Supporting Information

Competition and conversion between pnicogen bond and hydrogen bond involving prototype organophosphorus compounds

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Table S1 Binding energies (kJ·mol^{-1}), main geometrical parameters (Å) calculated at the MP2 level for the pnicogen-bonded complexes[a]

Complexes	Basis set	ΔE	d(P···N)	$r_{1C\text{-}5O}$	$r_{5O\text{-}6P}$	$r_{6P\text{-}7O}$	$r_{6P\text{-}8O}$	$r_{9N\text{-}10H}$	$r_{9N\text{-}11H}$	$r_{9N\text{-}12H}$
$H_3N\cdots CH_3OPO_2$	aug-cc-pVTZ	-92.5	1.9333	1.4374	1.6108	1.4846	1.4787	1.0156	1.0161	1.0166
	aug-cc-pV(T+d)Z	-91.9	1.9222	1.4375	1.6027	1.4763	1.4706	1.0156	1.0160	1.0166
		ΔE	d(P···O)	$r_{1C\text{-}5O}$	$r_{5O\text{-}6P}$	$r_{6P\text{-}7O}$	$r_{6P\text{-}8O}$	$r_{9N\text{-}10H}$	$r_{9N\text{-}11H}$	
$H_2O\cdots CH_3OPO_2$	aug-cc-pVTZ	-44.3	2.0740	1.4425	1.5865	1.4802	1.4746	0.9693	0.9698	
	aug-cc-pV(T+d)Z	-43.7	2.0497	1.4420	1.5782	1.4724	1.4670	0.9696	0.9700	
		ΔE	d(P···C)	$r_{1C\text{-}5O}$	$r_{5O\text{-}6P}$	$r_{6P\text{-}7O}$	$r_{6P\text{-}8O}$	$r_{11C\text{-}10N}$	$r_{10N\text{-}9H}$	
$HNC\cdots CH_3OPO_2$	aug-cc-pVTZ	-44.3	2.0077	1.4392	1.6005	1.4822	1.4774	1.1622	1.0005	
	aug-cc-pV(T+d)Z	-43.5	1.9793	1.4390	1.5921	1.4745	1.4700	1.1618	1.0005	
		ΔE	d(P···C)	$r_{1C\text{-}5O}$	$r_{5O\text{-}6P}$	$r_{6P\text{-}7O}$	$r_{6P\text{-}8O}$	$r_{9C\text{-}10H}$	$r_{9C\text{-}11C}$	$r_{11C\text{-}12H}$
$HCCH\cdots CH_3OPO_2$	aug-cc-pVTZ	-20.9	2.8753	1.4478	1.5832	1.4766	1.4703	1.0637	1.2155	1.0639
	aug-cc-pV(T+d)Z	-20.6	2.8574	1.4475	1.5746	1.4685	1.4624	1.0637	1.2156	1.0639
		ΔE	d(P···N)	$r_{1C\text{-}5O}$	$r_{5O\text{-}6P}$	$r_{6P\text{-}7O}$	$r_{8N\text{-}9H}$	$r_{8N\text{-}10H}$	$r_{8N\text{-}11H}$	
$H_3N\cdots CH_3PO_2$	aug-cc-pVTZ	-69.7	1.9768	1.8076	1.4877	1.4877	1.0157	1.0157	1.0176	
	aug-cc-pV(T+d)Z	-69.1	1.9606	1.8029	1.4793	1.4793	1.0156	1.0156	1.0177	
		ΔE	d(P···O)	$r_{1C\text{-}5P}$	$r_{5P\text{-}6O}$	$r_{5P\text{-}7O}$	$r_{8O\text{-}9H}$	$r_{8O\text{-}10H}$		
$H_2O\cdots CH_3PO_2$	aug-cc-pVTZ	-35.0	2.1516	1.7971	1.4817	1.4817	0.9693	0.9693		
	aug-cc-pV(T+d)Z	-34.3	2.1218	1.7922	1.4737	1.4737	0.9695	0.9695		
		ΔE	d(P···C)	$r_{1C\text{-}5P}$	$r_{5P\text{-}6O}$	$r_{5P\text{-}7O}$	$r_{8H\text{-}9N}$	$r_{9N\text{-}10C}$		
$HNC\cdots CH_3PO_2$	aug-cc-pVTZ	-24.1	2.1915	1.7982	1.4834	1.4834	1.0001	1.1661		
	aug-cc-pV(T+d)Z	-22.8	2.1228	1.7936	1.4763	1.4763	1.0003	1.1650		
		ΔE	d(P···C8)	$r_{1C\text{-}5P}$	$r_{5P\text{-}6O}$	$r_{5P\text{-}7O}$	$r_{8C\text{-}9H}$	$r_{8C\text{-}10C}$	$r_{10C\text{-}11H}$	
$HCCH\cdots CH_3PO_2$	aug-cc-pVTZ	-16.6	2.9709	1.8002	1.4779	1.4779	1.0635	1.2147	1.0635	
	aug-cc-pV(T+d)Z	-16.4	2.9675	1.7951	1.4693	1.4693	1.0635	1.2148	1.0635	
		ΔE	d(P···N)	$r_{3C\text{-}2O}$	$r_{2O\text{-}1P}$	$r_{1P\text{-}7O}$	$r_{8N\text{-}9H}$	$r_{8N\text{-}10H1}$	$r_{8N\text{-}11H}$	
$H_3N\cdots$*trans*-CH_3OPO	aug-cc-pVTZ	-16.0	2.5097	1.4322	1.6442	1.4902	1.0137	1.0149	1.0137	

	aug-cc-pV(T+d)Z	-16.0	2.5130	1.4328	1.6338	1.4824	1.0137	1.0149	1.0136
		ΔE	d(P···O)	$r_{3C\text{-}2O}$	$r_{2O\text{-}1P}$	$r_{1P\text{-}7O}$	$r_{8O\text{-}9H}$	$r_{8O\text{-}10H}$	
H_2O···*trans*-CH_3OPO	aug-cc-pVTZ	-14.1	2.8906	1.4398	1.6253	1.4886	0.9627	0.9651	
	aug-cc-pV(T+d)Z	-14.1	2.8916	1.4402	1.6158	1.4804	0.9627	0.9650	
		ΔE	d(P···N)	$r_{3C\text{-}2O}$	$r_{2O\text{-}1P}$	$r_{1P\text{-}7O}$	$r_{8N\text{-}9H}$	$r_{8N\text{-}10H1}$	$r_{8N\text{-}11H}$
H_3N···*cis*-CH_3OPO	aug-cc-pVTZ	-12.9	2.5190	1.4361	1.6335	1.4976	1.0143	1.0133	1.0133
	aug-cc-pV(T+d)Z	-12.9	2.5271	1.4365	1.6228	1.4896	1.0143	1.0133	1.0133

[a] ΔE Binding energies calculated at the CCSD(T)/aug-cc-pV(T+d)Z level basing on the MP2/aug-cc-pVTZ and MP2/aug-cc-pV(T+d)Z optimized geometries.

