Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting Information

Evidence of Strong O-H···C Interactions Involving Apical Pyramidane Carbon Atom as Hydrogen Atom Acceptor

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Computational Details: All molecular structures were optimized using the MP2 (second-order Møller-Plesset perturbation theory) method in combination with the correlation-consistent cc-pVTZ basis set. The convergence criteria for SCF calculations used in this work were: RMS change in the density matrix: 10^{-8}, Maximum change in the density matrix: 10^{-6}, Energy change: 10^{-6}. 28 For the DZ-TZ extrapolation, the aug-cc-pVDZ and aug-cc-pVTZ basis sets were used. We used Helgaker two-point formula where total energy was extrapolated separately for Hartree-Fock and correlation energy contributions. The Hartree-Fock part was calculated using the equation (1):

$$E_{HF}^{CBS} = E_{HF}(n) + A \cdot e^{-Bn} \qquad (1)$$

as defined in reference [28a]. In this equation, n in the exponent is the basis set cardinal number (n = 2 for cc-pVDZ and n = 3 for cc-pVTZ basis set), while B in the exponent is the constant with the value 1.63, as suggested in reference [28c].

The correlation part was calculated using the equation (2):

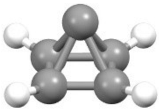
$$E_{corr}^{CBS} = E_{corr}(n) + C \cdot n^{-3} \qquad (2)$$

as defined in reference [28a]. In provided equation, n is the basis set cardinal number (n = 2 for cc-pVDZ and n = 3 for cc-pVTZ basis set), while 3 was used as exponent, as suggested in reference [28a].

Vibrational frequency calculations were performed for all optimized geometries to ensure that they correspond to true minima on the potential energy surface, confirmed by the absence of imaginary frequencies. The Supporting Information (ESI) includes the XYZ coordinates of the optimized geometries for the studied pyramidanes (Tables S1-S6) and their corresponding theoretical IR spectra (Figures S1-S6).

XYZ coordinates of optimized molecules

Table S1. Coordinates for optimized P-H molecule



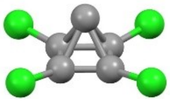
C	-0.02963	1.02429	-0.24803
C	0.00017	0.00000	1.04833
C	-1.02442	-0.02957	-0.24888
C	1.02436	0.02959	-0.24879
C	0.02952	-1.02430	-0.24801
H	-0.06030	2.08589	-0.08240
H	-2.08569	-0.06025	-0.08097
H	2.08578	0.06019	-0.08185
H	0.06017	-2.08591	-0.08249

Table S2. Coordinates for optimized P-F molecule

C	0.00258	-1.02257	-0.19563
C	-0.00013	0.00003	1.08678
C	1.02295	0.00254	-0.19878
C	-1.02295	-0.00256	-0.19829
C	-0.00253	1.02257	-0.19553
F	0.00588	-2.32386	-0.04972
F	2.32394	0.00578	-0.04967
F	-2.32405	-0.00581	-0.04986

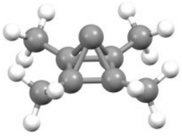
F	-0.00571	2.32388	-0.04976

Table S3. Coordinates for optimized P-Cl molecule



C	1.02639	0.01580	-0.18435
C	-0.00002	-0.00003	1.12548
C	-0.01578	1.02653	-0.18610
C	0.01585	-1.02660	-0.18575
C	-1.02632	-0.01582	-0.18426
Cl	2.70443	0.04168	-0.03437
Cl	-0.04161	2.70440	-0.03354
Cl	0.04173	-2.70438	-0.03359
Cl	-2.70458	-0.04166	-0.03439

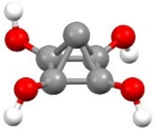
Table S4. Coordinates for optimized P-CH_3 molecule



