Experimental and computational study of the crystal packing of isoelectronic 4,11-diaza[5]helicene and 4,7,8,11-tetraaza[5]helicene

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Contribution submitted for the special issue of Structural Chemistry honoring the career of Angelo Gavezzotti

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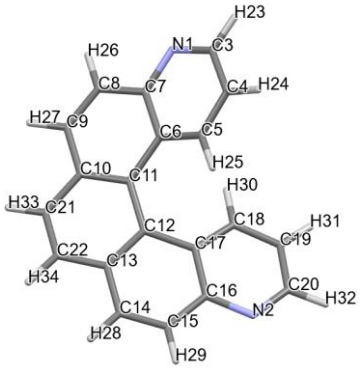
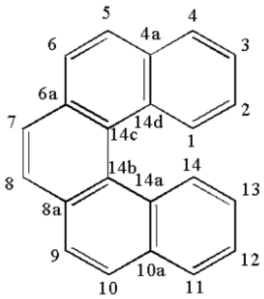
SUPPORTING INFORMATION

Section S1. Relevant topologies and steering parameters for classical simulations

Table S1. Topology of DNH at RT. ESP charges from MP2/6-31G(p,d) wavefunction at the expt geometry. See MiCMoS user's manual for details. [1,2] The scheme below shows the atom labelling in MiCMoS input (left) and the conventional numbering (right).






```
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    3   -0.58739    2.42555   -3.36403   12     0.4532
    4   -1.12362    2.53358   -2.07755   12    -0.4754
    5   -0.90865    1.51611   -1.18641   12     0.1753
    6   -0.18432    0.37547   -1.57447   14    -0.2722
    7    0.19036    0.31126   -2.94417   12     0.6738
    8    0.67074   -0.92001   -3.47769   12    -0.3351
    9    0.66963   -2.03425   -2.72609   12    -0.1663
   10    0.33136   -2.00917   -1.33712   14     0.1418
   11    0.04738   -0.77108   -0.71529   14    -0.0445
   12   -0.08736   -0.75977    0.72271   14     0.0616
   13   -0.34779   -1.98217    1.38758   14     0.0600
   14   -0.67685   -1.98610    2.77429   12    -0.1451
   15   -0.66282   -0.85794    3.50646   12    -0.3411
   16   -0.17512    0.35181    2.93795   12     0.6796
   17    0.15600    0.40106    1.55916   14    -0.3084
   18    0.87877    1.53580    1.13269   12     0.1838
   19    1.09814    2.56641    2.00128   12    -0.4724
   20    0.61525    2.46917    3.31239   12     0.4533
   21    0.22302   -3.21571   -0.59678   12    -0.1908
   22   -0.19830   -3.20648    0.68735   12    -0.1288
   23   -0.68930    3.26816   -4.03175    2     0.0190
   24   -1.69672    3.40326   -1.79179    2     0.1778
   25   -1.29710    1.59029   -0.18146    2     0.0711
   26    1.03802   -0.95792   -4.49254    2     0.1700
   27    0.93189   -2.97619   -3.18476    2     0.1402
   28   -0.94419   -2.91853    3.24918    2     0.1386
   29   -1.02141   -0.87028    4.52511    2     0.1712
   30    1.25725    1.58887    0.12253    2     0.0705
   31    1.63744    3.44572    1.68108    2     0.1743
   32    0.73508    3.32064    3.96576    2     0.0202
   33    0.48069   -4.15361   -1.06616    2     0.1260
   34   -0.42292   -4.13869    1.18422    2     0.1178
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    0  ncore-v
    0  nslav-v
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    1     7    1.360   5378.2    N- C
    2    16    1.364   5293.8    N- C
    2    20    1.313   6491.0    N- C
    3     4    1.398   4713.5    C- C
    3    23    1.080   3600.0    C- H
    4     5    1.370   5312.0    C- C
    4    24    1.080   3600.0    C- H
    5     6    1.406   4547.9    C- C
    5    25    1.080   3600.0    C- H
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    7     8    1.425   4137.6    C- C
    8     9    1.344   5848.7    C- C
    8    26    1.080   3600.0    C- H