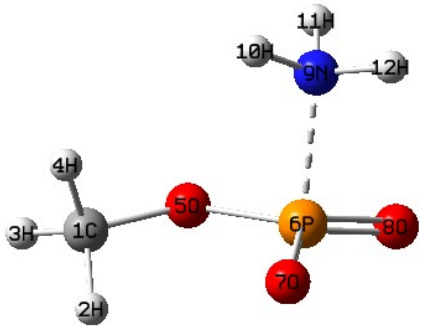
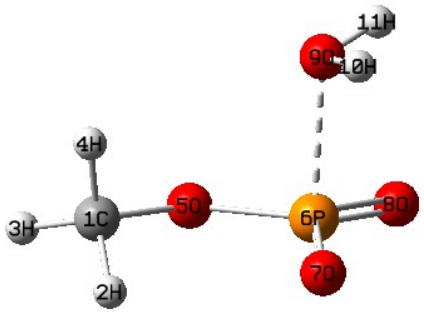
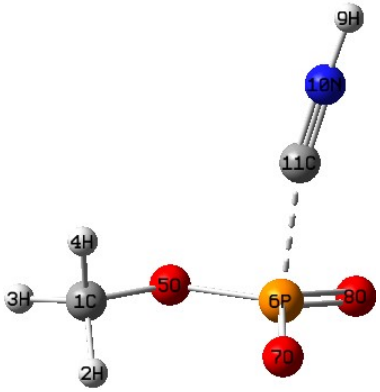
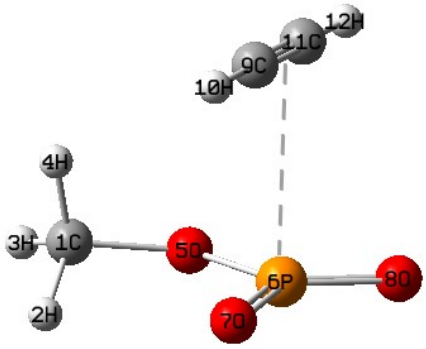
Table S2 Binding energies (kJ·mol^{-1}), main geometrical parameters (Å) calculated at the MP2 level for the hydrogen-bonded complexes[a]

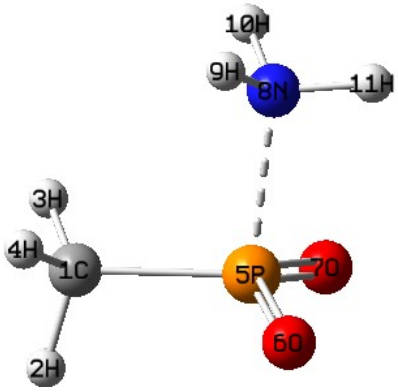
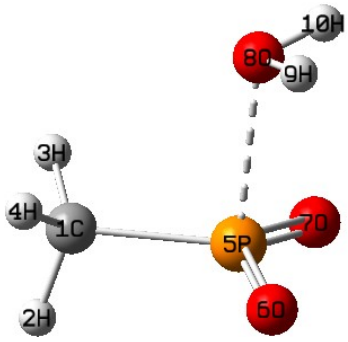
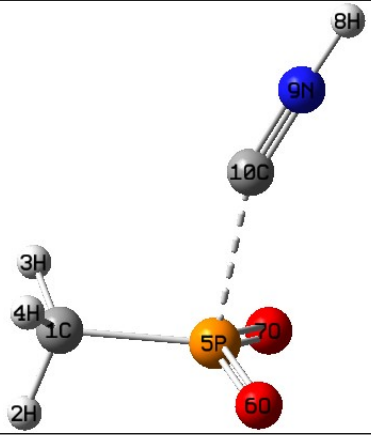
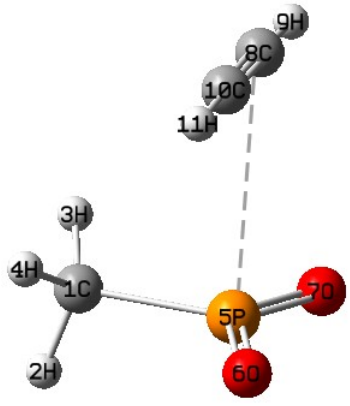
Complexes	Basis set	ΔE	d(O···H)	$r_{1C\text{-}5O}$	$r_{5O\text{-}6P}$	$r_{6P\text{-}7O}$	$r_{6P\text{-}8O}$	$r_{9O\text{-}10N}$	$r_{10N\text{-}11C}$	
CH_3OPO_2···HNC	aug-cc-pVTZ	-25.3	1.8190	1.4569	1.5712	1.4725	1.4752	1.0127	1.1764	
	aug-cc-pV(T+d)Z	-25.2	1.8194	1.4572	1.5629	1.4642	1.4672	1.0127	1.1764	
		ΔE	d(O···H)	$r_{1C\text{-}5O}$	$r_{5O\text{-}6P}$	$r_{6P\text{-}7O}$	$r_{6P\text{-}8O}$	$r_{12H\text{-}11C}$	$r_{11C\text{-}9C}$	$r_{9C\text{-}10H}$
CH_3OPO_2···HCCH	aug-cc-pVTZ	-9.0	2.2375	1.4528	1.5761	1.4752	1.4725	1.0658	1.2135	1.0620
	aug-cc-pV(T+d)Z	-8.9	2.2383	1.4526	1.5675	1.4670	1.4645	1.0658	1.2135	1.0620
		ΔE	d(O···H)	$r_{1C\text{-}5P}$	$r_{5P\text{-}6O}$	$r_{5P\text{-}7O}$	$r_{9H\text{-}8O}$	$r_{8O\text{-}10H}$		
CH_3PO_2···H_2O	aug-cc-pVTZ	-21.0	1.9676	1.7973	1.4823	1.4763	0.9691	0.9607		
	aug-cc-pV(T+d)Z	-20.9	1.9762	1.7918	1.4736	1.4677	0.9688	0.9607		
		ΔE	d(O···H)	$r_{1C\text{-}5P}$	$r_{5P\text{-}6O}$	$r_{5P\text{-}7O}$	$r_{8H\text{-}9N}$	$r_{9N\text{-}10C}$		
CH_3PO_2···HNC	aug-cc-pVTZ	-27.1	1.7941	1.7974	1.4843	1.4736	1.0167	1.1771		
	aug-cc-pV(T+d)Z	-27.1	1.7985	1.7920	1.4755	1.4651	1.0162	1.1771		
		ΔE	d(O···H)	$r_{1C\text{-}5P}$	$r_{5P\text{-}6O}$	$r_{5P\text{-}7O}$	$r_{9H\text{-}8C}$	$r_{8C\text{-}10C}$	$r_{10C\text{-}11H}$	
CH_3PO_2···HCCH	aug-cc-pVTZ	-12.7	2.2732	1.7994	1.4770	1.4800	1.0665	1.2139	1.0623	
	aug-cc-pV(T+d)Z	-12.6	2.2753	1.7940	1.4683	1.4713	1.0664	1.2139	1.0623	
		ΔE	d(O···H)	$r_{2O\text{-}3C}$	$r_{1P\text{-}2O}$	$r_{1P\text{-}7O}$	$r_{9H\text{-}8O}$	$r_{8O\text{-}10H}$		
trans-CH_3OPO···H_2O	aug-cc-pVTZ	-14.7	1.9712	1.4426	1.6171	1.4890	0.9683	0.9605		
	aug-cc-pV(T+d)Z	-14.7	1.9713	1.4432	1.6071	1.4809	0.9683	0.9605		
		ΔE	d(O···H)	$r_{2O\text{-}3C}$	$r_{1P\text{-}2O}$	$r_{1P\text{-}7O}$	$r_{8H\text{-}9N}$	$r_{9N\text{-}10C}$		
trans-CH_3OPO···HNC	aug-cc-pVTZ	-31.5	1.7893	1.4457	1.6133	1.4906	1.0161	1.1763		
	aug-cc-pV(T+d)Z	-31.5	1.7886	1.4462	1.6036	1.4824	1.0159	1.1763		
		ΔE	d(O···H)	$r_{2O\text{-}3C}$	$r_{1P\text{-}2O}$	$r_{1P\text{-}7O}$	$r_{9H\text{-}8C}$	$r_{8C\text{-}10C}$	$r_{10C\text{-}11H}$	
trans-CH_3OPO···HCCH	aug-cc-pVTZ	-10.5	2.1684	1.4421	1.6219	1.4870	1.0671	1.2136	1.0619	
	aug-cc-pV(T+d)Z	-10.5	2.1690	1.4427	1.6119	1.4790	1.0672	1.2136	1.0619	
		ΔE	d(O···H)	$r_{2O\text{-}3C}$	$r_{1P\text{-}2O}$	$r_{1P\text{-}7O}$	$r_{10H\text{-}8N}$	$r_{8N\text{-}9H}$	$r_{8N\text{-}11H}$	
cis-CH_3OPO···NH_3	aug-cc-pVTZ	-5.7	2.2080	1.4466	1.6148	1.4940	1.0146	1.0117	1.0117	