C	-0.15338	-1.01889	-0.22350
C	-0.00000	0.00001	1.05860
C	1.01888	-0.15337	-0.22336
C	-1.01888	0.15337	-0.22336
C	0.15338	1.01891	-0.22350
C	-0.37255	-2.47496	-0.04434
C	2.47499	-0.37256	-0.04465
C	-2.47499	0.37254	-0.04464
C	0.37256	2.47498	-0.04435
H	0.45279	-2.91524	0.51405

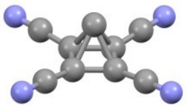
H	-0.44840	-2.97811	-1.00797
H	-1.29081	-2.65277	0.51423
H	2.65296	-1.29113	0.51337
H	2.91537	0.45248	0.51408
H	2.97788	-0.44787	-1.00845
H	-2.97790	0.44779	-1.00844
H	-2.65300	1.29111	0.51335
H	-2.91534	-0.45251	0.51411
H	1.29082	2.65279	0.51420
H	-0.45277	2.91526	0.51405
H	0.44838	2.97811	-1.00798

Table S5. Coordinates for optimized P-OH molecule



C	0.00173	1.02453	-0.23685
C	0.00000	0.01862	1.05051
C	-1.03265	-0.00276	-0.21481
C	1.03260	-0.00629	-0.21470
C	-0.00178	-1.04054	-0.17082
O	-0.00411	-2.36823	0.08787
O	-2.36334	0.01118	0.03234
O	0.00412	2.36949	-0.11729
O	2.36336	0.00296	0.03236
H	-0.00351	-2.83379	-0.75716
H	-2.81823	0.08583	-0.81533
H	0.00377	2.58473	0.82541
H	2.81840	0.07864	-0.81513

Table S6. Coordinates for optimized P-CN molecule



C	-0.97498	0.32785	-0.19418
C	-0.00002	-0.00002	1.14452
C	-0.32790	-0.97502	-0.19487
C	0.32789	0.97505	-0.19456
C	0.97496	-0.32786	-0.19412
C	-2.30662	0.77563	-0.07016
N	-3.41837	1.14947	-0.01960
C	0.77570	2.30656	-0.06939
N	1.14953	3.41829	-0.01800
C	2.30659	-0.77566	-0.07014
N	3.41834	-1.14952	-0.01963
C	-0.77565	-2.30653	-0.06945
N	-1.14947	-3.41824	-0.01790

Table S7. Coordinates for calculated optimal geometry for P-H/H_2O system

C	-1.145918	0.73601	0.724314
C	0.130269	-0.023252	-0.000583
C	-1.185471	-0.712667	0.725329
C	-1.147401	0.735189	-0.724934
C	-1.185327	-0.713587	-0.723904
H	-0.959914	1.48277	1.474728
H	-1.037295	-1.467168	1.476462

H	-0.960845	1.480792	-1.476393
H	-1.040299	-1.469212	-1.474471
H	2.229396	-0.083813	-0.00034
O	3.190014	-0.110905	-0.000228
H	3.451925	0.813715	0.000505

Table S8. Coordinates for calculated optimal geometry for P-F/H_2O system

C	-0.695861	0.737539	0.746035
C	0.535689	-0.043176	-0.005005
C	-0.788333	-0.70537	0.707615
C	-0.705983	0.777232	-0.699808
C	-0.79256	-0.666091	-0.738248
F	-0.488642	1.62162	1.689495
F	-0.691565	-1.657361	1.601578
F	-0.505779	1.710981	-1.595874
F	-0.708665	-1.56824	-1.683635
H	2.730723	-0.190556	-0.015454
O	3.68961	-0.254091	-0.019992
H	3.986532	0.659466	0.007786

Table S9. Coordinates for calculated optimal geometry for P-Cl/H_2O system

C	-0.710188	-0.71072	-0.602304
C	-0.019932	-0.000464	0.735046
C	0.740368	-0.739229	-0.549667
C	-0.681994	0.740829	-0.60121

