

Electronic Supplementary Information

Exceptional proton affinities of push-pull nitriles substituted by the guanidino and phosphazeno groups

Ewa D. Raczynska,* Jean-François Gal and Pierre-Charles Maria

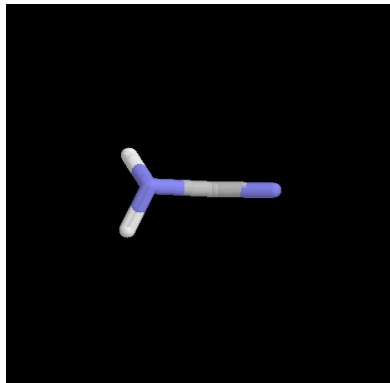
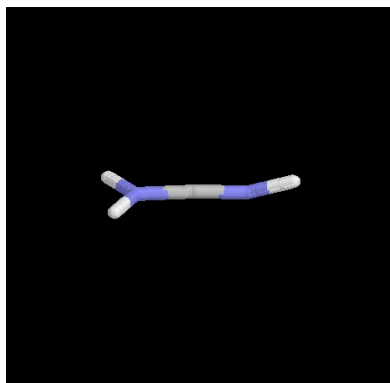
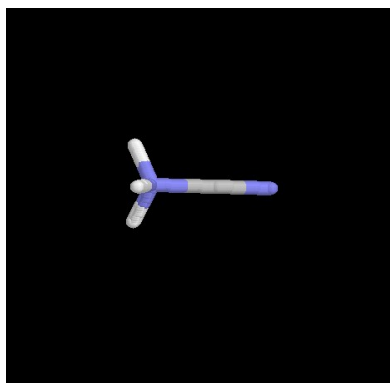
^a *Department of Chemistry, Warsaw University of Life Sciences (SGGW),
ul. Nowoursynowska 159c, 02-776 Warszawa, Poland*

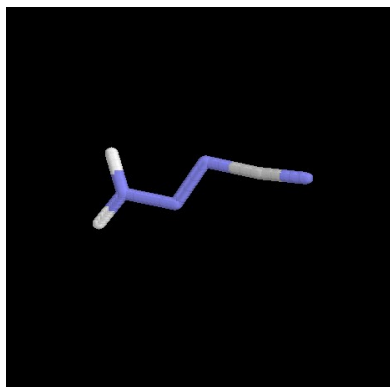
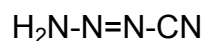
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Parc Valrose, 06108 Nice Cedex 2, France*

(e-mails: gal@unice.fr, pcmaria@unice.fr; Tel.: 33 492076361)

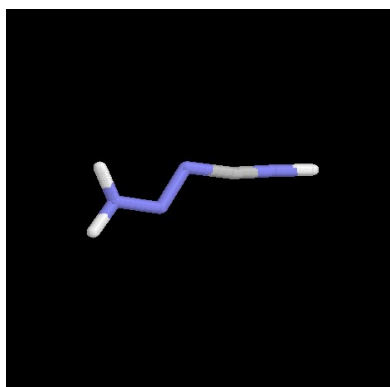
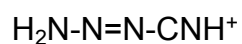
Table S1. Structures, electronic energies (in Hartree), and atom coordinates (in Å) for the neutral and protonated forms of push-pull nitriles

