Supporting Information

Atomistic Scale Investigation of the Carbonization Process for C/H/O/N-based Polymers with the ReaxFF Reactive Force Field

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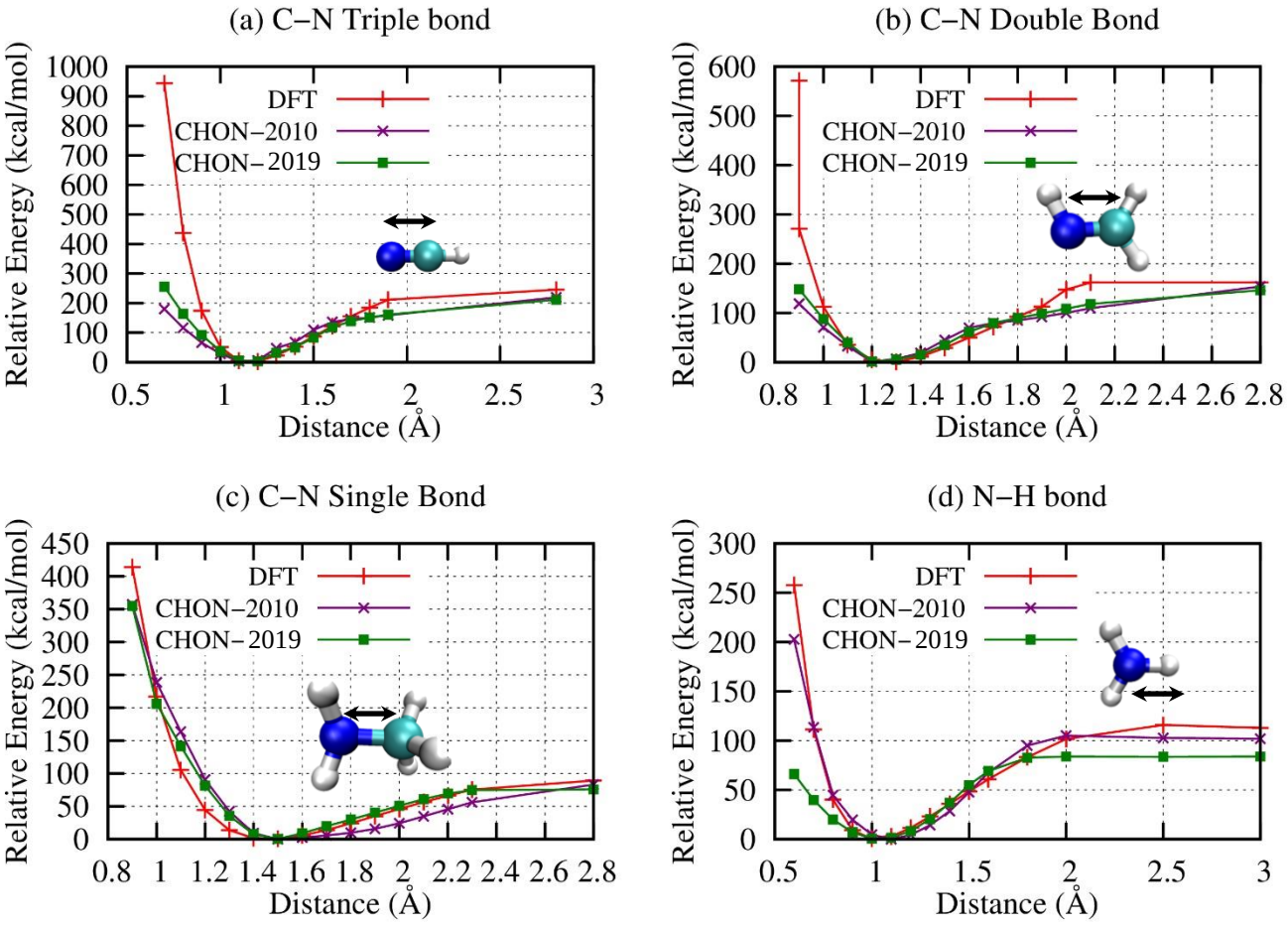

Figure S1: DFT(6-311G**/B3LYP) and ReaxFF (CHNO-2010 and CHNO-2019) bond dissociation energies for (a) C-N triple bond, (b) C-N double bond, (c) C-N single bond and (d) N-H bond. Cyan, red, blue and white spheres represent carbon, oxygen, nitrogen and hydrogen atom respectively