C	0.768474	0.71228	-0.545334
Cl	-1.924562	-1.87416	-0.498928
Cl	1.897015	-1.948934	-0.354807
Cl	-1.85004	1.950133	-0.491564
Cl	1.971796	1.875543	-0.349064
H	-0.09433	-0.005577	2.933782
O	-0.127609	-0.007796	3.894203
H	-1.066711	0.007884	4.097582

Table S10. Coordinates for calculated optimal geometry for P-CH_3/H_2O system

C	0.586097	0.853646	-0.737054
C	-0.511408	-0.124025	0.001257
C	0.896264	-0.570052	-0.723023
C	0.586028	0.867975	0.720024
C	0.896471	-0.555676	0.734071
C	0.189279	1.822484	-1.787845
C	0.943336	-1.635667	-1.753794
C	0.189722	1.857489	1.751545
C	0.943199	-1.60082	1.785624
H	-0.270637	1.302046	-2.627162
H	1.054153	2.375739	-2.153081
H	-0.536264	2.532444	-1.392417
H	0.312379	-1.369638	-2.601115
H	0.577241	-2.575602	-1.342332
H	1.96164	-1.785542	-2.111668
H	1.054793	2.417878	2.105251

H	-0.269741	1.353849	2.601282
H	-0.536027	2.55945	1.342452
H	0.577246	-2.548659	1.392591
H	0.311943	-1.318199	2.627329
H	1.961371	-1.743649	2.14673
H	-2.563263	-0.571099	0.005738
O	-3.50223	-0.775688	0.007789
H	-3.930914	0.084358	-0.000734

Table S11. Coordinates for calculated optimal geometry for P-OH/H_2O system

C	-0.761731	-0.411692	0.941986
C	0.517074	-0.047724	-0.007402
C	-0.819504	-0.882699	-0.436624
C	-0.670495	0.96566	0.472571
C	-0.70652	0.496375	-0.913075
O	-0.455357	1.066635	-2.113661
O	-0.668882	-2.094241	-1.020998
O	-0.635543	-1.01316	2.144288
O	-0.328078	2.136141	1.059743
H	-1.300476	1.326267	-2.499908
H	-1.546759	-2.481199	-1.124132
H	0.30575	-1.167713	2.3027
H	-1.140159	2.562399	1.359504
H	2.611388	-0.197023	-0.046915
O	3.569785	-0.265346	-0.064997
H	3.861905	0.59753	-0.370992

Table S12. Coordinates for calculated optimal geometry for P-CN/H_2O system

C	0.7687	-0.723942	-0.632704
C	-0.018963	-0.000084	0.673351
C	0.762364	0.730754	-0.633361
C	-0.684676	-0.730409	-0.69591
C	-0.691034	0.724319	-0.695437
C	1.76022	-1.712994	-0.465916
N	2.590301	-2.538716	-0.379602
C	-1.678145	-1.728103	-0.613777
N	-2.50528	-2.561134	-0.598269
C	-1.693246	1.713332	-0.614455
N	-2.527683	2.539051	-0.599794
C	1.744957	1.728422	-0.46514
N	2.567629	2.561418	-0.377805
H	-0.11818	-0.000598	2.97121
O	-0.159635	-0.000813	3.931316
H	-1.100565	-0.005006	4.126648

