**Supporting Information**

**Atomic Charges, Surface Electrostatic Potential Analysis, and Bond Order Analysis on Nitriles and Isocyanides**

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**Table S1** The Schönflies symbols of point groups, the lowest frequencies (in cm-1) and their vibrational mode assignments, and the absolute values (in a.u.) of electronic and zero-point energies *E*, thermal enthalpies *H* and thermal free energies *G* optimized at B3LYP-D3(BJ)/def2-QZVP level for the selected nitriles R-C≡N and isocyanides R-N≡C in vacuum

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Species | Point group | Freq | Mode assignment | *E* | *H* | *G* |
| R-C≡N | R=-AlH2 | Cs | 205 | Molecular twist | -336.534473 | -336.528982 | -336.560336 |
| R=-BeH | C∞v | 238 | Molecular twist | -108.229232 | -108.224467 | -108.251277 |
| R=-BH2 | Cs | 285 | Molecular twist | -118.906790 | -118.902014 | -118.930718 |
| R=-C≡CH | C∞v | 239 | Molecular twist | -169.630962 | -169.625988 | -169.654261 |
| R=-CF3 | C3v | 193 | Molecular twist | -430.650421 | -430.644364 | -430.678256 |
| R=-CH3 | C3v | 380 | Molecular twist | -132.779077 | -132.774518 | -132.802052 |
| R=-Cl | C∞v | 404 | Molecular bend | -553.095865 | -553.091855 | -553.118545 |
| R=-C≡N | D∞h | 250 | Molecular twist | -185.726847 | -185.722131 | -185.749373 |
| R=-COOH | C1 | 205 | Molecular twist | -282.101003 | -282.095502 | -282.128497 |
| R=-F | C∞v | 483 | Molecular bend | -192.722444 | -192.718641 | -192.744036 |
| R=-H | C∞v | 760 | Molecular bend | -93.455488 | -93.452001 | -93.474845 |
| R=-Li | C∞v | 174 | Molecular twist | -100.421891 | -100.417240 | -100.443888 |
| R=-MgH | C∞v | 170 | Molecular twist | -293.583636 | -293.578084 | -293.607620 |
| R=-Na | C∞v | 127 | Molecular twist | -255.203680 | -255.198665 | -255.227629 |
| R=-NH2 | C1 | 411 | Molecular twist | -148.830511 | -148.825974 | -148.854116 |
| R=-NO2 | C1 | 215 | Molecular twist | -298.016585 | -298.011342 | -298.043855 |
| R=-OH | Cs | 457 | Molecular twist | -168.704885 | -168.700598 | -168.728001 |
| R=-PH2 | C1 | 295 | Molecular twist | -435.450242 | -435.445357 | -435.475605 |
| R=-SH | Cs | 337 | Molecular twist | -491.695131 | -491.690521 | -491.719866 |
| R=-SiH3 | C1 | 256 | Molecular twist | -384.196796 | -384.191528 | -384.222611 |
| R=-CH=CH2 | C1 | 237 | Molecular bend | -170.869873 | -170.864779 | -170.895745 |
| :C=N-R | R=-AlH2 | Cs | 143 | Molecular twist | -336.538675 | -336.533043 | -336.564774 |
| R=-BeH | C∞v | 176 | Molecular twist | -108.238199 | -108.233262 | -108.260440 |
| R=-BH2 | Cs | 218 | Molecular twist | -118.904638 | -118.899730 | -118.928662 |
| R=-C≡CH | C∞v | 226 | Molecular twist | -169.591336 | -169.586195 | -169.614684 |
| R=-CF3 | C1 | 143 | Molecular twist | -430.628720 | -430.622479 | -430.657895 |
| R=-CH3 | C1 | 273 | Molecular twist | -132.741851 | -132.737062 | -132.766038 |
| R=-Cl | C∞v | 245 | Molecular twist | -553.030129 | -553.025730 | -553.053151 |
| R=-C≡N | C∞v | 212 | Molecular twist | -185.690989 | -185.686117 | -185.714283 |