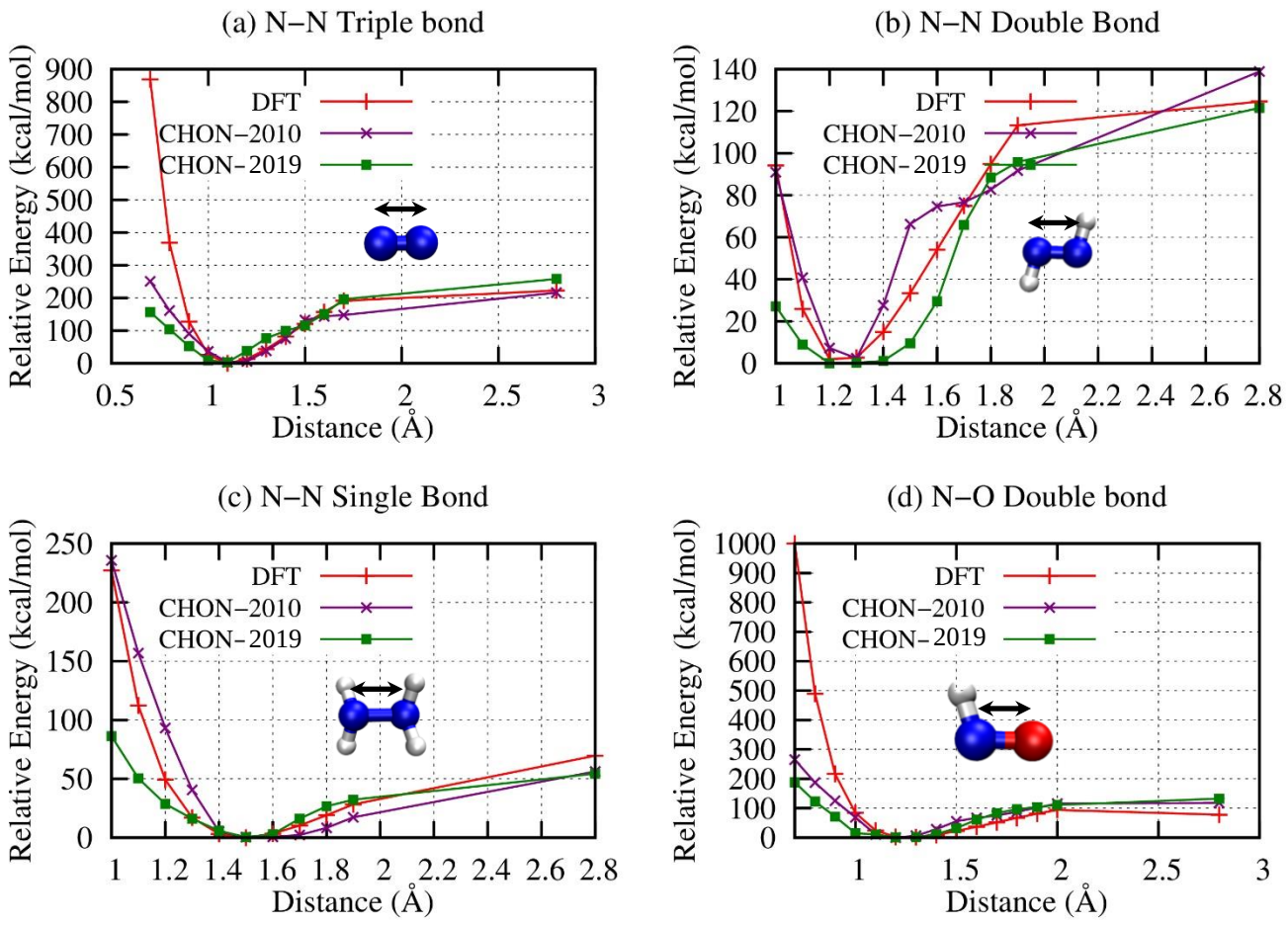

Figure S2: DFT(6-311G**/B3LYP) and ReaxFF (CHNO-2010 and CHNO-2019) bond dissociation energies for (a) N-N triple bond, (b) N-N double bond, (c) N-N single bond and (d) N-O double bond. Cyan, red, blue and white spheres represent carbon, oxygen, nitrogen and hydrogen atom respectively

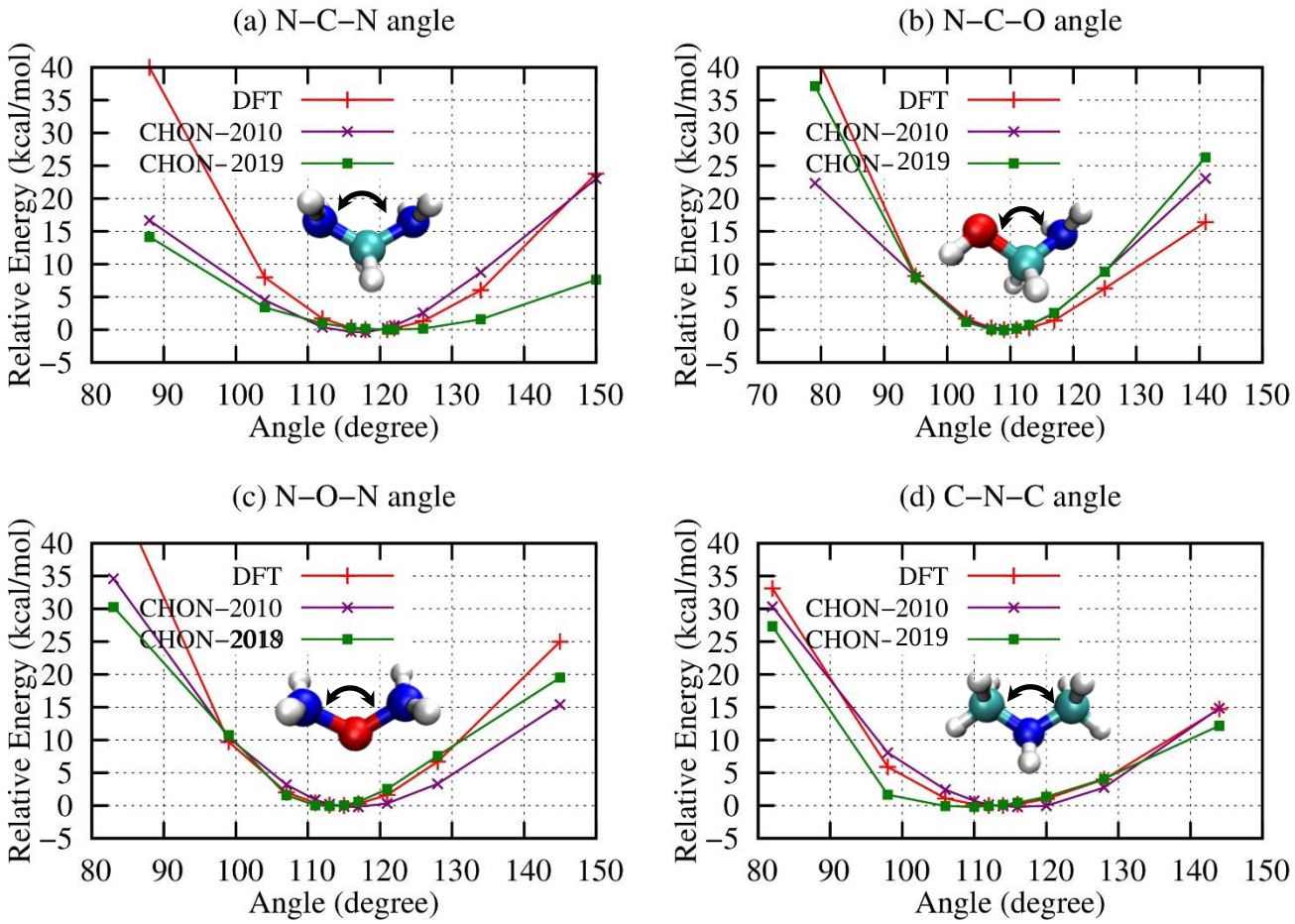

Figure S3: DFT(6-311G**/B3LYP) and ReaxFF (CHNO-2010 and CHNO-2019) valence angle distortion energies for (a) N-C-N angle, (b) N-C-O angle, (c) N-O-N angle and (d) C-N-C angle. Cyan, red, blue and white spheres represent carbon, oxygen, nitrogen and hydrogen atom respectively.