Theoretical IR Spectra for optimized geometries

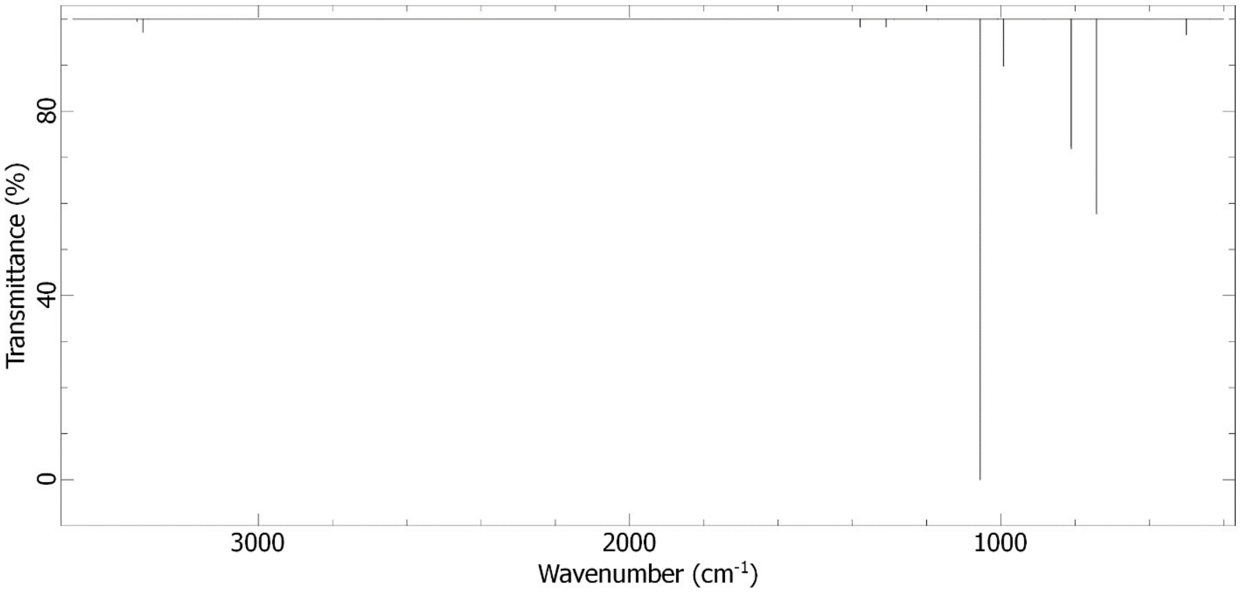


Figure S1. Calculated IR spectrum for the optimized geometry of P-H

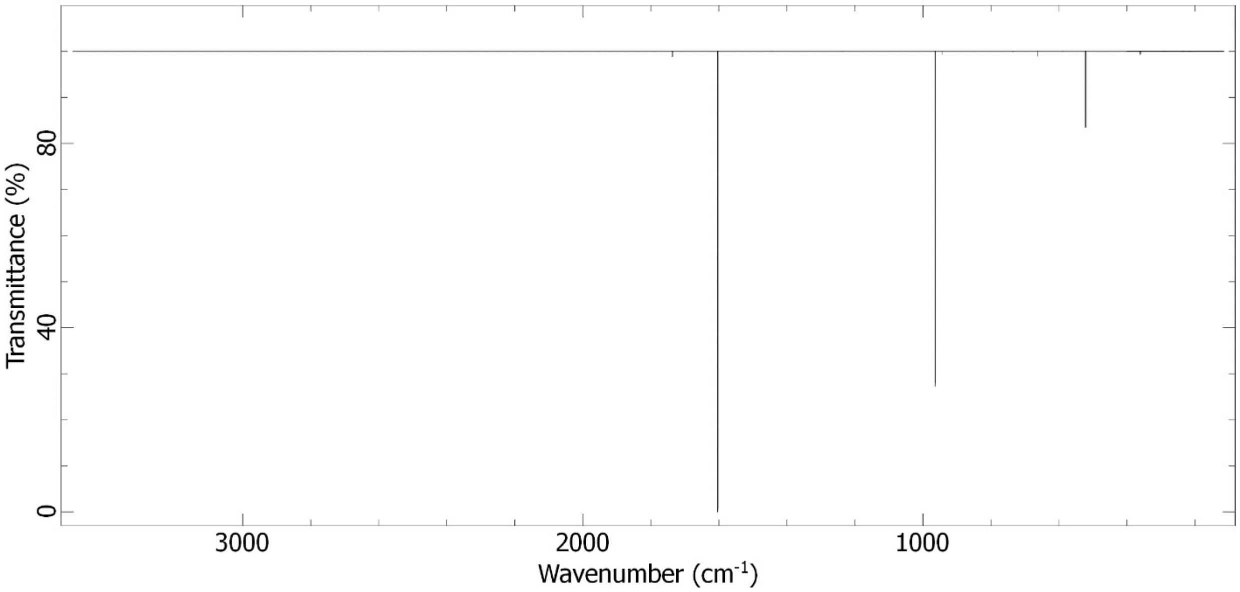