Structure	Electronic energy and atom coordinates																								
H₂N-CN 	scf done: -147.961184 <table><tr><td>C</td><td>-0.178991</td><td>0.418345</td><td>0.008707</td></tr><tr><td>N</td><td>-0.216312</td><td>1.597446</td><td>-0.056285</td></tr><tr><td>N</td><td>-0.170881</td><td>-0.936733</td><td>0.022614</td></tr><tr><td>H</td><td>0.759848</td><td>-1.335364</td><td>-0.044484</td></tr><tr><td>H</td><td>-0.694124</td><td>-1.335393</td><td>0.795249</td></tr></table>	C	-0.178991	0.418345	0.008707	N	-0.216312	1.597446	-0.056285	N	-0.170881	-0.936733	0.022614	H	0.759848	-1.335364	-0.044484	H	-0.694124	-1.335393	0.795249				
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H₂N-CN⁺ 	scf done: -148.284375 <table><tr><td>C</td><td>-0.109433</td><td>0.396511</td><td>0.135309</td></tr><tr><td>N</td><td>-0.175972</td><td>1.555485</td><td>0.019699</td></tr><tr><td>N</td><td>0.008969</td><td>-0.874464</td><td>0.336778</td></tr><tr><td>H</td><td>0.803544</td><td>-1.387190</td><td>-0.042639</td></tr><tr><td>H</td><td>-0.694046</td><td>-1.381810</td><td>0.872089</td></tr><tr><td>H</td><td>-0.379892</td><td>2.487718</td><td>-0.320445</td></tr></table>	C	-0.109433	0.396511	0.135309	N	-0.175972	1.555485	0.019699	N	0.008969	-0.874464	0.336778	H	0.803544	-1.387190	-0.042639	H	-0.694046	-1.381810	0.872089	H	-0.379892	2.487718	-0.320445
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H	-0.379892	2.487718	-0.320445																						
⁺H₃N-CN 	scf done: -148.234167 <table><tr><td>C</td><td>-0.184789</td><td>0.444410</td><td>0.003952</td></tr><tr><td>N</td><td>-0.229092</td><td>1.620068</td><td>-0.082638</td></tr><tr><td>N</td><td>-0.131550</td><td>-0.962782</td><td>0.107722</td></tr><tr><td>H</td><td>0.850226</td><td>-1.297898</td><td>0.110475</td></tr><tr><td>H</td><td>-0.582490</td><td>-1.287717</td><td>0.983657</td></tr><tr><td>H</td><td>-0.620394</td><td>-1.412511</td><td>-0.689128</td></tr></table>	C	-0.184789	0.444410	0.003952	N	-0.229092	1.620068	-0.082638	N	-0.131550	-0.962782	0.107722	H	0.850226	-1.297898	0.110475	H	-0.582490	-1.287717	0.983657	H	-0.620394	-1.412511	-0.689128
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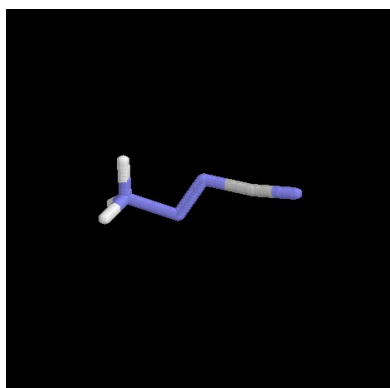
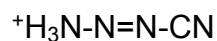
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N	-0.518803	1.678500	0.150171
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N	0.907448	-1.262915	-0.271758
N	0.957799	-2.582110	-0.324694
H	1.818932	-2.963197	-0.688681
H	0.086377	-3.108274	-0.374975



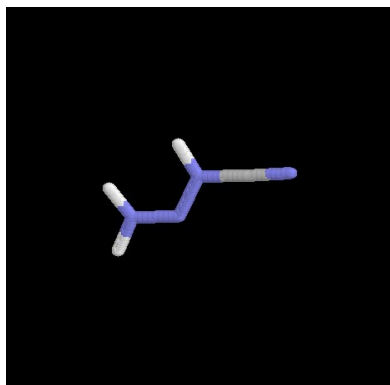
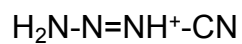
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N	-0.122818	-0.763325	0.072002
N	1.055677	-1.200570	-0.308571
N	1.120650	-2.475755	-0.282150
H	2.008094	-2.887517	-0.565609
H	0.321489	-3.051541	0.008974
H	-0.712922	2.660664	0.141292



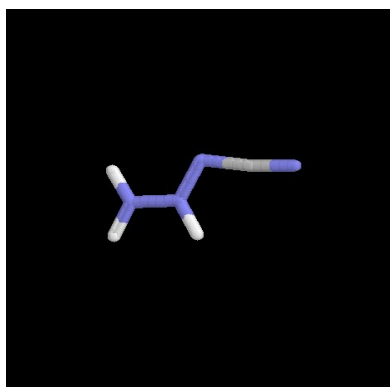
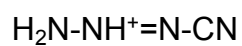
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N	-0.224235	-0.807694	-0.218515
N	0.965046	-1.193182	-0.096327
N	0.937073	-2.680753	-0.307090
H	1.563608	-2.894098	-1.100851
H	-0.027619	-3.012248	-0.495716
H	1.320361	-3.122696	0.544904