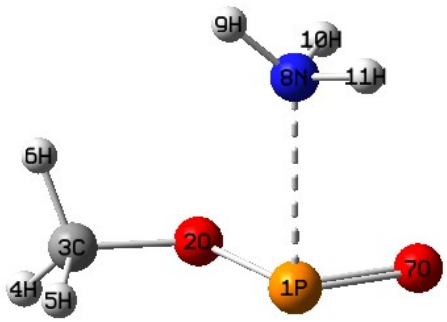
	aug-cc-pV(T+d)Z	-5.7	2.2080	1.4473	1.6049	1.4856	1.0146	1.0117	1.0117
		ΔE	d(O···H)	$r_{2O\text{-}3C}$	$r_{1P\text{-}2O}$	$r_{1P\text{-}7O}$	$r_{10H\text{-}8N}$	$r_{8N\text{-}9H}$	
cis-$CH_3OPO\cdots H_2O$	aug-cc-pVTZ	-19.9	1.9161	1.4545	1.6054	1.4971	0.9703	0.9607	
	aug-cc-pV(T+d)Z	-19.9	1.9148	1.4552	1.5956	1.4890	0.9703	0.9606	
		ΔE	d(O···H)	$r_{2O\text{-}3C}$	$r_{1P\text{-}2O}$	$r_{1P\text{-}7O}$	$r_{8H\text{-}9N}$	$r_{9N\text{-}10C}$	
cis-$CH_3OPO\cdots HNC$	aug-cc-pVTZ	-32.0	1.7531	1.4532	1.6027	1.4993	1.0194	1.1769	
	aug-cc-pV(T+d)Z	-32.1	1.7534	1.4539	1.5930	1.4911	1.0194	1.1769	
		ΔE	d(O···H)	$r_{2O\text{-}3C}$	$r_{1P\text{-}2O}$	$r_{1P\text{-}7O}$	$r_{9H\text{-}8C}$	$r_{8C\text{-}10C}$	$r_{10C\text{-}11H}$
cis-$CH_3OPO\cdots HCCH$	aug-cc-pVTZ	-12.7	2.1526	1.4505	1.6111	1.4955	1.0679	1.2140	1.0621
	aug-cc-pV(T+d)Z	-12.8	2.1525	1.4512	1.6012	1.4874	1.0680	1.2140	1.0622

[a] ΔE Binding energies calculated at the CCSD(T)/aug-cc-pV(T+d)Z level basing on the MP2/aug-cc-pVTZ and MP2/aug-cc-pV(T+d)Z optimized geometries.