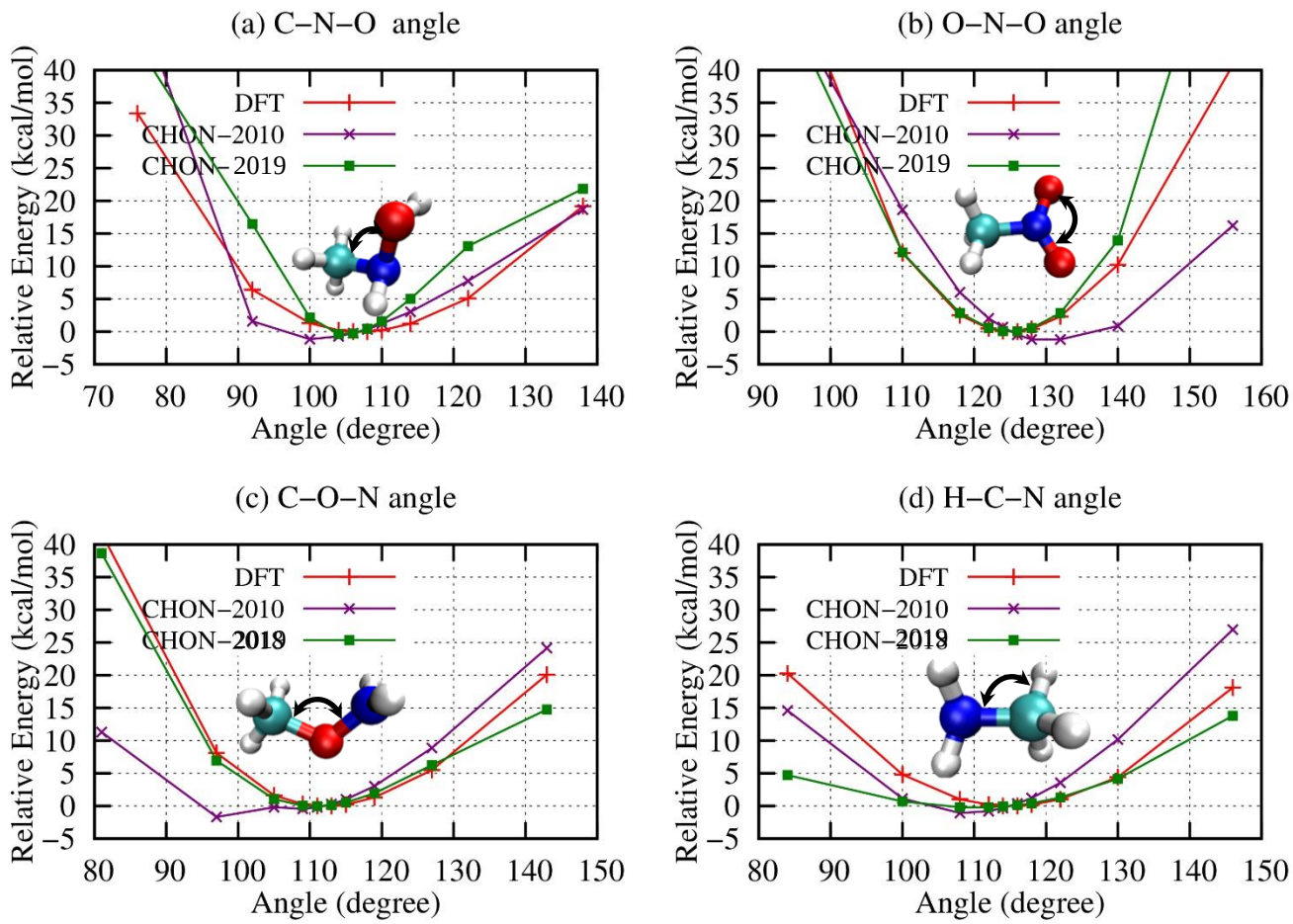

Figure S4: DFT(6-311G**/B3LYP) and ReaxFF (CHNO-2010 and CHNO-2019) valence angle distortion energies for (a) C-N-O angle, (b) O-C-O angle, (c) C-O-N angle and (d) H-C-N angle. Cyan, red, blue and white spheres represent carbon, oxygen, nitrogen and hydrogen atom respectively

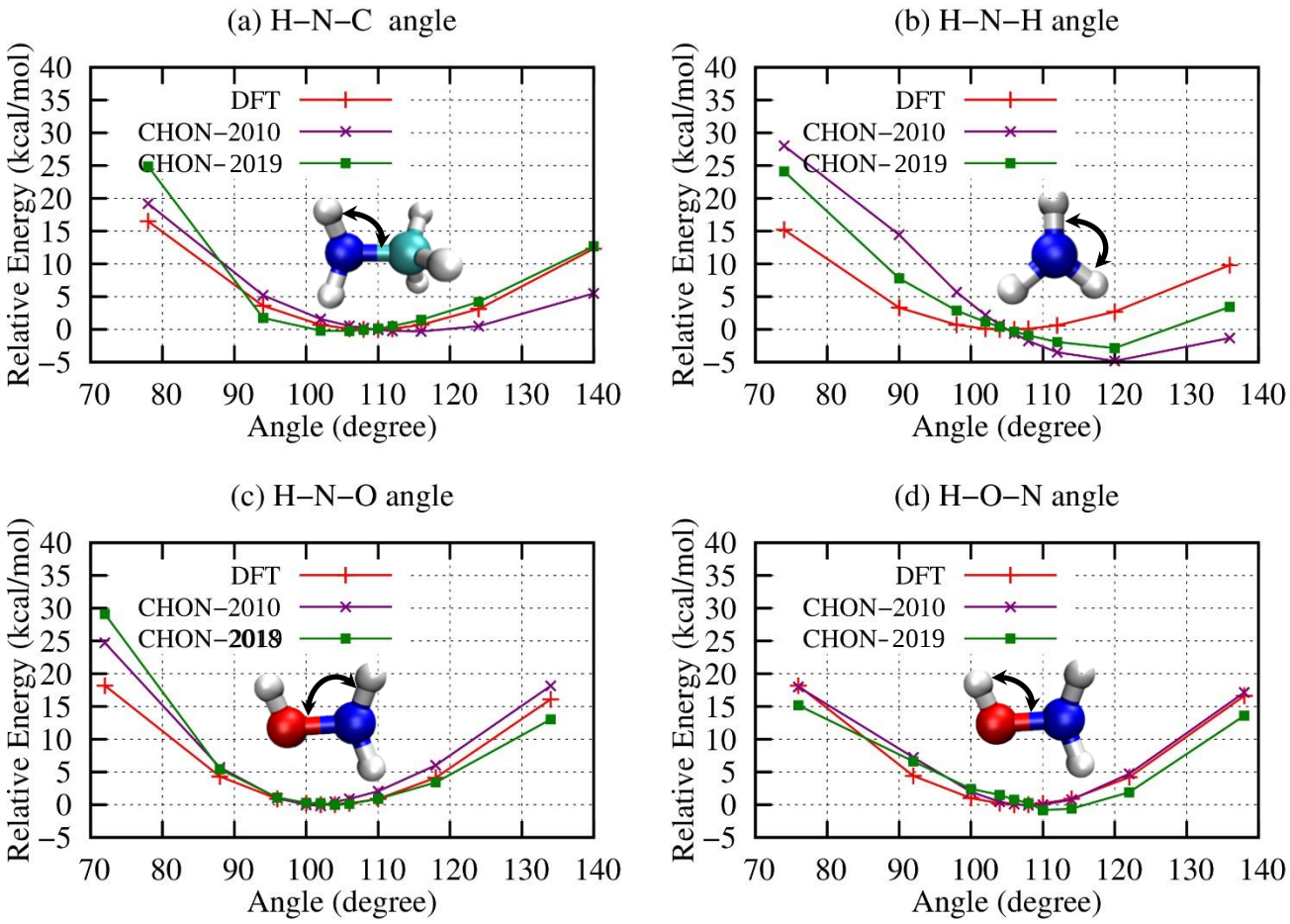

Figure S5: DFT(6-311G**/B3LYP) and ReaxFF (CHNO-2010 and CHNO-2019) valence angle distortion energie5 for (a) H-N-C angle, (b) H-N-H angle, (c) H-N-O angle and (d) H-O-N angle. Cyan, red, blue and white spheres represent carbon, oxygen, nitrogen and hydrogen atom respectively