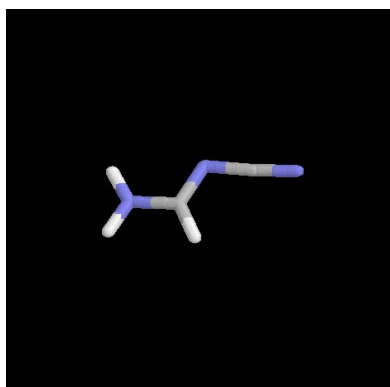
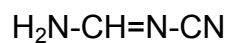
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N	-0.256797	-0.765011	-0.042446
N	0.885354	-1.296939	-0.329876
N	0.942284	-2.566133	-0.426103
H	1.866051	-2.938143	-0.654738
H	0.150907	-3.208174	-0.293553
H	-1.115720	-1.312531	0.111257



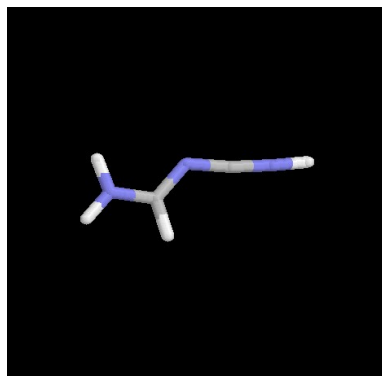
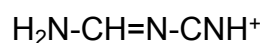
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N	-0.380613	-0.827197	-0.023867
N	0.764558	-1.328450	-0.326241
N	0.925166	-2.613089	-0.441004
H	1.845096	-2.977345	-0.681947
H	0.108159	-3.208368	-0.282765
H	1.605084	-0.741887	-0.490977



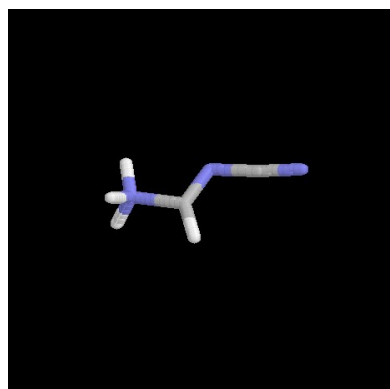
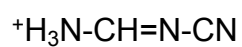
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N	-0.322533	-0.761355	-0.069923
C	0.841045	-1.292067	-0.288254
N	0.975452	-2.621044	-0.431417
H	1.767674	-0.717760	-0.369414
H	1.872995	-3.046394	-0.601142
H	0.154391	-3.208632	-0.366724



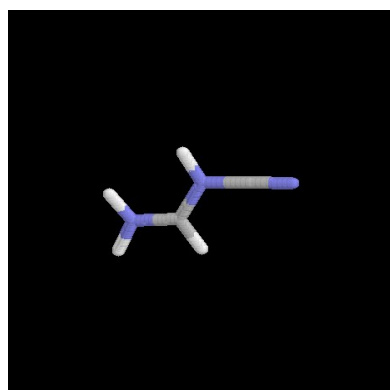
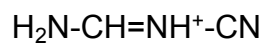
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C	-0.234128	0.640702	-0.061218
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N	-0.198074	-0.633958	-0.154997
C	0.914161	-1.354049	-0.137487
N	0.845213	-2.656685	-0.240128
H	1.907865	-0.916260	-0.040343
H	1.681672	-3.232076	-0.229497
H	-0.058583	-3.117518	-0.333205
H	-0.601384	2.783421	0.076458



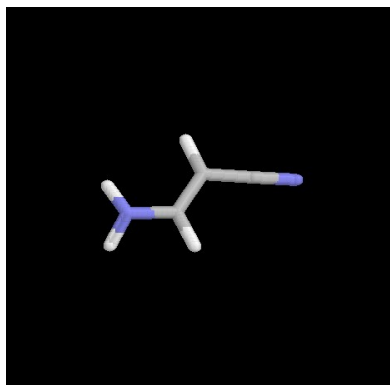
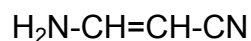
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C	-0.353985	0.498777	0.037773
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N	-0.197094	-0.821163	-0.227578
C	0.961509	-1.332009	-0.188123
N	0.986979	-2.783154	-0.498873
H	1.930198	-0.883642	0.034331
H	1.565715	-2.993495	-1.328471
H	0.016775	-3.088514	-0.690560
H	1.356599	-3.343064	0.286808