    9    10    1.430   4043.0    C- C
    9    27    1.080   3600.0    C- H
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   10    21    1.420   4255.0    C- C
   11    12    1.444   3736.4    C- C
   12    13    1.416   4340.1    C- C
   12    17    1.451   3589.0    C- C
   13    14    1.425   4139.1    C- C
   13    22    1.418   4284.7    C- C
   14    15    1.345   5828.4    C- C
   14    28    1.080   3600.0    C- H
   15    16    1.423   4188.5    C- C
   15    29    1.080   3600.0    C- H
   16    17    1.419   4273.4    C- C
   17    18    1.411   4431.1    C- C
   18    19    1.366   5395.6    C- C
   18    30    1.080   3600.0    C- H
   19    20    1.401   4657.8    C- C
   19    31    1.080   3600.0    C- H
   20    32    1.080   3600.0    C- H
   21    22    1.352   5691.3    C- C
   21    33    1.080   3600.0    C- H
   22    34    1.080   3600.0    C- H
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   62  nbend-u
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    1     3    23   118.00    530.0    N- C- H
    1     7     6   123.00    636.7    N- C- C
    1     7     8   117.00    580.9    N- C- C
    2    16    15   117.00    580.9    N- C- C
    2    16    17   123.00    636.7    N- C- C
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    2    20    32   118.00    530.0    N- C- H
    3     1     7   118.00    590.2    C- N- C
    3     4     5   119.00    576.7    C- C- C
    3     4    24   121.00    492.5    C- C- H
    4     3    23   118.00    530.0    C- C- H
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    4     5    25   120.00    505.0    C- C- H
    5     4    24   121.00    492.5    C- C- H
    5     6     7   116.00    555.7    C- C- C
    5     6    11   124.00    611.8    C- C- C
    6     5    25   120.00    505.0    C- C- H
    6     7     8   119.00    576.7    C- C- C
    6    11    10   118.00    569.7    C- C- C
    6    11    12   125.00    618.9    C- C- C
    7     6    11   120.00    583.8    C- C- C
    7     8     9   120.00    583.8    C- C- C
    7     8    26   120.00    505.0    C- C- H
    8     9    10   122.00    597.8    C- C- C
    8     9    27   119.00    517.5    C- C- H
    9     8    26   120.00    505.0    C- C- H
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   10     9    27   119.00    517.5    C- C- H
   10    11    12   118.00    569.7    C- C- C
   10    21    22   121.00    590.8    C- C- C
   10    21    33   120.00    505.0    C- C- H
   11    10    21   120.00    583.8    C- C- C
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   12    13    22   120.00    583.8    C- C- C
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 12   17   16  120.00   583.8   C- C- C
 12   17   18  124.00   611.8   C- C- C
 13   12   17  117.00   562.7   C- C- C
 13   14   15  122.00   597.8   C- C- C
 13   14   28  119.00   517.5   C- C- H
 13   22   21  121.00   590.8   C- C- C
 13   22   34  120.00   505.0   C- C- H
 14   13   22  120.00   583.8   C- C- C
 14   15   16  120.00   583.8   C- C- C
 14   15   29  120.00   505.0   C- C- H
 15   14   28  119.00   517.5   C- C- H
 15   16   17  120.00   583.8   C- C- C
 16    2   20  118.00   590.2   C- N- C
 16   15   29  120.00   505.0   C- C- H
 16   17   18  116.00   555.7   C- C- C