Table S3. Equilibrium geometries (Å) and zero point vibrational energies (a.u.) at the MP2/aug-cc-pV(T+d)Z level, total energies (a.u.) at the CCSD(T)/aug-cc-pV(T+d)Z//MP2/aug-cc-pV(T+d)Z level for the pnicogen- and hydrogen-bonded complexes

	$H_3N\cdots CH_3OPO_2$ $E_{CCSD(T)}$ = -662.748457 E_{ZPVE} =0.092313 1C -2.18601 0.14138 -0.08963 2H -2.30107 -0.54275 0.74567 3H -2.97997 0.00006 -0.81594 4H -2.21253 1.16629 0.28257 5O -0.95424 -0.11224 -0.78595 6P 0.38452 -0.33674 0.06608 7O 0.11818 -0.4598 1.51293 8O 1.42548 -0.96171 -0.76362 9N 0.97377 1.49025 -0.03305 10H 0.35005 2.12695 0.45369 11H 1.07225 1.76668 -1.00578 12H 1.88772 1.52373 0.41088
	$H_2O\cdots CH_3OPO_2$ $E_{CCSD(T)}$ = -682.590648 E_{ZPVE} = 0.077925 1C -2.16672 0.17475 -0.10919 2H -2.28266 -0.21219 0.89875 3H -2.98965 -0.13968 -0.74149 4H -2.10824 1.26106 -0.08613 5O -0.97383 -0.35889 -0.7187 6P 0.36914 -0.38012 0.10999 7O 0.18893 -0.20449 1.56074 8O 1.46691 -0.97429 -0.66074 9O 0.83006 1.57836 -0.28157 10H 1.12928 1.90832 0.57961 11H 1.61797 1.5104 -0.84324
	$HNC\cdots CH_3OPO_2$ $E_{CCSD(T)}$ = -699.504018 E_{ZPVE} = 0.070260 1C 1.86521 -1.34633 -0.09201 2H 2.3935 -0.92033 0.75575 3H 2.56189 -1.75855 -0.81451 4H 1.19246 -2.1288 0.25904 5O 1.12582 -0.32804 -0.79036 6P 0.16856 0.63097 0.06145 7O 0.44286 0.57822 1.5171 8O -0.36437 1.72323 -0.77864 9H -3.39677 -1.49442 -0.01036 10N -2.48837 -1.07513 -0.00997 11C -1.44778 -0.55765 -0.01244
	$HCCH\cdots CH_3OPO_2$ $E_{CCSD(T)}$ = -683.428446 E_{ZPVE} = 0.079776 1C 1.62498 -1.45936 -0.19921 2H 2.14819 -1.18429 0.71124 3H 2.31113 -1.85773 -0.93797 4H 0.84162 -2.18053 0.0207 5O 1.03088 -0.29073 -0.81355 6P 0.24856 0.74123 0.09724 7O 0.41314 0.52643 1.54879 8O -0.37221 1.81378 -0.69397 9C -1.89269 -1.12182 0.55681 10H -1.78852 -1.3644 1.58718 11C -2.01381 -0.81696 -0.61355

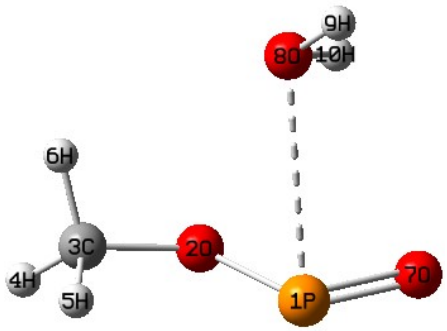
	12H -2.12621 -0.53867 -1.63422
	$H_3N\cdots CH_3PO_2$ $E_{CCSD(T)}$ = -587.594301 E_{ZPVE} = 0.086031 1C 0.52602 1.64443 0.00000 2H 1.60015 1.82598 0.00000 3H 0.10225 2.08797 0.89868 4H 0.10225 2.08797 -0.89868 5P 0.29647 -0.14855 0.00000 6O 0.52602 -0.75012 -1.34111 7O 0.52602 -0.75012 1.34111 8N -1.68035 -0.14888 0.00000 9H -2.07641 0.27213 -0.8352 10H -2.07641 0.27213 0.8352 11H -1.90898 -1.14046 0.00000
	$H_2O\cdots CH_3PO_2$ $E_{CCSD(T)}$ = -607.441539 E_{ZPVE} = 0.071569 1C 0.50117 1.65414 0.00000 2H 1.56405 1.89392 0.00000 3H 0.04433 2.0617 0.89693 4H 0.04433 2.0617 -0.89693 5P 0.35748 -0.13225 0.00000 6O 0.50117 -0.73955 -1.33504 7O 0.50117 -0.73955 1.33504 8O -1.76414 -0.10322 0.00000 9H -1.96384 -0.64994 -0.77531 10H -1.96384 -0.64994 0.77531
	$HNC\cdots CH_3PO_2$ $E_{CCSD(T)}$ = -624.350376 E_{ZPVE} = 0.063737 1C 0.83597 1.72767 0.00000 2H 1.90149 1.95669 0.00000 3H 0.38214 2.13732 0.89854 4H 0.38214 2.13732 -0.89854 5P 0.6627 -0.06218 0.00000 6O 0.83597 -0.67259 -1.34086 7O 0.83597 -0.67259 1.34086 8H -3.53253 -0.89954 0.00000 9N -2.61318 -0.50588 0.00000 10C -1.52879 -0.07707 0.00000
	$HCCH\cdots CH_3PO_2$ $E_{CCSD(T)}$ = -608.281319 E_{ZPVE} = 0.073431 1C 1.7584 -0.33917 0.00000 2H 2.3128 -1.27777 0.00000 3H 1.99538 0.22213 0.89833 4H 1.99538 0.22213 -0.89833 5P 0.00567 -0.74973 0.00000 6O -0.56332 -0.95559 -1.34831 7O -0.56332 -0.95559 1.34831 8C -0.56332 2.10227 0.60737 9H -0.58298 2.08832 1.67058 10C -0.56332 2.10227 -0.60737 11H -0.58298 2.08832 -1.67058



$H_3N\cdots$*trans*-CH_3OPO

$E_{CCSD(T)}$ = -587.549403 E_{ZPVE} = 0.083591

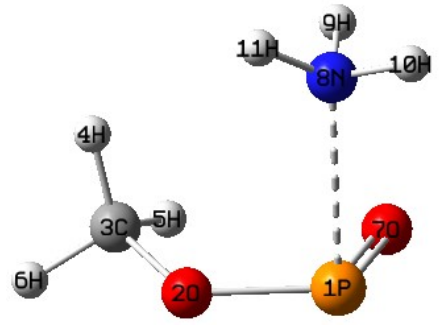
1P	0.28799	-0.61874	0.45685
2O	-0.96855	-0.28797	-0.53356
3C	-2.10692	0.35206	0.05583
4H	-2.99768	-0.17845	-0.26858
5H	-2.05386	0.33654	1.14647
6H	-2.15092	1.38435	-0.28642
7O	1.36873	-1.21248	-0.36602
8N	1.16897	1.68815	-0.00916
9H	0.79672	2.61874	0.1422
10H	1.22601	1.52627	-1.00938
11H	2.11707	1.66793	0.34879