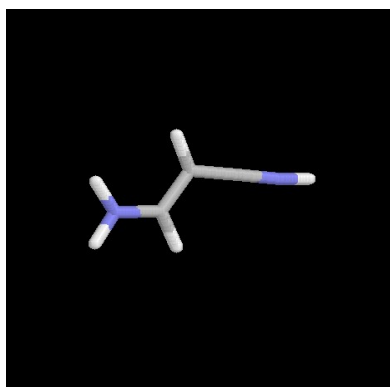
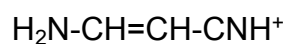
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C	-0.355605	0.671503	-0.041173
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N	-0.345282	-0.691472	-0.154135
C	0.795205	-1.378379	-0.143131
N	0.867896	-2.677770	-0.247080
H	1.715908	-0.809847	-0.040699
H	1.776993	-3.135028	-0.230816
H	0.054065	-3.282865	-0.346195
H	-1.250610	-1.157541	-0.247141



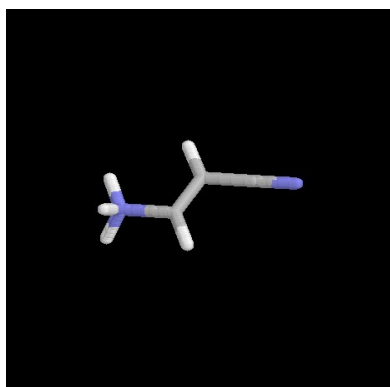
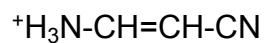
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C	-0.376362	0.702399	0.076980
N	-0.443892	1.881123	0.149127
C	-0.309082	-0.714394	-0.016284
C	0.869037	-1.336172	-0.245726
N	1.063350	-2.695711	-0.268362
H	1.774924	-0.747297	-0.366222
H	1.857054	-3.033625	-0.795278
H	0.238497	-3.275352	-0.366278
H	-1.230745	-1.274673	0.113953



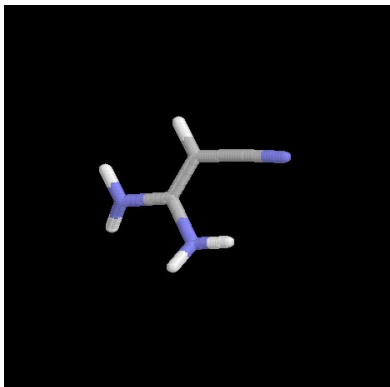
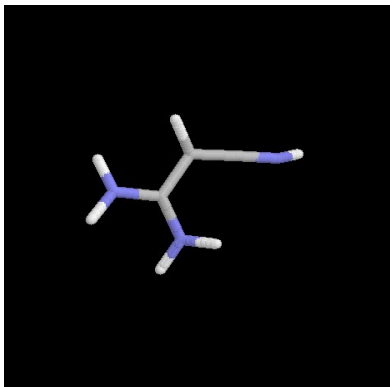
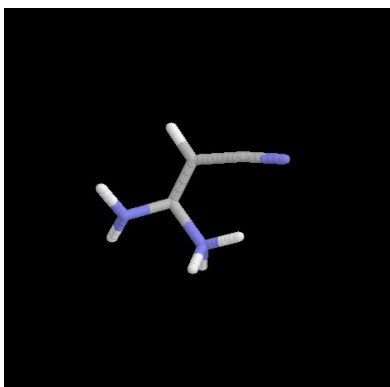
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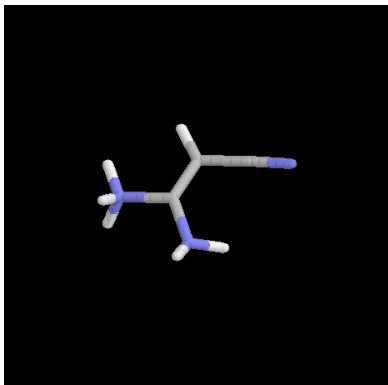
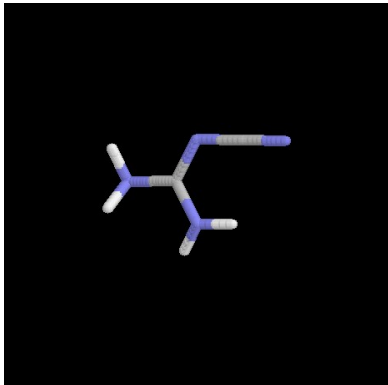
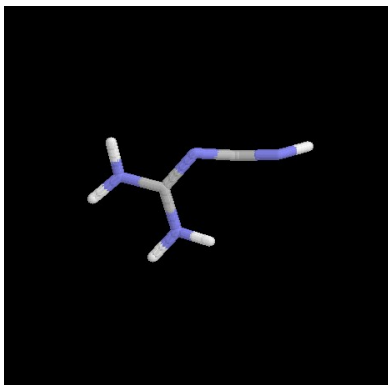
C	-0.356148	0.661154	0.132255
N	-0.440108	1.829551	0.263260
C	-0.241146	-0.706065	0.118269
C	0.960139	-1.277055	-0.267661
N	1.190746	-2.575535	-0.323964
H	1.797641	-0.642829	-0.549651
H	2.094980	-2.934498	-0.609202
H	-1.110148	-1.287641	0.410208
H	0.481478	-3.260357	-0.080330
H	-0.659794	2.758165	-0.075463