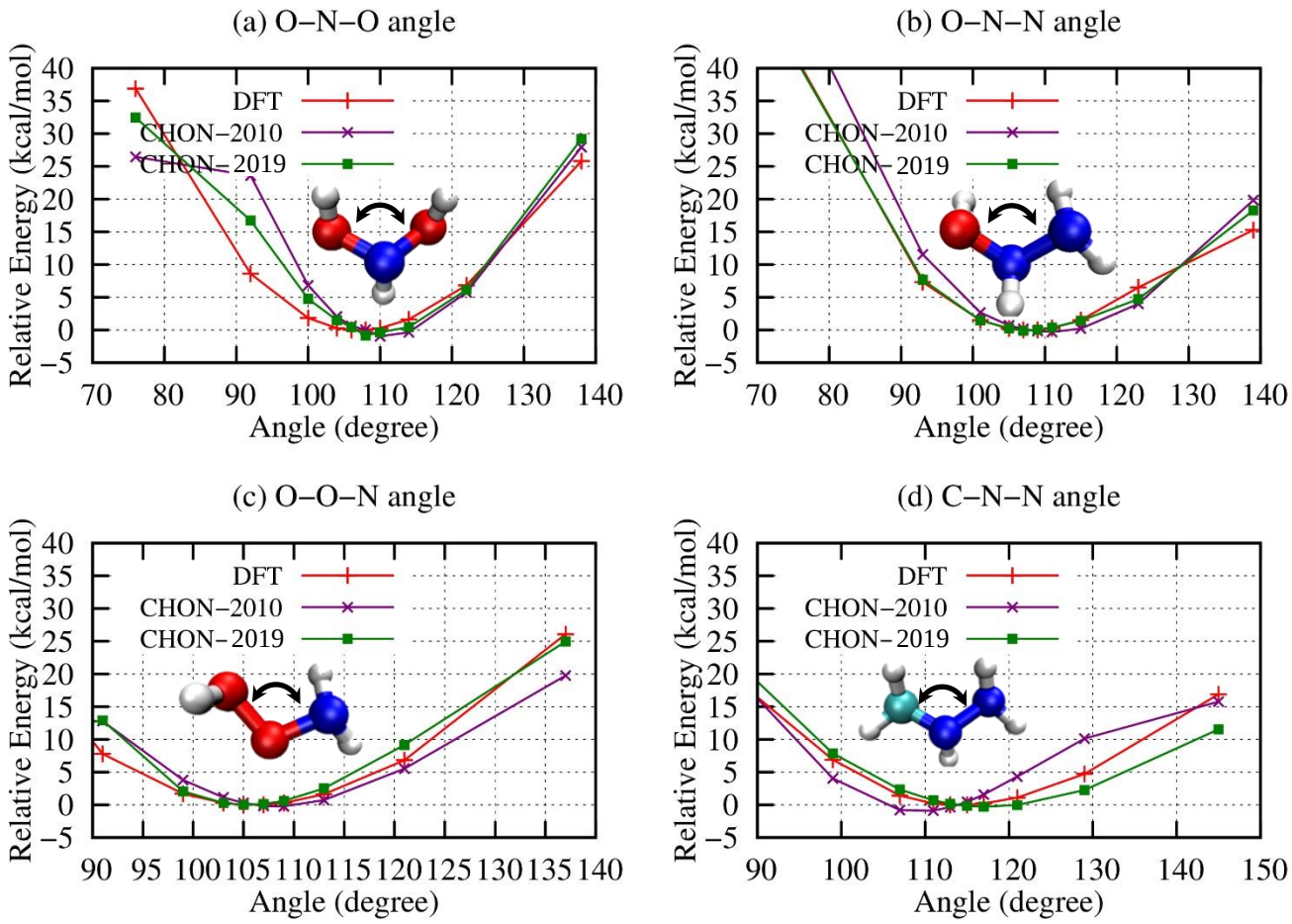

Figure S6: DFT(6-311G**/B3LYP) and ReaxFF (CHNO-2010 and CHNO-2019) valence angle distortion energies for (a) O-N-O angle, (b) O-N-N angle, (c) O-O-N angle and (d) C-N-N angle. Cyan, red, blue and white spheres represent carbon, oxygen, nitrogen and hydrogen atom respectively

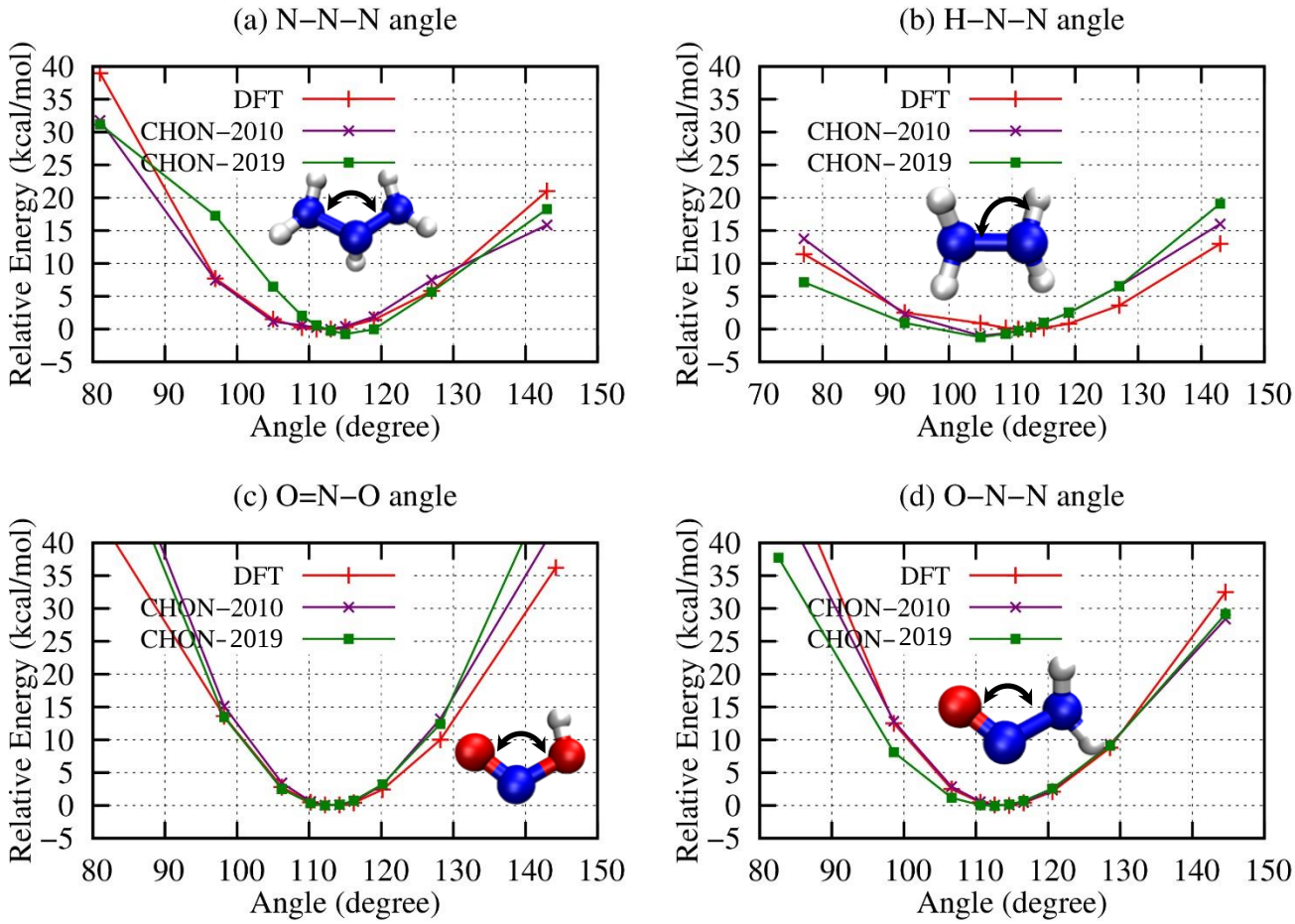

Figure S7: DFT(6-311G**/B3LYP) and ReaxFF (CHNO-2010 and CHNO-2019) valence angle distortion energies for (a) N-N-N angle, (b) H-N-N angle, (c) O=N-O angle and (d) O-N-N angle. Cyan, red, blue and white spheres represent carbon, oxygen, nitrogen and hydrogen atom respectively