| R=-COOH | C1 | 160 | Molecular twist | -282.078071 | -282.072374 | -282.105835 |
| R=-F | C∞v | 210 | Molecular twist | -192.613502 | -192.609065 | -192.635731 |
| R=-H | C∞v | 470 | Molecular twist | -93.434058 | -93.430258 | -93.453556 |
| R=-Li | C∞v | 115 | Molecular twist | -100.427356 | -100.422534 | -100.449747 |
| R-MgH | C∞v | 110 | Molecular twist | -293.587289 | -293.581554 | -293.611710 |
| R=-Na | C∞v | 47 | Molecular twist | -255.204880 | -255.199596 | -255.230189 |
| R=-NH2 | C1 | 265 | Molecular twist | -148.760310 | -148.755602 | -148.784108 |
| R=-NO2 | C1 | 57 | Molecular twist | -297.971966 | -297.966138 | -298.000641 |
| R=-OH | Cs | 261 | Molecular twist | -168.612795 | -168.608103 | -168.636271 |
| R=-PH2 | C1 | 209 | Molecular twist | -435.428215 | -435.423142 | -435.453755 |
| R=-SH | Cs | 225 | Molecular bend | -491.650538 | -491.645658 | -491.675500 |
| R=-SiH3 | C1 | 187 | Molecular twist | -384.191939 | -384.186527 | -384.217939 |
| R=-CH=CH2 | Cs | 206 | Molecular bend | -170.837196 | -170.831932 | -170.863170 |

**Table S2** Cartesian coordinates of all species obtained at B3LYP-D3BJ/def2-QZVP level. Charge and spin multiplicity are set to 0 and 1

|  |  |
| --- | --- |
| Species | Cartesian coordinates |
| R-C≡N | H2Al-C≡N |  C 0.00000000 0.80052700 0.00000000 N -0.00057800 1.95415000 0.00000000 Al 0.00027400 -1.13752800 0.00000000 H -1.39401800 -1.84712900 0.00000000 H 1.39450400 -1.84722500 0.00000000 |
| HBe-C≡N |  C 0.00000000 0.00000000 -0.08424200 N 0.00000000 0.00000000 -1.23775400 Be 0.00000000 0.00000000 1.57108400 H 0.00000000 0.00000000 2.88539700 |
| H2B-C≡N |  C 0.00000000 0.18576800 0.00000000 N -0.00002500 1.33925400 0.00000000 B 0.00002400 -1.33497000 0.00000000 H -1.03459600 -1.90727700 0.00000000 H 1.03465200 -1.90726100 0.00000000 |
| HC≡C-C≡N |  C 0.00000000 0.00000000 0.73701200 N 0.00000000 0.00000000 1.89111900 C 0.00000000 0.00000000 -0.63074100 C 0.00000000 0.00000000 -1.83049400 H 0.00000000 0.00000000 -2.89249300 |
| F3C-C≡N |  C 0.00000000 0.00000000 1.15982900 N 0.00000000 0.00000000 2.30530700 C 0.00000000 0.00000000 -0.32115300 F 0.00000000 1.25235900 -0.78404500 F -1.08457400 -0.62617900 -0.78404500 F 1.08457400 -0.62617900 -0.78404500 |
| H3C-C≡N |  C 0.00000000 0.00000000 0.28061000 N 0.00000000 0.00000000 1.42890700 C 0.00000000 0.00000000 -1.17342400 H 0.00000000 1.02197200 -1.54848900 H -0.88505400 -0.51098600 -1.54848900 H 0.88505400 -0.51098600 -1.54848900 |
| Cl-C≡N |  C 0.00000000 0.00000000 -0.65502800 N 0.00000000 0.00000000 -1.80698000 Cl 0.00000000 0.00000000 0.97523700 |
| N≡C-C≡N |  C 0.00000000 0.00000000 0.68734400 N 0.00000000 0.00000000 1.83835300 C 0.00000000 0.00000000 -0.68734400 N 0.00000000 0.00000000 -1.83835300 |
| HOOC-C≡N |  C 1.00527400 0.01828900 -0.00002200 N 2.15204100 0.06370600 0.00001300 C -0.45258200 -0.12001400 -0.00000400 O -1.00683500 -1.17863700 0.00000400 O -1.04072900 1.08122600 0.00000200 H -1.99992600 0.94370000 0.00001400 |