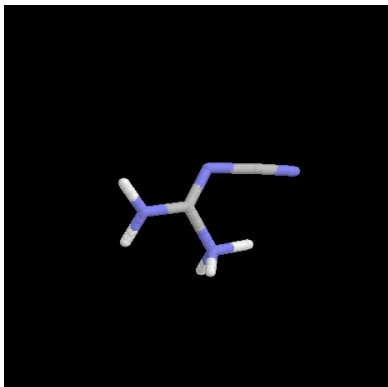
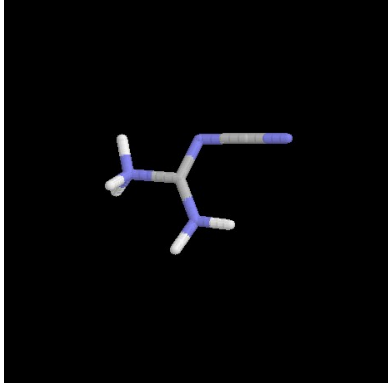
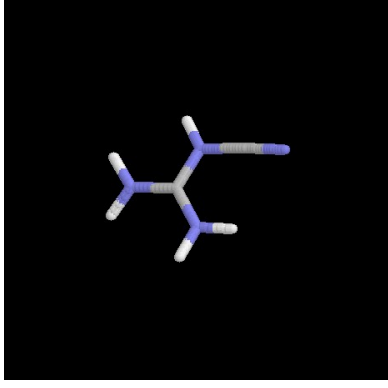


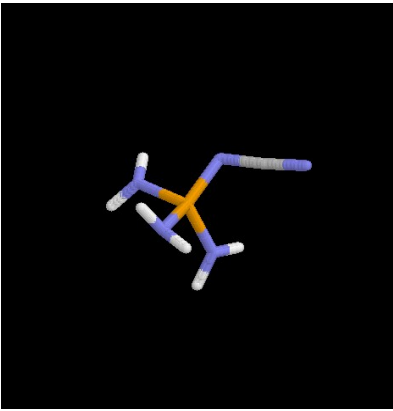
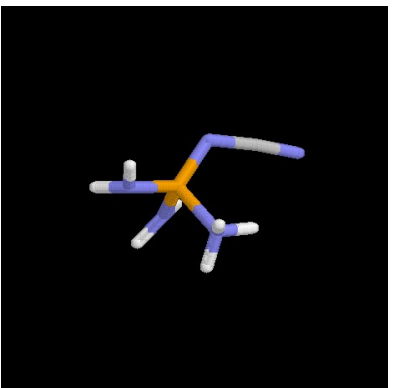
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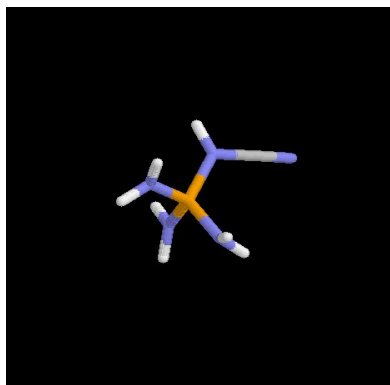
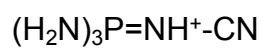
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N	-0.513306	1.889250	0.146072
C	-0.305513	-0.700457	-0.089948
C	0.896657	-1.282337	-0.140260
N	1.007281	-2.748082	-0.273876
H	1.850071	-0.768797	-0.091129
H	1.519031	-3.013534	-1.130120
H	0.081843	-3.200178	-0.317391
H	-1.232983	-1.269573	-0.144101
H	1.515074	-3.164485	0.522529