Figure S2. Calculated IR spectrum for the optimized geometry of P-F

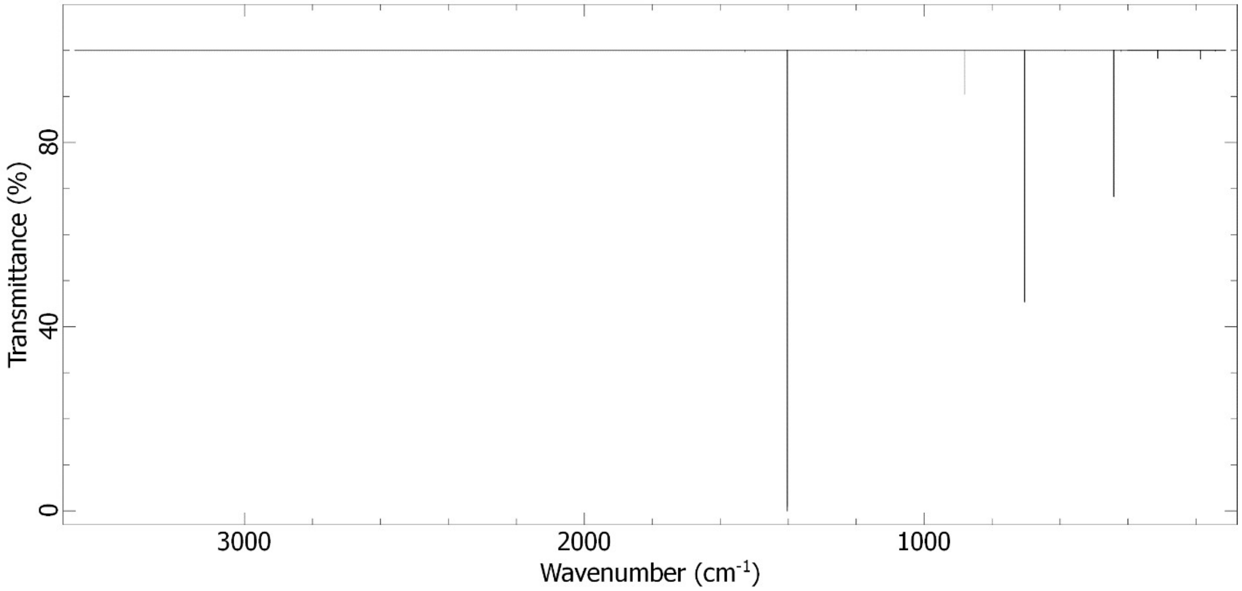


Figure S3. Calculated IR spectrum for the optimized geometry of P-Cl

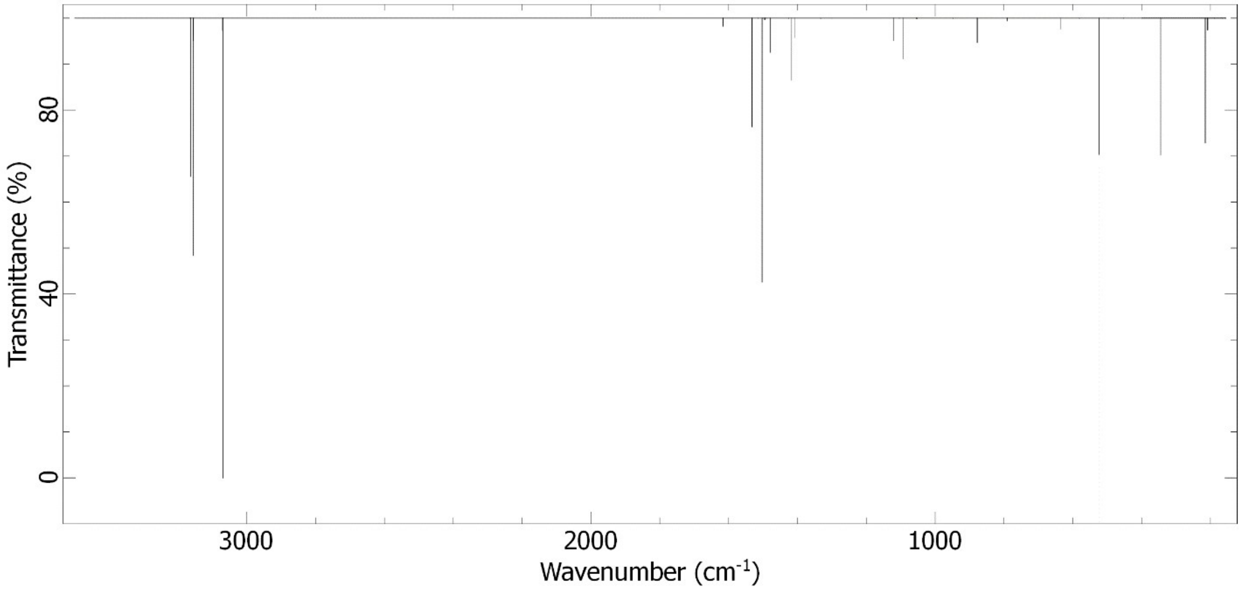