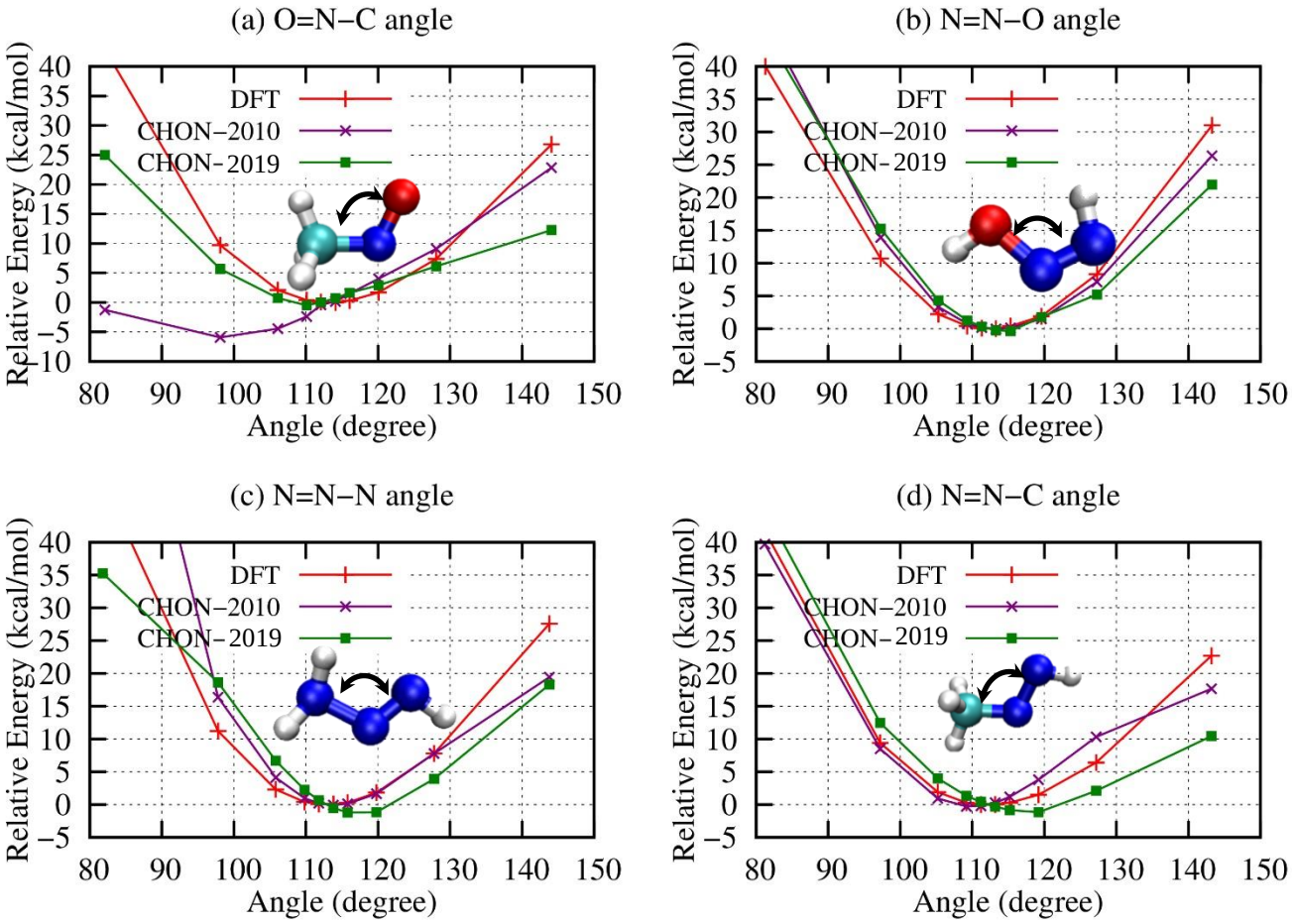

Figure S8: DFT(6-311G**/B3LYP) and ReaxFF (CHNO-2010 and CHNO-2019) valence angle distortion energies for (a) O=N-C angle, (b) N=N-O angle, (c) N=N-N angle and (d) N=N-C angle. Cyan, red, blue and white spheres represent carbon, oxygen, nitrogen and hydrogen atom respectively