$(\text{H}_2\text{N})_2\text{C}=\text{CH}-\text{CN}$ 	scf done: -279.947493 C -0.912241 0.315783 0.072228 N -0.828776 1.495969 0.122191 C -0.947885 -1.097754 -0.003307 C 0.206168 -1.797953 -0.179966 N 0.284235 -3.178595 -0.070447 N 1.425263 -1.218811 -0.487613 H -1.902495 -1.604454 0.071427 H 1.417839 -0.203443 -0.464225 H 2.203364 -1.608456 0.034926 H 0.843249 -3.609981 -0.800018 H -0.612592 -3.638075 0.039784
$(\text{H}_2\text{N})_2\text{C}=\text{CH}-\text{CNH}^+$ 	scf done: -280.308269 C -0.999851 0.281195 0.023839 N -0.993099 1.483624 0.051421 C -0.946813 -1.055395 0.167107 C 0.240970 -1.780977 -0.151546 N 0.163378 -3.094545 -0.350703 N 1.425071 -1.173388 -0.247804 H -1.835104 -1.576854 0.505501 H 1.551412 -0.226031 0.086562 H 2.252891 -1.656508 -0.576792 H 0.985495 -3.679447 -0.447170 H -0.736680 -3.555107 -0.403460 H -1.255799 2.179962 -0.644144
$^+\text{H}_3\text{N}_{\text{syn}}(\text{H}_2\text{N})\text{C}=\text{CH}-\text{CN}$ 	scf done: -280.262901 C -0.873529 0.322291 0.081753 N -0.649128 1.484261 0.130280 C -0.966853 -1.092562 -0.024800 C 0.144815 -1.821220 -0.258273 N 0.345405 -3.173377 -0.181116 N 1.430665 -1.092601 -0.447170 H -1.927469 -1.584836 0.091097 H 1.297615 -0.072491 -0.322446 H 2.124258 -1.423710 0.242186 H 0.796874 -3.636148 -0.968033 H -0.456295 -3.703592 0.150985 H 1.828722 -1.238425 -1.387544