Figure S4. Calculated IR spectrum for the optimized geometry of P-CH_3

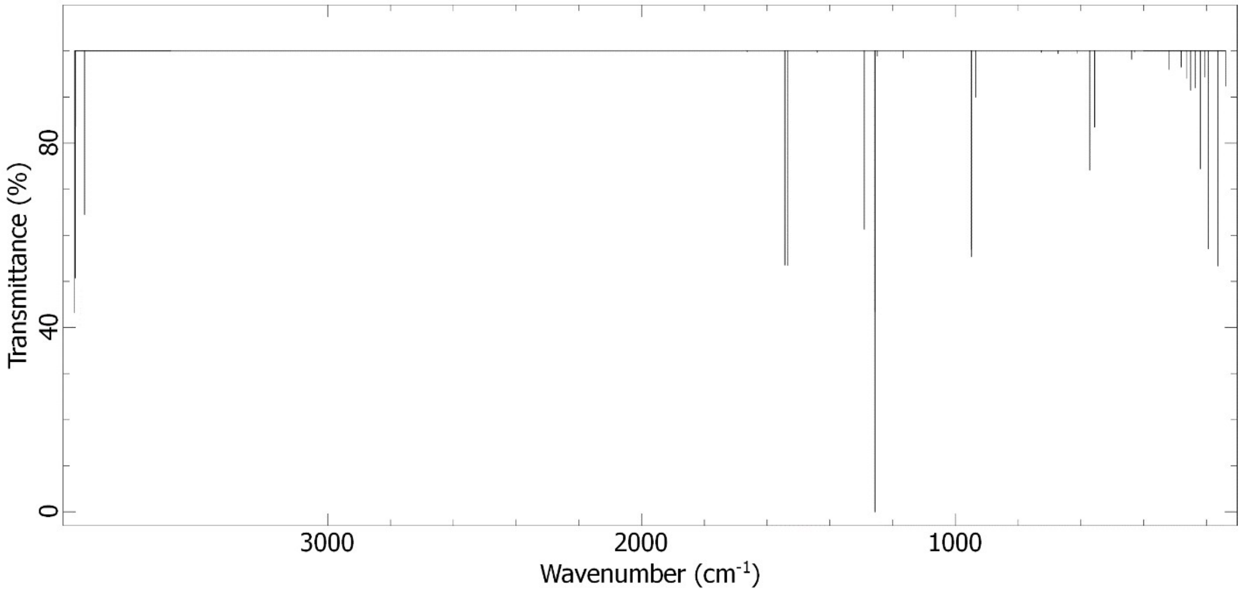


Figure S5. Calculated IR spectrum for the optimized geometry of P-OH

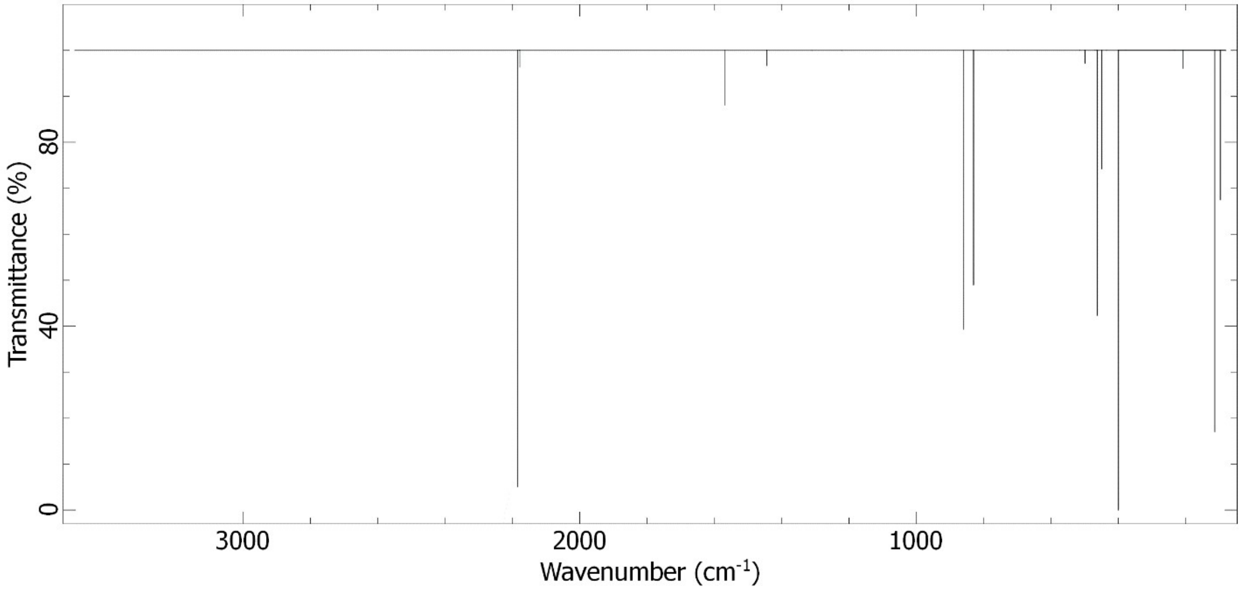


Figure S6. Calculated IR spectrum for the optimized geometry of P-CN

Correlation between values in molecular electrostatic potential critical points and electron density in hydrogen bond critical points