 17   18   19  120.00   583.8   C- C- C
 17   18   30  120.00   505.0   C- C- H
 18   19   20  119.00   576.7   C- C- C
 18   19   31  120.00   505.0   C- C- H
 19   18   30  120.00   505.0   C- C- H
 19   20   32  118.00   530.0   C- C- H
 20   19   31  120.00   505.0   C- C- H
 21   22   34  120.00   505.0   C- C- H
 22   21   33  120.00   505.0   C- C- H
  0  nbend-v
 46  ntors-u
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  3    1    7    6  50.00   -1.0    1.0   C- N- C- C
 20    2   16   15  50.00    1.0    1.0   C- N- C- C
 16    2   20   19  50.00   -1.0    1.0   C- N- C- C
  1    3    4    5  50.00   -1.0    1.0   N- C- C- C
  3    1    4   23 100.00   -1.0    1.0   C- N- C- H
  3    4    5    6  50.00   -1.0    1.0   C- C- C- C
  4    3    5   24 100.00   -1.0    1.0   C- C- C- H
  4    5    6    7  50.00   -1.0    1.0   C- C- C- C
  5    4    6   25 100.00   -1.0    1.0   C- C- C- H
  5    6    7    1  50.00   -1.0    1.0   C- C- C- N
  5    6   11   10  50.00    1.0    1.0   C- C- C- C
  6    5    7   11 100.00   -1.0    1.0   C- C- C- C
  1    7    8    9  50.00    1.0    1.0   N- C- C- C
  7    1    6    8 100.00   -1.0    1.0   C- N- C- C
  7    8    9   10  50.00   -1.0    1.0   C- C- C- C
  8    7    9   26 100.00   -1.0    1.0   C- C- C- H
  8    9   10   11  50.00   -1.0    1.0   C- C- C- C
  9    8   10   27 100.00   -1.0    1.0   C- C- C- H
  9   10   11    6  50.00   -1.0    1.0   C- C- C- C
  9   10   21   22  50.00    1.0    1.0   C- C- C- C
 10    9   11   21 100.00   -1.0    1.0   C- C- C- C
  6   11   12   13  50.00    1.0    1.0   C- C- C- C
 11    6   10   12 100.00   -1.0    1.0   C- C- C- C
 11   12   13   14  50.00    1.0    1.0   C- C- C- C
 11   12   17   16  50.00    1.0    1.0   C- C- C- C
 12   11   13   17 100.00   -1.0    1.0   C- C- C- C
 12   13   14   15  50.00   -1.0    1.0   C- C- C- C
 12   13   22   21  50.00   -1.0    1.0   C- C- C- C
 13   12   14   22 100.00   -1.0    1.0   C- C- C- C
 13   14   15   16  50.00   -1.0    1.0   C- C- C- C
 14   13   15   28 100.00   -1.0    1.0   C- C- C- H
 14   15   16    2  50.00    1.0    1.0   C- C- C- N
 15   14   16   29 100.00   -1.0    1.0   C- C- C- H
  2   16   17   12  50.00    1.0    1.0   N- C- C- C
 16    2   15   17 100.00   -1.0    1.0   C- N- C- C
 12   17   18   19  50.00    1.0    1.0   C- C- C- C
 17   12   16   18 100.00   -1.0    1.0   C- C- C- C
 17   18   19   20  50.00   -1.0    1.0   C- C- C- C
 18   17   19   30 100.00   -1.0    1.0   C- C- C- H
 18   19   20    2  50.00   -1.0    1.0   C- C- C- N
 19   18   20   31 100.00   -1.0    1.0   C- C- C- H
 20    2   19   32 100.00   -1.0    1.0   C- N- C- H
 10   21   22   13  50.00   -1.0    1.0   C- C- C- C
 21   10   22   33 100.00   -1.0    1.0   C- C- C- H
 22   13   21   34 100.00   -1.0    1.0   C- C- C- H
  0  ntors-v
  4  nlist-u
 18 25 5 30 5 18 25 30
  0  nlist-v
 0.410   235.0   650.0   77000.0
  0  nextr
```
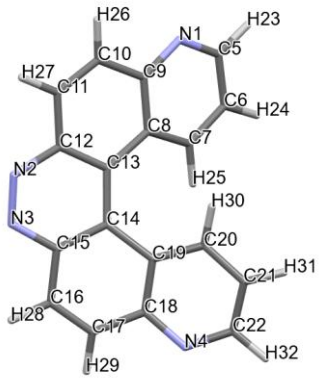
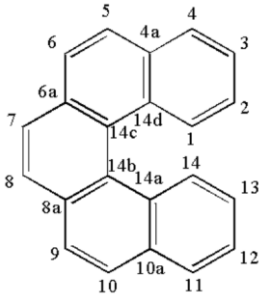

Table S2. Topology of TNH at RT. ESP charges from MP2/6-31G(p,d) wavefunction at the expt geometry. See MiCMoS user's manual for details. [1,2] The scheme below shows the atom labelling in MiCMoS input (left) and the conventional numbering (right).