${}^+\text{H}_3\text{N}_{\text{anti}}(\text{H}_2\text{N})\text{C}=\text{CH}-\text{CN}$ 	scf done: -280.258501 <table><tr><td>C</td><td>-0.949474</td><td>0.347149</td><td>0.017080</td></tr><tr><td>N</td><td>-0.885714</td><td>1.528857</td><td>0.004762</td></tr><tr><td>C</td><td>-0.956701</td><td>-1.074533</td><td>0.018808</td></tr><tr><td>C</td><td>0.217545</td><td>-1.728669</td><td>-0.072993</td></tr><tr><td>N</td><td>0.193036</td><td>-3.215965</td><td>-0.050592</td></tr><tr><td>N</td><td>1.470343</td><td>-1.260536</td><td>-0.375002</td></tr><tr><td>H</td><td>-1.911259</td><td>-1.591667</td><td>0.060036</td></tr><tr><td>H</td><td>1.488815</td><td>-0.269487</td><td>-0.613061</td></tr><tr><td>H</td><td>2.230143</td><td>-1.494886</td><td>0.262403</td></tr><tr><td>H</td><td>0.600919</td><td>-3.583352</td><td>-0.925733</td></tr><tr><td>H</td><td>-0.764180</td><td>-3.583867</td><td>0.048412</td></tr><tr><td>H</td><td>0.747877</td><td>-3.599564</td><td>0.730271</td></tr></table>	C	-0.949474	0.347149	0.017080	N	-0.885714	1.528857	0.004762	C	-0.956701	-1.074533	0.018808	C	0.217545	-1.728669	-0.072993	N	0.193036	-3.215965	-0.050592	N	1.470343	-1.260536	-0.375002	H	-1.911259	-1.591667	0.060036	H	1.488815	-0.269487	-0.613061	H	2.230143	-1.494886	0.262403	H	0.600919	-3.583352	-0.925733	H	-0.764180	-3.583867	0.048412	H	0.747877	-3.599564	0.730271
C	-0.949474	0.347149	0.017080																																														
N	-0.885714	1.528857	0.004762																																														
C	-0.956701	-1.074533	0.018808																																														
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H	0.747877	-3.599564	0.730271																																														
$(\text{H}_2\text{N})_2\text{C}=\text{N}-\text{CN}$ 	scf done: -295.966926 <table><tr><td>C</td><td>-0.400858</td><td>0.536226</td><td>-0.044680</td></tr><tr><td>N</td><td>-0.386691</td><td>1.720872</td><td>0.036209</td></tr><tr><td>N</td><td>-0.446741</td><td>-0.799378</td><td>-0.130224</td></tr><tr><td>C</td><td>0.710500</td><td>-1.405692</td><td>-0.180749</td></tr><tr><td>N</td><td>0.732260</td><td>-2.755485</td><td>-0.418099</td></tr><tr><td>N</td><td>1.934115</td><td>-0.818318</td><td>-0.011694</td></tr><tr><td>H</td><td>1.448883</td><td>-3.284274</td><td>0.064194</td></tr><tr><td>H</td><td>-0.189172</td><td>-3.175515</td><td>-0.376533</td></tr><tr><td>H</td><td>1.936460</td><td>0.196518</td><td>0.001678</td></tr><tr><td>H</td><td>2.715514</td><td>-1.237014</td><td>-0.500213</td></tr></table>	C	-0.400858	0.536226	-0.044680	N	-0.386691	1.720872	0.036209	N	-0.446741	-0.799378	-0.130224	C	0.710500	-1.405692	-0.180749	N	0.732260	-2.755485	-0.418099	N	1.934115	-0.818318	-0.011694	H	1.448883	-3.284274	0.064194	H	-0.189172	-3.175515	-0.376533	H	1.936460	0.196518	0.001678	H	2.715514	-1.237014	-0.500213								
C	-0.400858	0.536226	-0.044680																																														
N	-0.386691	1.720872	0.036209																																														
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H	1.448883	-3.284274	0.064194																																														
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H	2.715514	-1.237014	-0.500213																																														
$(\text{H}_2\text{N})_2\text{C}=\text{N}-\text{CNH}^+$ 	scf done: -296.329111 <table><tr><td>C</td><td>-0.375799</td><td>0.598973</td><td>0.035416</td></tr><tr><td>N</td><td>-0.540878</td><td>1.769946</td><td>0.175746</td></tr><tr><td>N</td><td>-0.288679</td><td>-0.658198</td><td>0.056919</td></tr><tr><td>C</td><td>0.834095</td><td>-1.388139</td><td>-0.137227</td></tr><tr><td>N</td><td>0.648973</td><td>-2.692528</td><td>-0.279628</td></tr><tr><td>N</td><td>2.056843</td><td>-0.858695</td><td>-0.174344</td></tr><tr><td>H</td><td>1.410910</td><td>-3.351840</td><td>-0.383319</td></tr><tr><td>H</td><td>-0.299269</td><td>-3.051640</td><td>-0.261714</td></tr><tr><td>H</td><td>2.204702</td><td>0.125271</td><td>0.013622</td></tr><tr><td>H</td><td>2.885137</td><td>-1.428767</td><td>-0.303658</td></tr><tr><td>H</td><td>-0.877574</td><td>2.623437</td><td>-0.247325</td></tr></table>	C	-0.375799	0.598973	0.035416	N	-0.540878	1.769946	0.175746	N	-0.288679	-0.658198	0.056919	C	0.834095	-1.388139	-0.137227	N	0.648973	-2.692528	-0.279628	N	2.056843	-0.858695	-0.174344	H	1.410910	-3.351840	-0.383319	H	-0.299269	-3.051640	-0.261714	H	2.204702	0.125271	0.013622	H	2.885137	-1.428767	-0.303658	H	-0.877574	2.623437	-0.247325				
C	-0.375799	0.598973	0.035416																																														
N	-0.540878	1.769946	0.175746																																														
N	-0.288679	-0.658198	0.056919																																														
C	0.834095	-1.388139	-0.137227																																														
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H	2.885137	-1.428767	-0.303658																																														
H	-0.877574	2.623437	-0.247325																																														