| F-C≡N |  C 0.00000000 0.00000000 -0.15152200 N 0.00000000 0.00000000 -1.30094000 F 0.00000000 0.00000000 1.11285700 |
| H-C≡N |  C 0.00000000 0.00000000 -0.49640700 N 0.00000000 0.00000000 0.64862100 H 0.00000000 0.00000000 -1.56190000 |
| Li-C≡N |  C 0.00000000 0.00000000 -0.14943000 N 0.00000000 0.00000000 1.00942200 Li 0.00000000 0.00000000 -2.05645900 |
| HMg- C≡N |  C 0.00000000 0.00000000 -0.77806900 N 0.00000000 0.00000000 -1.93355100 Mg 0.00000000 0.00000000 1.27125700 H 0.00000000 0.00000000 2.94818200 |
| Na-C≡N |  C 0.00000000 0.00000000 -0.68758700 N 0.00000000 0.00000000 -1.84733500 Na 0.00000000 0.00000000 1.55062400 |
| H2N-C≡N |  C 0.22114000 0.00018500 0.00031300 N 1.37463600 -0.00008400 -0.01240700 N -1.11572400 -0.00004500 0.07942600 H -1.56968000 0.84310200 -0.23552200 H -1.56954800 -0.84331000 -0.23548400 |
| O2N-C≡N |  C 0.91998900 -0.00026900 0.00000300 N 2.06765200 -0.00002400 -0.00010600 N -0.50274100 0.00000700 0.00029400 O -1.02985200 -1.09227700 -0.00008300 O -1.02943600 1.09249300 -0.00008500 |
| HO-C≡N |  C 0.00000000 0.18092600 0.00000000 N 0.05018400 1.33201700 0.00000000 O -0.13464900 -1.10783000 0.00000000 H 0.72590300 -1.54703400 0.00000000 |
| H2P-C≡N |  C -0.75375000 0.00005300 -0.02775900 N -1.90520200 -0.00003900 -0.00194900 P 1.02639800 -0.00002700 0.12140000 H 1.23162200 -1.03624600 -0.82057300 H 1.23131900 1.03661200 -0.82022700 |
| HS-C≡N |  C 0.00000000 0.69487800 0.00000000 N 0.03273900 1.84776700 0.00000000 S 0.06499500 -0.99596900 0.00000000 H -1.26910000 -1.16812900 0.00000000 |
| H3Si-C≡N |  C -0.82446700 0.00004100 0.00000400 N -1.97541900 -0.00000900 0.00000100 Si 1.02601600 -0.00000800 -0.00000500 H 1.47024400 0.88106600 -1.09331200 H 1.47024300 0.50629700 1.30970300 H 1.47002700 -1.38744000 -0.21635700 |
| H2C=CH-C≡N |  C -0.78044100 0.08860200 0.00000500 N -1.88892200 -0.22268700 -0.00000300 C 0.58326200 0.50260300 0.00000000 C 1.59951000 -0.35583900 -0.00000100 H 0.75005300 1.57167400 -0.00000300 H 2.61919800 -0.00112900 -0.00000500 H 1.43921400 -1.42393500 0.00000300 |
| :C=N-R | :C=N-AlH2 |  C -0.00026500 1.94041300 0.00000000 N 0.00000000 0.76790700 0.00000000 Al 0.00010400 -1.04126100 0.00000000 H -1.39810600 -1.74075700 0.00000000 H 1.39835000 -1.74068200 0.00000000 |
| :C=N-BeH |  C 0.00000000 0.00000000 1.27795300 N 0.00000000 0.00000000 0.10428500 Be 0.00000000 0.00000000 -1.41647600 H 0.00000000 0.00000000 -2.73181000 |
| :C=N-BeH2 |  C 0.00542400 1.37577600 0.00000000 N 0.00000000 0.20193500 0.00000000 B -0.00417100 -1.22009300 0.00000000 H -1.04689600 -1.78077500 0.00000000 H 1.03520700 -1.78696300 0.00000000 |
| :C=N-C≡CH |  C 0.00000000 0.00000000 1.91996500 N 0.00000000 0.00000000 0.74454500 C 0.00000000 0.00000000 -0.56040600 C 0.00000000 0.00000000 -1.75835200 H 0.00000000 0.00000000 -2.81905600 |
| :C=N-CF3 |  C -2.29310400 -0.00003700 -0.00006300 N -1.12438700 0.00003800 -0.00010300 C 0.27827500 0.00004000 -0.00007300 F 0.73934900 -0.97714800 -0.77957700 F 0.73930200 1.16389300 -0.45616100 F 0.73909100 -0.18677700 1.23590800 |