$H_2O\cdots$*trans*-CH_3OPO

$E_{CCSD(T)}$ = -607.410050 E_{ZPVE} = 0.070009

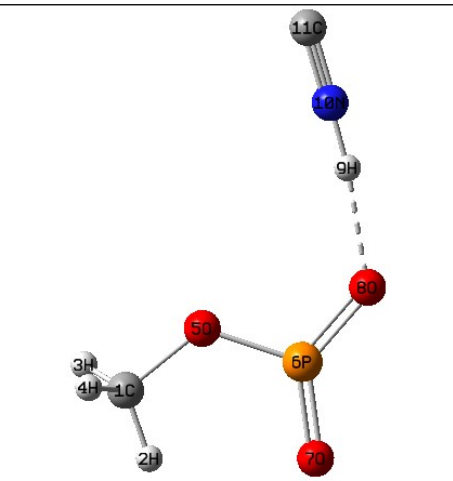
1P	0.36288	-0.76493	0.4464
2O	-0.85492	-0.35906	-0.5505
3C	-2.06809	0.13799	0.04455
4H	-2.90068	-0.36814	-0.43389
5H	-2.09009	-0.05336	1.11844
6H	-2.11936	1.20846	-0.13321
7O	1.57277	-1.01177	-0.38489
8O	0.72078	2.07353	0.0333
9H	1.43975	2.55961	0.44992
10H	1.1267	1.6779	-0.74774



$H_3N\cdots$*cis*-CH_3OPO

$E_{CCSD(T)}$ = -587.554003 E_{ZPVE} = 0.083524

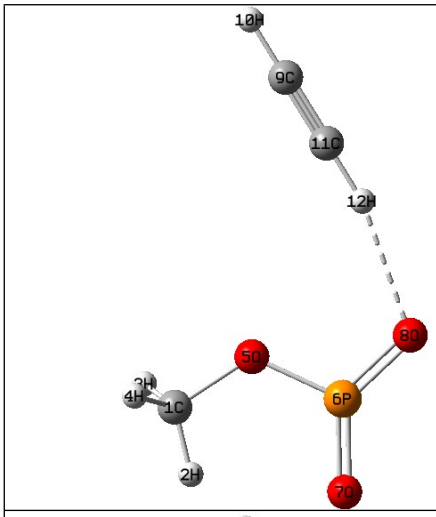
1P	-0.19891	-0.77405	-0.50793
2O	0.98809	0.31681	-0.69344
3C	1.70158	0.84628	0.4354
4H	1.2062	1.75416	0.77788
5H	1.73184	0.11974	1.24403
6H	2.705	1.08469	0.09655
7O	-0.23048	-1.29047	0.88896
8N	-1.81956	1.07257	0.08355
9H	-1.72346	1.02835	1.09231
10H	-2.76682	0.79234	-0.14222
11H	-1.70256	2.03504	-0.21099



$CH_3OPO_2\cdots HNC$

$E_{CCSD(T)}$ = -699.504018 E_{ZPVE} = 0.070260

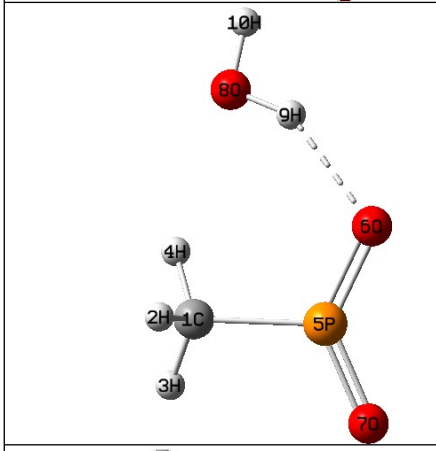
1C	1.86521	-1.34633	-0.09201
2H	2.3935	-0.92033	0.75575
3H	2.56189	-1.75855	-0.81451
4H	1.19246	-2.1288	0.25904
5O	1.12582	-0.32804	-0.79036
6P	0.16856	0.63097	0.06145
7O	0.44286	0.57822	1.5171
8O	-0.36437	1.72323	-0.77864
9H	-3.39677	-1.49442	-0.01036
10N	-2.48837	-1.07513	-0.00997
11C	-1.44778	-0.55765	-0.01244



$CH_3OPO_2\cdots HCCH$

$E_{CCSD(T)}$ = -683.423594 E_{ZPVE} = 0.079359

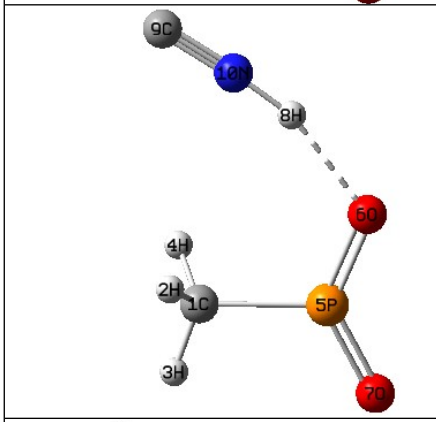
1C	0.26371	2.36093	0.000000
2H	1.33269	2.54883	0.000000
3H	-0.20331	2.76594	0.89112
4H	-0.20331	2.76594	-0.89112
5O	0.00000	0.93244	0.000000
6P	1.16187	-0.11968	0.000000
7O	2.52127	0.43174	0.000000
8O	0.65102	-1.49219	0.000000
9C	-3.83701	-1.29735	0.000000
H10	-4.88795	-1.14437	0.000000
11C	-2.63698	-1.47737	0.000000
12H	-1.58278	-1.63428	0.000000



$CH_3PO_2\cdots H_2O$

$E_{CCSD(T)}$ = -607.434626 E_{ZPVE} = 0.069779

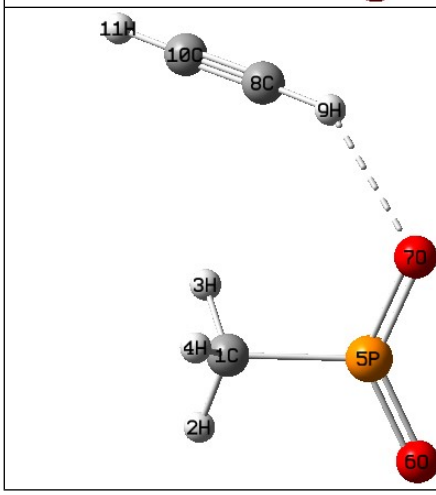
1C	-0.07109	1.5093	0.10671
2H	-0.11362	1.81647	1.15195
3H	-0.68002	2.18102	-0.49033
4H	0.96749	1.47562	-0.21355
5P	-0.76636	-0.14555	0.01622
6O	0.22288	-1.23277	0.20756
7O	-2.22406	-0.206	-0.20928
8O	2.75945	0.03246	-0.13562
9H	2.09423	-0.65502	0.01911
10H	3.58766	-0.44021	-0.25198