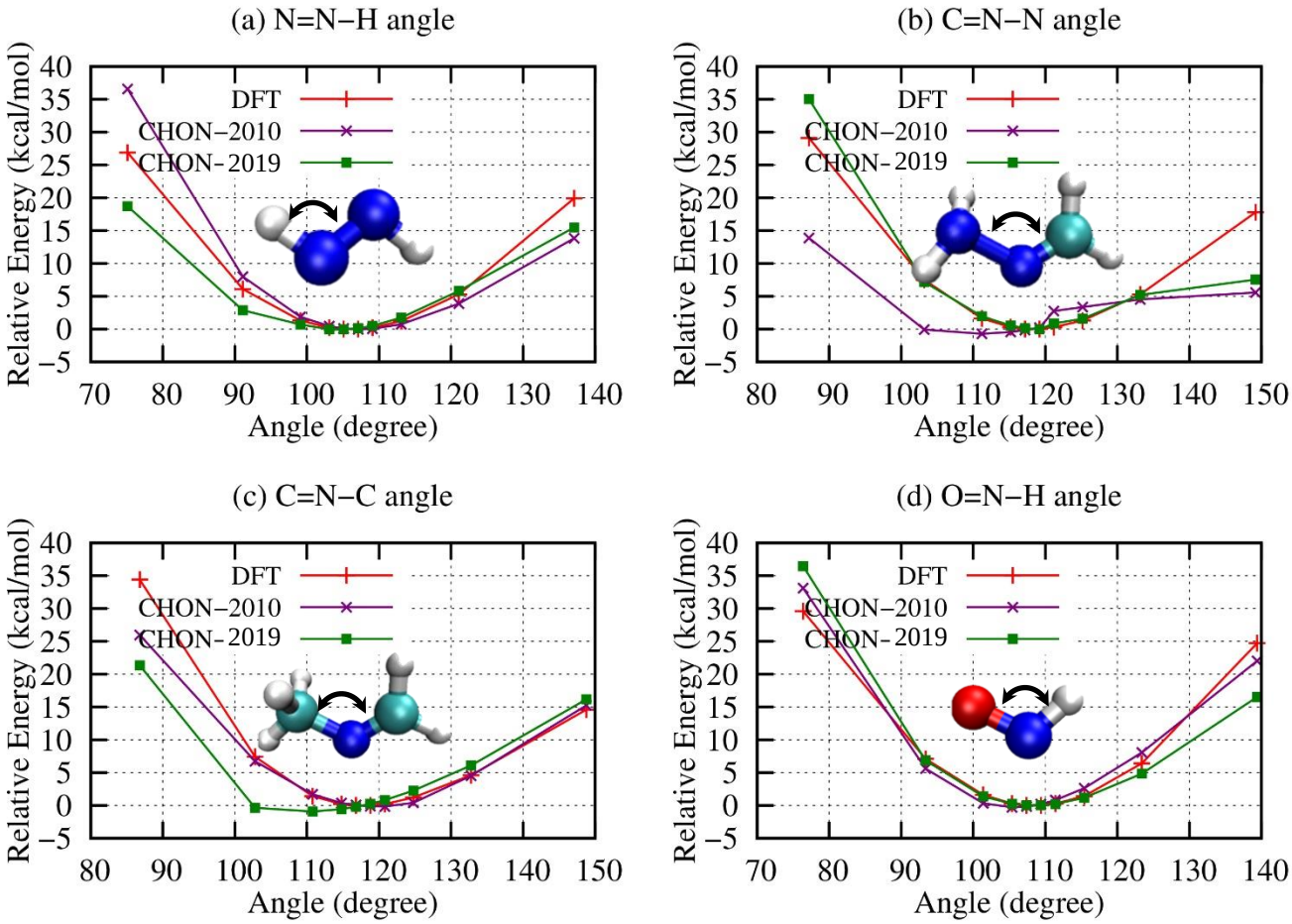

Figure S9: DFT(6-311G**/B3LYP) and ReaxFF (CHNO-2010 and CHNO-2019) valence angle distortion energies for (a) N=N-H angle, (b) C=N-N angle, (c) C=N-C angle and (d) O=N-H angle. Cyan, red, blue and white spheres represent carbon, oxygen, nitrogen and hydrogen atom respectively

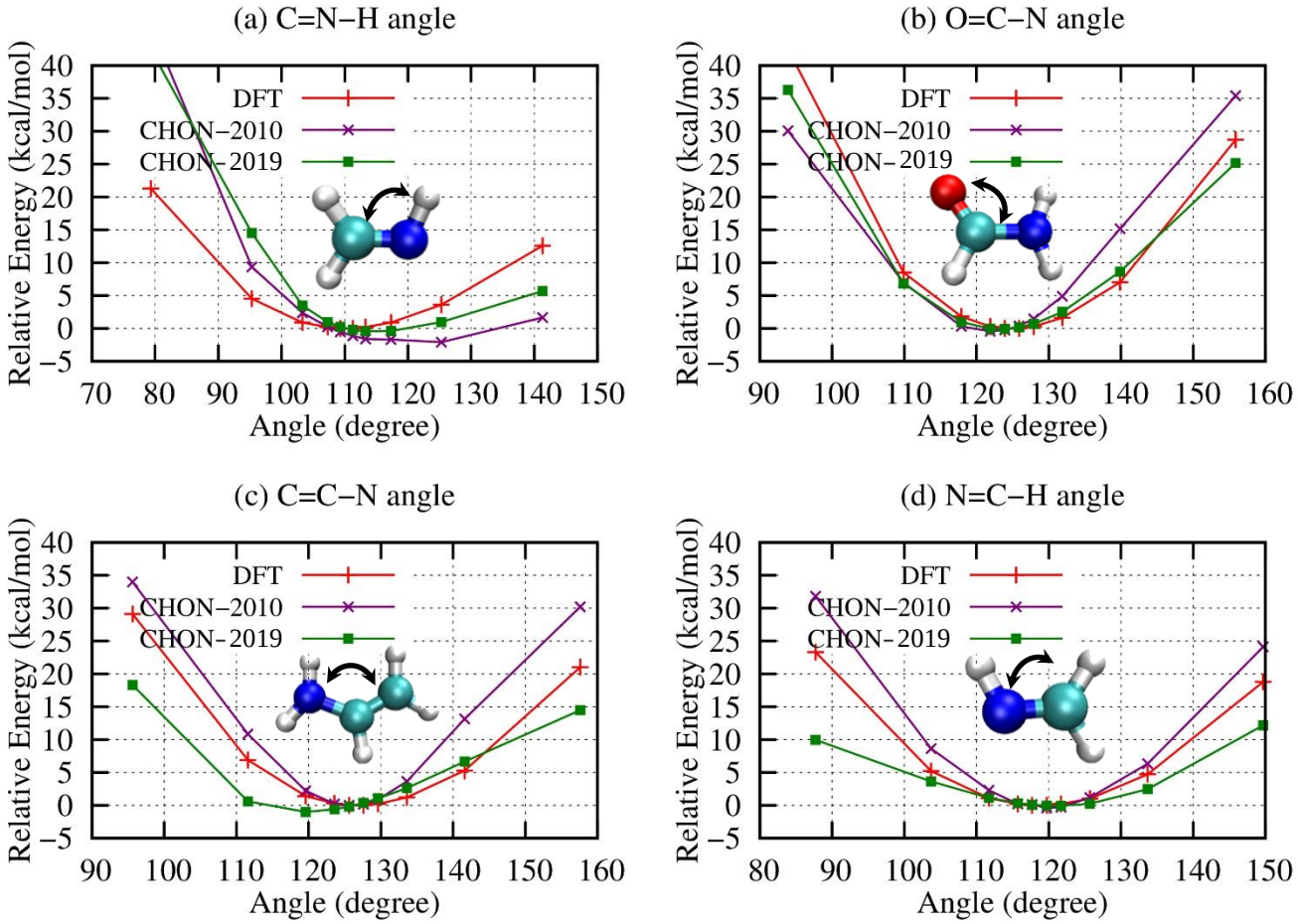

Figure S2: DFT(6-311G**/B3LYP) and ReaxFF (CHNO-2010 and CHNO-2019) valence angle distortion energies for (a) C=N-H angle, (b) O=C-N angle, (c) C=C-N angle and (d) N=C-H angle. Cyan, red, blue and white spheres represent carbon, oxygen, nitrogen and hydrogen atom respectively