$^+H_3N_{\text{syn}}(H_2N)C=N-CN$ 	scf done: -296.258216 C 1.568795 -3.498719 -0.075377 N 2.576384 -4.125816 -0.091803 N 0.470692 -2.724955 -0.052548 C 0.626709 -1.455763 -0.095881 N -0.351323 -0.549344 -0.177169 N 2.012242 -0.840166 -0.135255 H -0.225560 0.439332 0.003821 H -1.304987 -0.903670 -0.154762 H 2.713947 -1.607024 -0.153540 H 2.148371 -0.262886 -0.980151 H 2.207732 -0.258409 0.694617
$^+H_3N_{\text{anti}}(H_2N)C=N-CN$ 	scf done: -296.262960 C -0.512943 0.515754 -0.322911 N -0.600664 1.697631 -0.315104 N -0.423231 -0.833221 -0.333603 C 0.743745 -1.329175 -0.143561 N 0.723622 -2.819086 -0.175771 N 1.945070 -0.783487 0.072473 H 1.304883 -3.209834 -0.933902 H 1.022588 -3.241723 0.717149 H 2.803155 -1.304499 0.209160 H 2.011346 0.232517 0.103423 H -0.260670 -3.087556 -0.349253
$(H_2N)_2C=NH^+-CN$ 	scf done: -296.315214 C -0.425011 0.601779 0.037679 N -0.348979 1.771319 0.182452 N -0.423641 -0.744649 -0.132960 C 0.744189 -1.443930 -0.184173 N 0.686633 -2.769508 -0.227819 N 1.890995 -0.784738 -0.192325 H 1.518551 -3.328970 -0.379391 H -0.172812 -3.273126 -0.040203 H 1.915167 0.229614 -0.261538 H 2.778834 -1.263672 -0.087868 H -1.306447 -1.206851 -0.339953

$(\text{H}_2\text{N})_3\text{P}=\text{N}-\text{CN}$ 	scf done: -654.535874 C -0.874019 0.599687 -0.329987 N -1.124444 1.736410 -0.573737 N -0.670965 -0.689734 -0.064229 P 0.793027 -1.288168 -0.038079 N 0.537844 -2.926162 0.057034 H 1.339398 -3.542336 -0.001661 H -0.290278 -3.265810 -0.418039 N 1.708026 -0.649632 -1.268476 N 1.911434 -1.130254 1.197656 H 1.230974 -0.344869 -2.108441 H 2.678730 -0.910554 -1.388746 H 2.278024 -0.189671 1.315523 H 1.610677 -1.531246 2.081533
$(\text{H}_2\text{N})_3\text{P}=\text{N}-\text{CNH}^+$ 	scf done: -654.923186 C -0.666346 0.812116 -0.034332 N -0.939173 1.970652 0.086653 N -0.447410 -0.419595 0.006226 P 0.936210 -1.283591 -0.095925 N 0.341452 -2.781870 -0.358577 H 0.965256 -3.579059 -0.431321 H -0.602470 -2.994850 -0.052351 N 2.034601 -1.101429 -1.288909 N 1.802078 -0.852077 1.231914 H 1.831435 -1.471195 -2.212265 H 2.690522 -0.327195 -1.264321 H 1.302450 -0.630496 2.088069 H 2.718852 -1.263462 1.384971 H -1.315756 2.750892 -0.431092
$^+\text{H}_3\text{N}(\text{H}_2\text{N})_2\text{P}=\text{N}-\text{CN}$ 	scf done: -654.854247 C -0.925307 0.281325 0.050987 N -1.923013 0.237274 0.693327 N 0.198801 0.212975 -0.682474 P 1.165261 -0.970881 -0.408386 N 0.000496 -2.447248 -0.120649 H 0.449425 -3.246464 0.343561 H -0.786509 -2.126572 0.470443 N 2.077846 -1.526469 -1.636142 N 2.083019 -1.013212 0.933723 H 3.080633 -1.359535 -1.594792 H 1.704965 -1.454534 -2.581319 H 2.850812 -1.658968 1.094775 H 1.999766 -0.252675 1.603918 H -0.410705 -2.784847 -1.001393



scf done: -654.900797

C	-0.826509	0.634189	-0.000340
N	-0.950345	1.761239	0.329873
N	-0.624317	-0.666954	-0.340243
P	0.896770	-1.343532	-0.179819
N	0.527558	-2.930766	-0.176606
H	1.234527	-3.609062	-0.446889
H	-0.210322	-3.299931	0.417157
N	1.861895	-0.878616	-1.397970
N	1.679794	-0.832253	1.152367
H	1.513442	-0.768523	-2.345177
H	2.872055	-0.879708	-1.293944
H	2.005283	0.130314	1.214901
H	1.481400	-1.263169	2.051232
H	-1.341050	-1.129008	-0.899654