$CH_3PO_2\cdots HNC$

$E_{CCSD(T)}$ = -624.351127 E_{ZPVE} = 0.062819

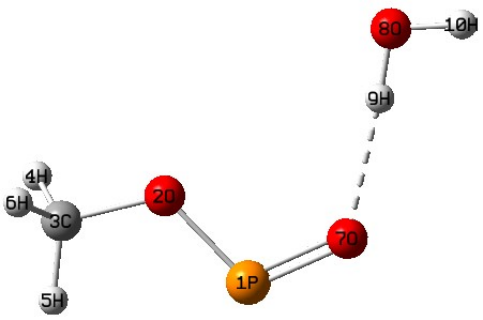
1C	1.55205	0.21629	0.00000
2H	1.5732	-0.4262	0.8794
3H	2.38159	0.91476	0.00000
4H	1.5732	-0.4262	-0.8794
5P	0.00000	1.11202	0.00000
6O	-1.18053	0.22687	0.00000
7O	0.09641	2.57394	0.00000
8H	-1.02405	-1.56478	0.00000
9C	-0.11246	-3.55796	0.00000
10N	-0.63837	-2.50491	0.00000



$CH_3PO_2\cdots HCCH$

$E_{CCSD(T)}$ = -608.279665 E_{ZPVE} = 0.073228

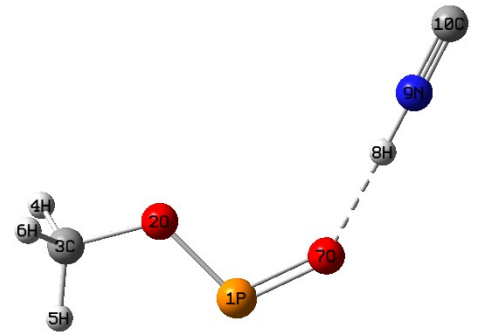
1C	-0.30078	1.41786	0.39946
2H	-0.81417	2.25708	-0.05726
3H	0.72606	1.32142	0.0501
4H	-0.28373	1.5231	1.4837
5P	-1.17354	-0.10829	0.01635
6O	-2.50608	0.0678	-0.59583
7O	-0.42328	-1.3287	0.38802
8C	2.64141	-0.52292	-0.03527
9H	1.83782	-1.181	0.20679
10C	3.53367	0.2511	-0.31517
11H	4.32618	0.9147	-0.56023



trans-$CH_3OPO\cdots H_2O$

$E_{CCSD(T)}$ = -607.410305 E_{ZPVE} = 0.070297

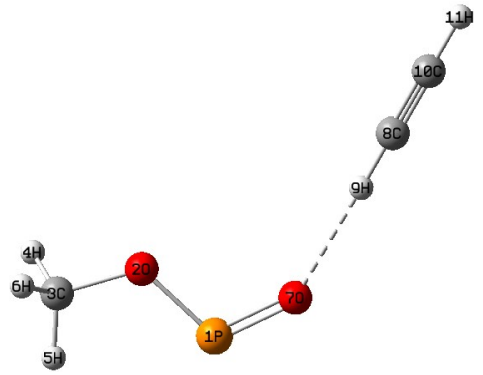
1P	1.10233	-0.08196	0.00000
2O	0.00000	1.08753	0.00000
3C	0.43617	2.4632	0.00000
4H	0.03535	2.93719	0.8901
5H	1.52434	2.53313	0.00000
6H	0.03535	2.93719	-0.8901
7O	0.41136	-1.39182	0.00000
8O	-2.48798	-1.86859	0.00000
9H	-1.52666	-1.75256	0.00000
10H	-2.60738	-2.82167	0.00000



trans-$CH_3OPO\cdots HNC$

$E_{CCSD(T)}$ = -624.331761 E_{ZPVE} = 0.063994

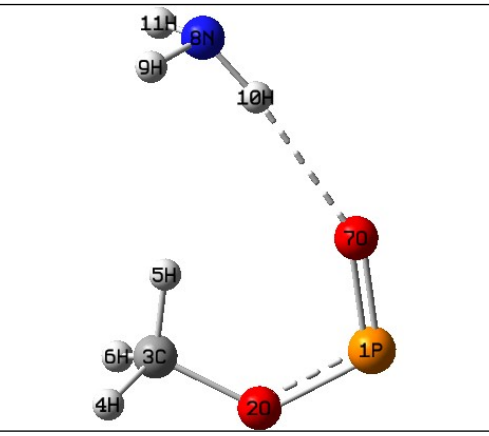
1P	-1.27402	0.46684	0.00000
2O	-0.90556	-1.1038	0.00000
3C	-1.97722	-2.07416	0.00000
4H	-1.86865	-2.68448	0.89046
5H	-2.95195	-1.58584	0.00000
6H	-1.86865	-2.68448	-0.89046
7O	0.00000	1.24071	0.00000
8H	1.77488	1.01387	0.00000
9N	2.78121	0.87342	0.00000
10C	3.94401	0.69567	0.00000



trans-$CH_3OPO\cdots HCCH$

$E_{CCSD(T)}$ = -608.257586 E_{ZPVE} = 0.074176

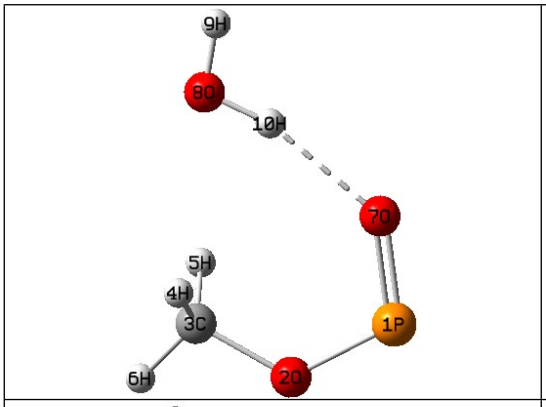
1P	-1.35627	0.57309	0.00000
2O	-1.23257	-1.03409	0.00000
3C	-2.44163	-1.82123	0.00000
4H	-2.43437	-2.44228	0.89007
5H	-3.32772	-1.18558	0.00000
6H	-2.43437	-2.44228	-0.89007
7O	0.00000	1.163	0.00000
8C	3.19224	0.63229	0.00000
9H	2.14127	0.81742	0.00000
10C	4.38717	0.42037	0.00000
11H	5.43305	0.23642	0.00000