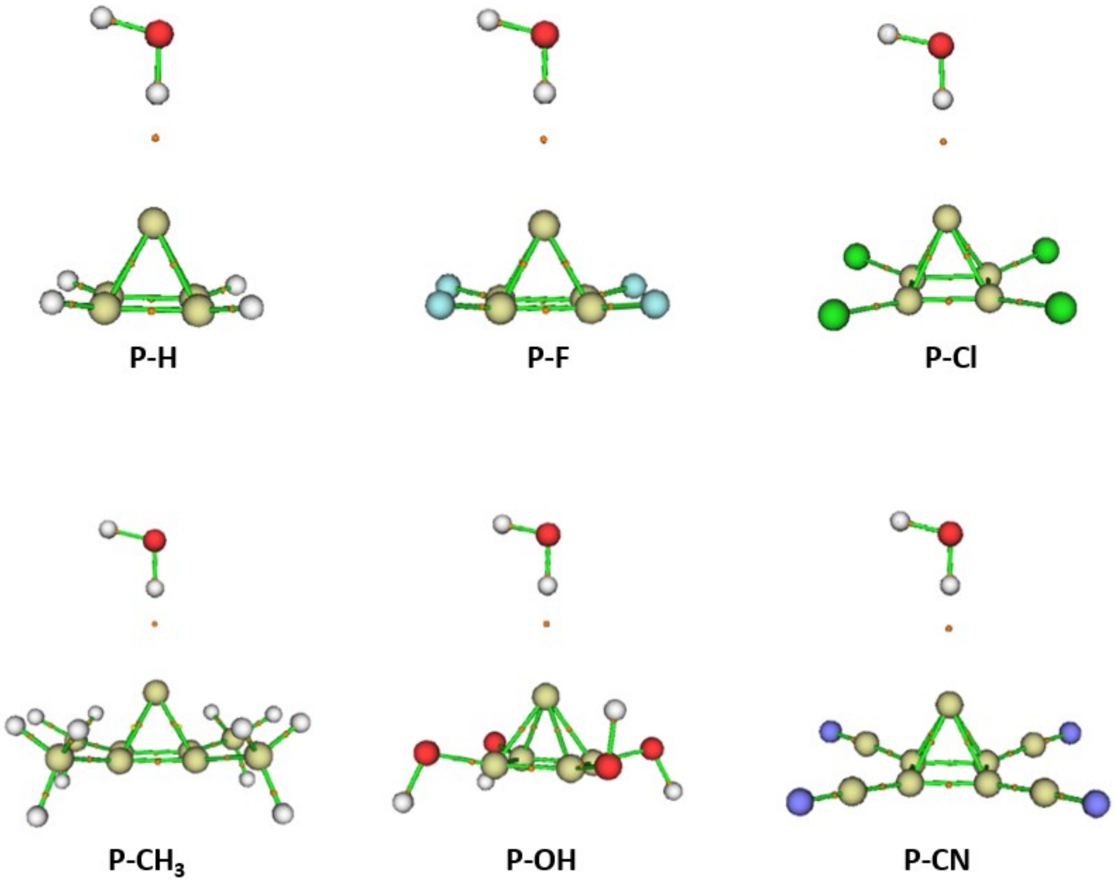


Figure S7. Calculated hydrogen bond critical points for studied systems

Table S13. Calculated values of electrostatic potential in critical points above apical carbon atom and electron density in hydrogen bond critical point

Model system	Energy in electrostatic potential critical point (kcal/mol)	Electron density in hydrogen bond critical point (a.u.)
P-H	-45.06	0.0234
P-F	-30.23	0.0178
P-Cl	-32.49	0.0181
P-CH_3	-48.76	0.0237

P-OH	-45.14	0.0228
P-CN	-7.97	0.0142

Influence of Basis Set Superposition Error on Interaction energy values

Table S14. Comparison of interaction energy values calculated at MP2/aug-cc-pVTZ level with and without BSSE correction:

Model system	**O-H···C distance (Å)**	**BSSE corrected energy (kcal/mol)**	**Energy without BSSE correction (kcal/mol)**
P-H	**2.1**	-6.41	-7.08
P-F	**2.2**	-3.90	-4.65
P-Cl	**2.2**	-4.54	-5.32
P-CH_3	**2.1**	-7.40	-8.21
P-OH	**2.1**	-5.83	-6.61
P-CN	**2.3**	-2.05	-2.69