Force Field developed in this study (ReaxFF CHON-2019)

```
Reactive MD-force field: Combustion C/H/O force field + atom type N
(May11, 2018)
40       ! Number of general parameters
   50.0000 !p(boc1)
    9.5469 !p(boc2)
   26.5405 !p(coa2)
    0.6863 !p(trip4)
    2.7295 !p(trip3)
   70.0000 !kc2
    1.0588 !p(ovun6)
    4.1262 !p(trip2)
   12.1176 !p(ovun7)
   13.3056 !p(ovun8)
  -68.9784 !p(trip1)
    0.0000 !Lower Taper-radius (swa)
   10.0000 !Upper Taper-radius (swb)
    0.0000 !not used
   33.8667 !p(val7)
    6.0891 !p(lp1)
    1.0563 !p(val9)
    2.0384 !p(val10)
    6.1431 !not used
    6.9290 !p(pen2)
    0.3989 !p(pen3)
    3.9954 !p(pen4)
    0.0000 !not used
    5.7796 !p(tor2)
   10.0000 !p(tor3)
    1.9487 !p(tor4)
    0.0000 !not used
    2.1645 !p(cot2)
    1.5591 !p(vdW1)
    0.1000 !Cutoff for bond order*100 (cutoff)
    2.1365 !p(coa4)
    0.6991 !p(ovun4)
   50.0000 !p(ovun3)
    1.8512 !p(val8)
    0.0000 !not used
    0.0000 !not used
    0.0000 !not used
    1.0000 !not used
    2.6962 !p(coa3)
    2.0000 !triple bond on/off (0 for CO, 1 for CO and N2, 2 for all)
  4   ! Nr of atoms; atomID;ro(sigma); Val;atom mass;Rvdw;Dij;gamma
            alfa;gamma(w);Val(angle);p(ovun5);n.u.;chiEEM;etaEEM;n.u.
            ro(pipi);p(lp2);Heat
increment;p(boc4);p(boc3);p(boc5),n.u.;n.u.
            p(ovun2);p(val3);n.u.;Val(boc);p(val5);n.u.;n.u.;n.u.
 C    1.3674   4.0000  12.0000   2.0453   0.1444   0.9500   1.1706
4.0000
      9.0000   1.5000   4.0000  27.5134  79.5548   5.0191   7.0500
0.0000
```

```
      1.1168   0.0000      NaN  14.2732  24.4406   6.7313   0.8563
0.0000
     -4.1021   5.0000   1.0564   4.0000   2.9663   0.0000   0.0000
0.0000
 H    0.9479   1.0000   1.0080   1.1364   0.0232   0.9900  -0.1000
1.0000
      9.0643   4.7746   1.0000   0.0000 121.1250   4.7757   9.7732
1.0000
     -0.1000   0.0000      NaN   2.5194   2.3785   0.2223   1.0698
0.0000
    -15.7683   2.1488   1.0338   1.0000   2.8793   0.0000   0.0000
0.0000
 O    1.1939   2.0000  15.9990   1.9289   0.1201   0.9900   1.0981
6.0000
     10.4842   8.2916   4.0000  28.8967 116.0768   7.9703   7.0500
2.0000
      1.0479  20.0000      NaN  10.0338   2.2024   0.9942   0.9745
0.0000
     -3.6141   2.7025   1.0493   4.0000   2.9225   0.0000   0.0000
0.0000
 N    1.3638   3.0000  14.0000   1.7000   0.0967   0.8537   1.1943
5.0000
      9.8544  10.4284   4.0000  41.8891 100.0000   7.7391   7.5000
2.0000
      1.0200   0.0700      NaN   1.5271   2.9480   2.6234   0.9745
0.0000
     -5.6116   2.0047   1.0183   4.0000   2.5196   0.0000   0.0000
0.0000
 10     ! Nr of bonds; at1;at2;De(sigma);De(pi);De(pipi);p(be1);p(b
                    p(be2);p(bo3);p(bo4);n.u.;p(bo1);p(bo2)
  1  1  80.8865 107.9944  52.0636   0.5218  -0.3636   1.0000  34.9876
0.7769
         6.1244  -0.1693   8.0804   1.0000  -0.0586   8.1850   1.0000
0.0000
  1  2 179.5195   0.0000   0.0000  -0.5242   0.0000   1.0000   6.0000
0.7187
         5.4740   1.0000   0.0000   1.0000  -0.1144   6.7029   0.0000
0.0000
  2  2 113.9232   0.0000   0.0000  -0.5971   0.0000   1.0000   6.0000
0.9093
         1.7152   1.0000   0.0000   1.0000  -0.0450   6.0710   0.0000
0.0000
  1  3 136.4945 164.1201   5.5000  -0.9159  -0.1075   1.0000  10.6519
0.8644
         0.6858  -0.4602   9.5754   1.0000  -0.1745   4.5987   0.0000
0.0000
  3  3 148.0798 155.2406  20.1160  -1.0000  -0.1254   1.0000  33.0027
0.7790
         0.7673  -0.1697   7.0028   1.0000  -0.1300   5.1959   1.0000
0.0000
  2  3 169.1351   0.0000   0.0000  -0.8810   0.0000   1.0000   6.0000
0.5757
         1.5482   1.0000   0.0000   1.0000  -0.1788   4.6622   0.0000
0.0000
```

```
  1  4 146.4220 161.9411  83.1445  -0.0673  -0.7385   1.0000  20.5574
0.3439
         1.1554  -0.7615   6.3243   1.0000  -0.1692   5.3062   1.0000
0.0000
  2  4 131.9942   0.0000   0.0000  -0.2031   0.0000   1.0000   4.0000
0.4507
        10.2925  -0.3653   0.0000   1.0000  -0.0527   8.0000   0.0000
0.0000
  3  4  78.7524 155.4183 100.4654   1.0000  -1.0000   1.0000  40.0000
0.1723
         0.1607  -0.5703   5.5634   1.0000  -0.1969   4.9725   1.0000
0.0000
  4  4  81.3043  99.0989 144.9704  -0.6110  -0.7864   1.0000   5.0000
0.1000
         1.0202  -0.1368   8.0395   1.0000  -0.1463   3.8325   1.0000
0.0000
  6   ! Nr of off-diagonal terms. at1;at2;Dij;RvdW;alfa;ro(sigma);r
  1  2   0.1253   1.5717   9.9736   1.2057  -1.0000  -1.0000
  2  3   0.1125   1.6311   8.7528   1.0929  -1.0000  -1.0000
  1  3   0.0953   1.7397   8.8986   1.4256   1.1067   1.1265
  1  4   0.1425   1.8737  10.3522   1.4256   1.3259   1.2082
  2  4   0.0660   1.5027   8.8662   1.0548  -1.0000  -1.0000
  3  4   0.1263   1.5263  10.0075   1.3841   1.2535   1.0000
 41   ! Nr of angles. at1;at2;at3;Thetao,o;p(val1);p(val2);p(coa1);
  1  1  1  76.1370  34.6920   1.1328   0.0000   0.0050   0.3556   1.8065
  1  1  2  68.0572   9.9461   4.7000   0.0000   0.4566   0.0000   1.8532
  2  1  2  65.6815  35.0000   1.8622   0.0000   0.0490   0.0000   1.0937
  1  2  2   0.0000   4.0000   7.2043   0.0000   0.0000   0.0000   1.0728
  1  2  1   0.0000   3.4110   7.7350   0.0000   0.0000   0.0000   1.0400
  2  2  2   0.0000  30.0000   5.6235   0.0000   0.0000   0.0000   1.0400
  1  1  3  78.3624  13.0773   9.0480   0.0000   0.1270  52.1129   2.3964
  3  1  3  76.7101  24.3833   5.8613 -21.8559   2.6395 -32.6534   3.6179
  2  1  3  79.1288  30.0000   1.4632   0.0000   0.2065   0.0000   2.0000
  1  3  1  80.7352  16.4130   4.9987   0.0000   0.0843   0.0000   1.0137
  1  3  3  85.4436  14.4937   3.9928   0.0000   1.4350  44.5320   1.1348
  3  3  3  89.9282  32.1199   2.7181   0.0000   0.3323  57.6122   1.0000
  1  3  2  82.9640  32.4874   0.8777   0.0000   0.9627   0.0000   1.0010
  2  3  3  85.7838  17.3139   1.9157   0.0000   3.6306   0.0000   2.1858
  2  3  2  84.2527  33.1226   0.6730   0.0000   0.7238   0.0000   2.4348
  1  2  3   0.0000  14.4588   3.1507   0.0000   3.4571   0.0000   1.0149
  3  2  3   0.0000   0.9696   3.6303   0.0000   0.0000   0.0000   1.6987
  2  2  3   0.0000   0.5797   1.9739   0.0000   0.0000   0.0000   2.4494
  1  1  4  89.5412  10.0000   3.1804   0.0000   0.1000   2.0000   2.0000
  3  1  4  75.6717  34.2176   2.4651   0.0000   0.2576   0.0000   1.3080
  4  1  4  56.7950  21.2889   1.1348   0.0000   0.1000   0.0000   2.0000
  2  1  4  57.5770  16.8737   1.6684   0.0000   0.9500   0.0000   1.0100
  1  2  4   0.0000   0.0100   5.6777   0.0000   0.0000   0.0000   1.2703
  1  3  4  77.6218  14.9138   3.5216   0.0000   0.6416   0.0000   1.5611
  3  3  4  87.1336  29.3985   2.1764   0.0000   0.6955   0.0000   1.8914
  4  3  4  70.2689  19.9584   4.2797   0.0000   0.6998   0.0000   1.6913
  2  3  4  73.7577  44.4943   0.5753   0.0000   3.0692   0.0000   1.5996
  1  4  1  81.0255  35.0000   0.7103   0.0000   1.6888   0.0000   1.0100
  1  4  3  90.0000  25.5053   4.4541   0.0000   2.1016   0.0000   1.2203
  1  4  4  67.3194  22.7804   1.8415   0.0000   2.0063   0.0000   1.0100
```

```
  3  4  3  74.8496  50.0000   1.6227  -6.6718   3.0000  50.0000   1.0100
  3  4  4  74.6195  47.0693   0.9622  -3.4101   2.1852   0.0000   1.7988
  4  4  4  66.6498  17.4122   7.0441   0.0000   1.1587   0.0000   1.2779
  1  4  2  90.0000  20.9302   1.2522   0.0000   0.6402   0.0000   3.0000
  2  4  3  83.0567  36.8198   1.0207   0.0000   0.8674   0.0000   3.0000
  2  4  4  79.0108  22.2517   3.0204   0.0000   0.4118   0.0000   2.9985
  2  4  2  49.0517  14.1263   7.4919   0.0000   0.1000   0.0000   1.0100
  1  2  4   0.0000   0.0019   6.0000   0.0000   0.0000   0.0000   1.0400
  3  2  4   0.0000   0.0019   6.0000   0.0000   0.0000   0.0000   1.0400
  4  2  4   0.0000   0.0019   6.0000   0.0000   0.0000   0.0000   1.0400
  2  2  4   0.0000   0.0019   6.0000   0.0000   0.0000   0.0000   1.0400
 30    ! Nr of torsions. at1;at2;at3;at4;;V1;V2;V3;p(tor1);p(cot1);n
  1  1  1  1   2.0474  32.6719   0.5282  -9.0000  -2.6449   0.0000
0.0000
  1  1  1  2   1.6328  78.4995  -0.1514  -6.9161  -2.9986   0.0000
0.0000
  2  1  1  2   2.4142  78.7025   0.3506  -8.8640  -6.9283   0.0000
0.0000
  1  1  1  3  -0.7104  22.6038   0.5309  -2.0000  -0.6614   0.0000
0.0000
  2  1  1  3   1.9323  52.9368   0.6554  -8.8118  -3.9854   0.0000
0.0000
  3  1  1  3  -1.2500   1.1248  -0.1230  -9.9453  -3.9000   0.0000
0.0000
  1  1  3  1  -0.6848  56.7751  -1.2733  -2.2937  -4.0000   0.0000
0.0000
  1  1  3  2  -1.4557  78.6279   0.9945  -3.2742  -2.4240   0.0000
0.0000
  2  1  3  1   0.6928  78.1546   0.5608  -3.1713  -3.7301   0.0000
0.0000
  2  1  3  2  -1.4343  77.0699   0.9875  -3.4139  -1.4053   0.0000
0.0000
  1  1  3  3   0.5153   2.1584   0.2000  -6.5859  -3.0000   0.0000
0.0000
  2  1  3  3   0.2018  80.0000   0.3778  -2.5000  -2.8750   0.0000
0.0000
  3  1  3  1  -1.9875  79.2591   1.0000  -2.4206  -3.9342   0.0000
0.0000
  3  1  3  2  -1.1000  78.8002  -1.0000  -2.6282  -4.0000   0.0000
0.0000
  3  1  3  3  -1.0000  83.5323   4.3660  -2.6805  -1.2938   0.0000
0.0000
  1  3  3  1   3.4682   0.0781   0.9887  -6.1195  -0.5004   0.0000
0.0000
  1  3  3  2   1.0000  16.5478  -1.0313  -2.0000  -2.6888   0.0000
0.0000
  2  3  3  2   4.0818  -3.2744  -0.9664  -7.1634  -3.0000   0.0000
0.0000
  1  3  3  3   4.2014 -10.0642   1.8690  -2.4805  -2.5000   0.0000
0.0000
  2  3  3  3   1.0000 -10.0500  -1.0000  -2.1946  -0.5300   0.0000
0.0000
  3  3  3  3   1.0000   1.6871   3.0000  -6.2660  -0.5500   0.0000
0.0000
```