cis-$CH_3OPO\cdots H_3N$

$E_{CCSD(T)}$ = -587.550473 E_{ZPVE} = 0.082735

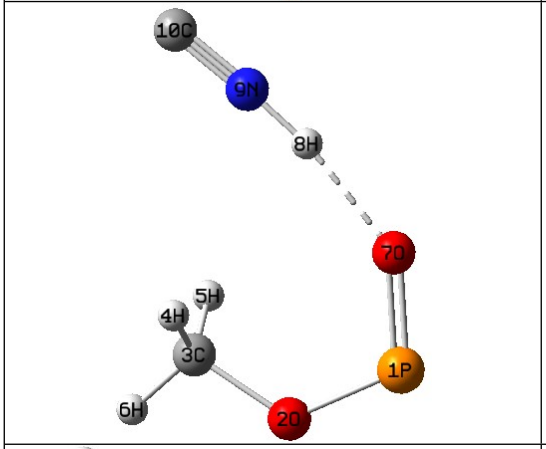
1P	1.37473	0.57019	0.00000
2O	1.33678	-1.04419	0.00000
3C	0.10942	-1.80989	0.00000
4H	0.11358	-2.43188	0.88978
5H	-0.75258	-1.14729	0.00000
6H	0.11358	-2.43188	-0.88978
7O	0.00000	1.15507	0.00000
8N	-3.2025	0.83786	0.00000
9H	-3.41256	0.27511	0.81404
10H	-2.20357	1.01531	0.00000
11H	-3.41256	0.27511	-0.81404



cis-$CH_3OPO\cdots H_2O$

$E_{CCSD(T)}$ = -607.418987 E_{ZPVE} = 0.070878

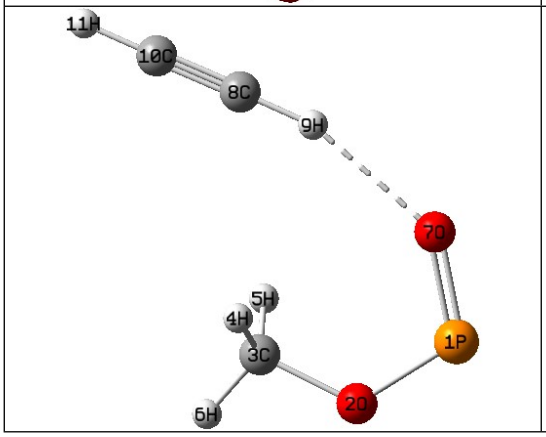
1P	1.31605	0.59383	0.00000
2O	1.14809	-0.99288	0.00000
3C	-0.15224	-1.64612	0.00000
4H	-0.71028	-1.35592	0.88466
5H	-0.71028	-1.35592	-0.88466
6H	0.05148	-2.71034	0.00000
7O	0.00000	1.29035	0.00000
8O	-2.67922	0.28408	0.00000
9H	-3.36346	0.95836	0.00000
10H	-1.84572	0.7808	0.00000



cis-$CH_3OPO\cdots HNC$

$E_{CCSD(T)}$ = -624.337978 E_{ZPVE} = 0.064128

1P	1.45898	0.91249	0.00000
2O	1.67304	-0.67587	0.00000
3C	0.56521	-1.61628	0.00000
4H	-0.04178	-1.46938	0.88896
5H	-0.04178	-1.46938	-0.88896
6H	1.01221	-2.60319	0.00000
7O	0.00000	1.25762	0.00000
8H	-1.61319	0.57145	0.00000
9N	-2.47595	0.02857	0.00000
10C	-3.44068	-0.64553	0.00000

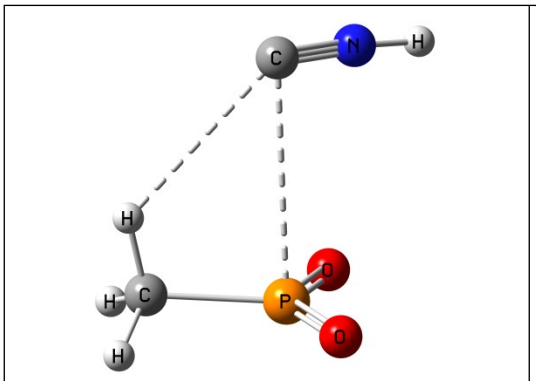
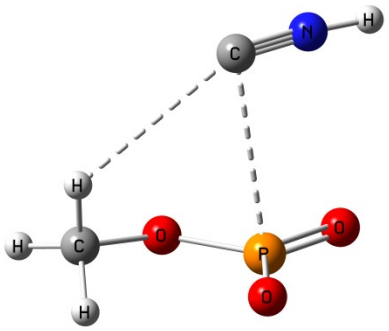
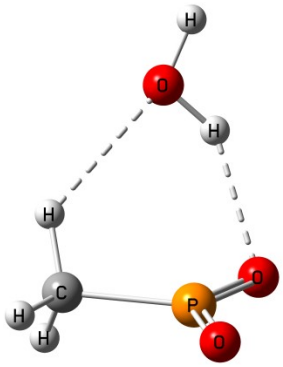


cis-$CH_3OPO\cdots HCCH$

$E_{CCSD(T)}$ = -608.264462 E_{ZPVE} = 0.074319

1P	1.46664	1.16043	0.00000
2O	1.79778	-0.40617	0.00000
3C	0.75283	-1.41314	0.00000
4H	0.13441	-1.30374	0.88627
5H	0.13441	-1.30374	-0.88627
6H	1.25943	-2.37138	0.00000
7O	0.00000	1.40786	0.00000
8C	-2.61953	-0.4083	0.00000
9H	-1.88297	0.36503	0.00000
10C	-3.44264	-1.30064	0.00000
11H	-4.17108	-2.07365	0.00000

Table S4 Geometries (Å) and imaginary frequencies (cm^{-1}) at the MP2/aug-cc-pVTZ level, total energies (a.u.) at the CCSD(T)/aug-cc-pV(T+d)Z//MP2/aug-cc-pVTZ level for the transition states.