| :C=N-CH3 |  C 1.47648500 -0.00003800 0.00000500 N 0.31303200 0.00006000 -0.00000700 C -1.10488800 -0.00001500 0.00000200 H -1.47363200 1.02036400 0.08125500 H -1.47358900 -0.58060200 0.84305100 H -1.47358800 -0.43986600 -0.92429800 |
| :C=N-Cl |  C 0.00000000 0.00000000 -1.85668300 N 0.00000000 0.00000000 -0.68458000 Cl 0.00000000 0.00000000 0.93718600 |
| :C=N-C≡N |  C 0.00000000 0.00000000 -1.86732700 N 0.00000000 0.00000000 -0.69056300 C 0.00000000 0.00000000 0.61303100 N 0.00000000 0.00000000 1.76567400 |
| :C=N-COOH |  C 2.15318000 -0.06634400 -0.00004000 N 0.98363900 -0.03287600 0.00005400 C -0.40061200 0.12223100 -0.00000400 O -0.94608700 1.18180000 -0.00000600 O -0.98615500 -1.07805900 -0.00000400 H -1.94294800 -0.93511800 -0.00002600 |
| :C=N-F |  C 0.00000000 0.00000000 1.38489200 N 0.00000000 0.00000000 0.21467600 F 0.00000000 0.00000000 -1.09023100 |
| :C=N-H |  C 0.00000000 0.00000000 -0.73583700 N 0.00000000 0.00000000 0.42734200 H 0.00000000 0.00000000 1.42362900 |
| :C=N-Li |  C 0.00000000 0.00000000 -1.06113400 N 0.00000000 0.00000000 0.10929700 Li 0.00000000 0.00000000 1.86724200 |
|  |   |
| :C=N-MgH |  C 0.00000000 0.00000000 1.92409000 N 0.00000000 0.00000000 0.75255900 Mg 0.00000000 0.00000000 -1.16441100 H 0.00000000 0.00000000 -2.83952300 |
| :C=N-Na |  C 0.00000000 0.00000000 -1.84383800 N 0.00000000 0.00000000 -0.67411100 Na 0.00000000 0.00000000 1.43470900 |
| :C=N-NH2 |  C 1.43377300 0.00002800 0.00811700 N 0.26723900 -0.00005200 0.01345400 N -1.07965200 0.00001100 -0.11455900 H -1.45780600 0.82833200 0.32949900 H -1.45793700 -0.82821400 0.32953100 |
| :C=N-NO2 |  C -2.11061700 0.00000000 0.00055100 N -0.93669600 -0.00000600 -0.00075400 N 0.48738100 0.00000100 0.00004000 O 0.98806200 -1.08828100 0.00010500 O 0.98805200 1.08828600 0.00010500 |
| :C=N-OH |  C -0.20227100 1.39078500 0.00000000 N 0.00000000 0.24033100 0.00000000 O 0.03067800 -1.08718900 0.00000000 H 0.96819900 -1.32950800 0.00000000 |
| :C=N-PH2 |  C 1.91763900 -0.00000700 -0.01193700 N 0.74840700 0.00001400 0.05243100 P -0.95453700 -0.00000100 -0.12771300 H -1.21328800 -1.02979100 0.81013400 H -1.21334100 1.02974700 0.81016200 |
| :C=N-SH |  C -0.11906100 1.87688600 0.00000000 N 0.00000000 0.71053000 0.00000000 S -0.03647700 -0.94502800 0.00000000 H 1.29800300 -1.11457600 0.00000000 |
| :C=N-SiH3 |  C 1.96799100 0.00001200 0.00001700 N 0.79759300 -0.00000700 -0.00004200 Si -0.94419100 -0.00000300 0.00001200 H -1.39076900 0.99025100 0.99353900 H -1.39072600 -1.35557300 0.36078700 H -1.39092700 0.36534000 -1.35430400 |
| :C=N-CH=CH2 |  C -1.13253400 -1.56610500 0.00000000 N -0.58603800 -0.53356100 0.00000000 C 0.00000000 0.71261700 0.00000000 C 1.31370100 0.89433500 0.00000000 H 1.71767000 1.89427200 0.00000000 H 2.00030300 0.06151600 0.00000000 H -0.70271100 1.53406000 0.00000000 |
|  |   |

**Fig. S1** The relative free energies (ΔG), optimized geometries and surface electrostatic potential maps of the triangular isomers of Na-C≡N/:C=N-Na and Li-C≡N/:C=N-Li at B3LYP-D3(BJ)/def2-QZVP level. Bond lengths are in Å. Relative energies and local electrostatic extrema are in kcal/mol