	^{1p}J(Cl-P2)
	-0.1	0.0	-2.0	-0.1	-2.2	J(Cl-P1)

Table. S5. P-P distances (R, Å) in hydrogen-, halogen-, and pnicogen-bonded complexes with molecular P_4

Pnicogen-bonded complexes with FH				
Interaction site	$R(P_1\text{-}P_2)$	$R(P_2\text{-}P_3)$	$R(P_1\text{-}P_4)$	$R(P_2\text{-}P_4)$
face	2.214	2.208		
vertex	2.214	2.210		
Pnicogen-bonded complexes with ClH				
face	2.213	2.211		
Pnicogen-bonded complexes with FCl				
parallel (face)	2.212	2.209	2.215	2.211
face	2.213	2.210		
Hydrogen-bonded complexes with FH				
Interaction site	$R(P_1\text{-}P_2)$	$R(P_2\text{-}P_3)$	$R(P_1\text{-}P_4)$	$R(P_2\text{-}P_4)$
bond	2.207	2.233	2.219	
face	2.208	2.222		
vertex	2.203	2.216		
Hydrogen-bonded complexes with ClH				
bond	2.209	2.226	2.217	
face	2.209	2.219		
Halogen-bonded complexes with ClF				
bond	2.209	2.235	2.219	
vertex (P···Cl)	2.201	2.219		
vertex (P···F)	2.213	2.211		

a) The P-P distance in the P_4 molecule is 2.211 Å.

Table S6. Components of $^1J(P_i\text{-}P_j)$ (Hz) for molecular P_4 and its hydrogen-, halogen-, and pnicogen-bonded complexes

Pnicogen-bonded complexes with FH

Site	PSO	DSO	FC	SD	J(P1-P2)
face	-14.0	0.2	-143.1	-4.1	-161.0
vertex	-16.9	0.2	-140.7	-4.2	-161.6
					J(P2-P3)
face	-17.3	0.2	-155.6	-4.6	-177.2
vertex	-16.9	0.2	-149.5	-4.5	-170.6

Pnicogen-bonded complexes with FCl

Site	PSO	DSO	FC	SD	J(P1-P2)
face	-15.2	0.2	-144.4	-4.2	-163.6
					J(P2-P3)
	-16.7	0.2	-151.6	-4.4	-172.5

Hydrogen-bonded complexes with FH

Site	PSO	DSO	FC	SD	J(P1-P2)
bond	-20.7	0.2	-152.7	-4.6	-177.7
face	-22.3	0.2	-151.7	-4.9	-178.7
vertex	-15.2	0.2	-160.4	-4.6	-180.0
					J(P2-P3)
bond	-9.4	0.2	-115.0	-3.0	-127.1
face	-13.1	0.2	-131.2	-3.6	-147.7
vertex	-14.5	0.2	-141.7	-4.0	-160.0
					J(P1-P4)
bond	-11.2	0.2	-140.6	-3.7	-155.3

Hydrogen-bonded complexes with ClH

Site	PSO	DSO	FC	SD	J(P1-P2)
bond	-19.5	0.2	-149.8	-4.6	-173.6
face	-21.0	0.2	-148.3	-4.8	-173.9
					J(P2-P3)
bond	-11.3	0.2	-126.3	-3.2	-140.6
face	-13.7	0.2	-137.3	-3.6	-154.4
					J(P1-P4)
bond	-13.3	0.2	-142.3	-3.9	-159.3

Halogen-bonded complexes with ClH

Site	PSO	DSO	FC	SD	J(P1-P2)
face	-16.2	0.2	-144.6	-4.4	-165.0
					J(P2-P3)
	-16.2	0.2	-149.9	-4.3	-170.1

Halogen-bonded complexes with ClF

Site	PSO	DSO	FC	SD	J(P1-P2)
bond	-20.7	0.2	-148.5	-4.3	-173.3
vertex (P…Cl)	-16.2	0.2	-167.0	-4.9	-187.8
					J(P2-P3)
bond	-9.2	0.3	-118.0	-2.7	-129.7
vertex (P…Cl)	-12.8	0.2	-140.1	-3.6	-156.3
					J(P1-P4)
bond	-12.6	0.2	-141.2	-4.0	-157.6
					J(P1-P2)
parallel	-16.0	0.2	-146.3	-4.4	-166.5
					J(P2-P3)
	-15.9	0.2	-150.6	-4.1	-170.5
					J(P1-P4)
	-15.5	0.2	-141.3	-4.0	-160.6
					J(P2-P4)
	-16.8	0.2	-151.9	-4.4	-172.8
					J(P1-P2)
vertex (P…F)	-16.7	0.2	-142.8	-4.3	-163.5
					J(P2-P3)
	-16.8	0.2	-148.4	-4.4	-169.3

P_4 monomer					^{1}J(P-P)
	-16.3	0.2	-147.3	-4.3	-167.8