	$CH_3PO_2\cdots HNC$ TSa freq = -83.53 cm^{-1} $E_{CCSD(T)}$ = -624.34657 E_{ZPVE} = 0.061876 C 1.24261700 1.46597400 0.25654000 H 0.37821000 2.04345500 -0.07276200 H 2.09550200 1.69762300 -0.37444700 H 1.44090500 1.66264500 1.30535200 P 0.79772700 -0.26260800 0.04122400 O 0.24250700 -0.91200300 1.24948400 O 1.04530600 -0.79475300 -1.31484400 H -2.86967100 -0.99267300 0.37299500 C -2.12762300 0.87572700 -0.45157700 N -2.57190300 -0.12401100 -0.02234200
	$CH_3OPO_2\cdots HNC$ TSb freq = -89.50 cm^{-1} $E_{CCSD(T)}$ = -699.493175 E_{ZPVE} = 0.068227 C -1.78157800 1.43254300 -0.14085100 H -2.46112800 0.97230700 0.56925800 H -2.32427600 1.95459500 -0.92018900 H -1.09285800 2.10003300 0.36844900 O -1.01179300 0.41092600 -0.83267200 P -0.33608700 -0.73650300 0.01235900 O -0.74388900 -0.80061800 1.42871400 O 0.55664900 -1.58002200 -0.80089400 H 3.17081100 -0.01622000 -0.33078300 N 2.53760600 0.67308700 0.02249700 C 1.71120800 1.41461200 0.40905300
	$CH_3PO_2\cdots H_2O$ TSc freq = -33.43 cm^{-1} $E_{CCSD(T)}$ = -607.435203 E_{ZPVE} = 0.069596 C -0.21344900 1.57134800 -0.31001300 H 0.81479200 1.66495600 0.03770400 H -0.88904100 2.21300900 0.24456100 H -0.24238200 1.79002100 -1.37568300 P -0.68086900 -0.14800200 -0.07994200 O 0.17138600 -1.10120800 -0.82872000 O -1.84344500 -0.38157800 0.80005200 O 2.48319700 0.00892500 0.45534400 H 2.07705700 -0.66082300 -0.11224000 H 3.24419800 -0.42433600 0.85145800

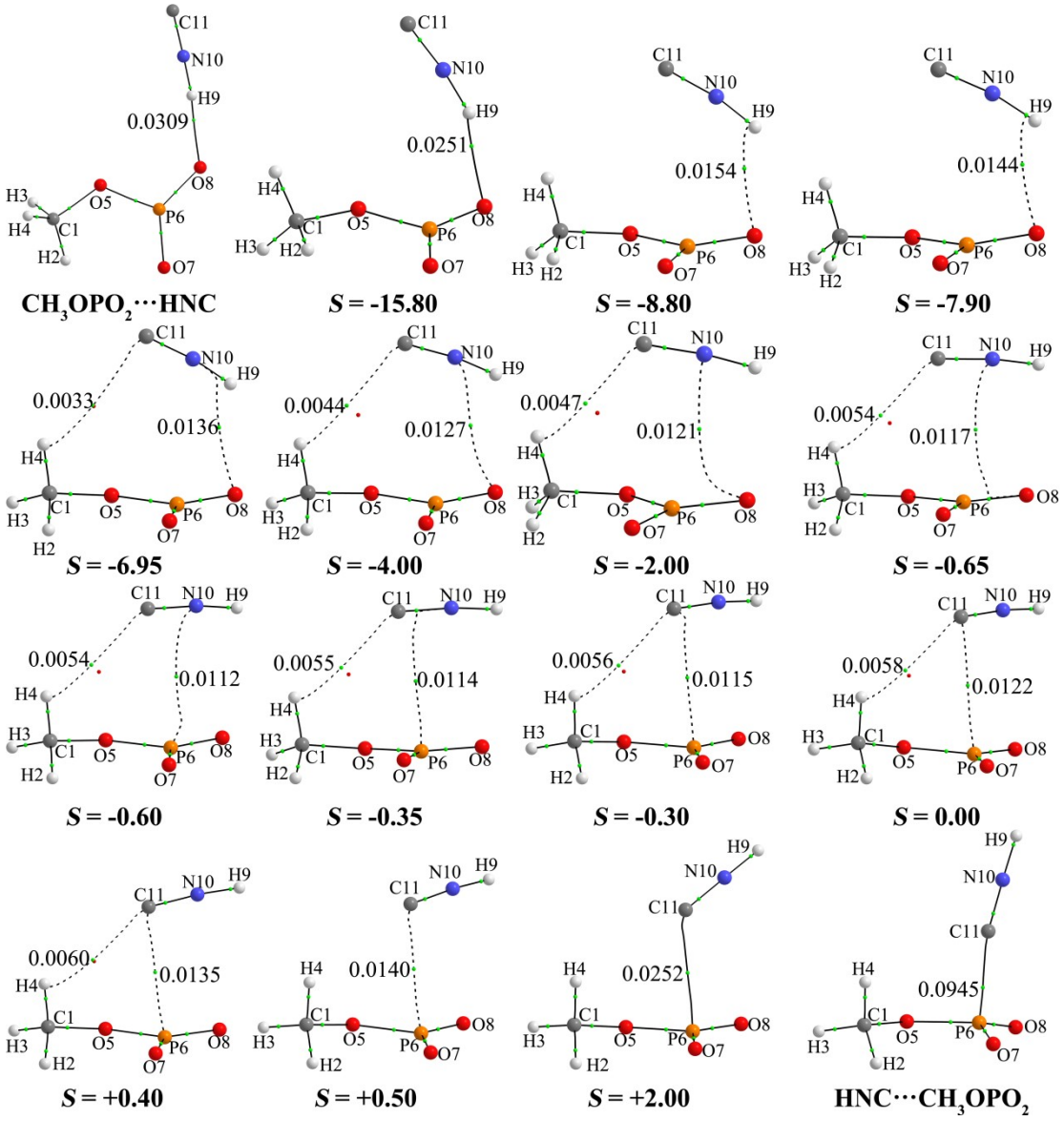


Figure S1. Molecular graphs of some points along the $CH_3OPO_2\cdots HNC \rightarrow TSb \rightarrow HNC\cdots CH_3OPO_2$ reaction pathway.