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  4  1  1  4   3.0000  80.0000   2.0000  -2.0000  -1.8773   0.0000
0.0000
  1  1  1  4   1.0676  41.9735  -0.6803  -6.3125  -3.0000   0.0000
0.0000
  2  1  1  4   3.0000  44.9653   1.7235  -3.0352  -1.0000   0.0000
0.0000
  0  1  4  0   1.4015  77.4788   1.0472  -6.9179  -1.7577   0.0000
0.0000
  0  2  4  0  -3.0000   0.1000   0.0200  -2.8105   0.0000   0.0000
0.0000
  0  3  4  0   3.0000  50.0719   0.2740  -8.0000  -1.0000   0.0000
0.0000
  0  4  4  0   0.8759  30.0000  -1.7701  -8.0000  -1.0000   0.0000
0.0000
  0  1  1  0   3.0000  38.1059   2.0000  -3.2272  -2.9827   0.0000
0.0000
  4  1  4  4  -3.0000  40.0000  -1.8678  -7.3019  -1.0000   0.0000
0.0000
  4    ! Nr of hydrogen bonds. at1;at2;at3;r(hb);p(hb1);p(hb2);p(hb3
  3  2  3   1.8130  -3.5409   2.3815  21.9463
  3  2  4   1.7753  -5.0000   3.0000   3.0000
  4  2  3   1.3884  -5.0000   3.0000   3.0000
  4  2  4   1.6953  -4.0695   3.0000   3.0000
```