```
#Tetraaza  LJC       topology
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    3  -0.16579  -3.12834  -0.61273  18   -0.3570
    4  -0.09843   1.27789  -3.88342  18   -0.6828
    5  -0.55708   2.43247   3.45858  12    0.5552
    6  -0.94542   2.65004   2.13400  12   -0.5533
    7  -0.73719   1.66255   1.21748  12    0.2334
    8  -0.12653   0.45657   1.60496  14   -0.1661
    9   0.16098   0.31002   2.98715  12    0.4809
   10   0.60015  -0.95957   3.49523  12   -0.0725
   11   0.60240  -2.04283   2.70914  12   -0.5223
   12   0.28717  -1.93489   1.31947  12    0.7397
   13   0.07024  -0.67536   0.72050  14   -0.2490
   14  -0.01700  -0.68748  -0.70225  14   -0.1647
   15  -0.26091  -1.94790  -1.29102  12    0.6965
   16  -0.62292  -2.05476  -2.66693  12   -0.5003
   17  -0.68633  -0.97476  -3.44925  12   -0.0782
   18  -0.22806   0.29030  -2.96454  12    0.4758
   19   0.16545   0.43302  -1.61053  14   -0.1993
   20   0.86892   1.60596  -1.27652  12    0.2234
   21   1.03734   2.58050  -2.22352  12   -0.5281
   22   0.50094   2.38383  -3.49225  12    0.5272
   23  -0.69579   3.23546   4.16734   2    0.0001
   24  -1.40240   3.58390   1.84161   2    0.1931
   25  -1.04189   1.80681   0.19149   2    0.0682
   26   0.93127  -1.04082   4.52002   2    0.1469
   27   0.84485  -3.00776   3.12914   2    0.2024
   28  -0.84947  -3.02559  -3.08252   2    0.1979
   29  -1.08439  -1.05655  -4.44993   2    0.1462
   30   1.27181   1.73578  -0.28294   2    0.0651
   31   1.57725   3.48613  -1.98972   2    0.1905
   32   0.58137   3.19208  -4.20398   2    0.0051
    0  nslav-u
   32
    1   0.01312  -1.29756  -3.89203  18   -0.7031
    2  -0.20728   3.12065  -0.62058  18   -0.3709
    3   0.21194   3.11942   0.61213  18   -0.3570
    4  -0.01067  -1.27816   3.89801  18   -0.6828
    5   0.60832  -2.39967  -3.47103  12    0.5552
    6   1.04084  -2.59669  -2.16682  12   -0.5533
    7   0.79669  -1.62621  -1.23476  12    0.2334
    8   0.12483  -0.44635  -1.60880  14   -0.1661
    9  -0.19876  -0.30911  -2.97973  12    0.4809
   10  -0.68876   0.94324  -3.47043  12   -0.0725
   11  -0.69279   2.03106  -2.68125  12   -0.5223
   12  -0.32628   1.93551  -1.30369  12    0.7397
   13  -0.07292   0.67875  -0.71237  14   -0.2490
   14   0.04747   0.68223   0.70969  14   -0.1647
   15   0.32454   1.93430   1.29230  12    0.6965
   16   0.71444   2.03024   2.66454  12   -0.5003
   17   0.70031   0.95107   3.45797  12   -0.0782
   18   0.18861  -0.29305   2.97787  12    0.4758
   19  -0.15459  -0.43306   1.61047  14   -0.1993
   20  -0.81616  -1.62258   1.24887  12    0.2234
   21  -1.02435  -2.59709   2.18305  12   -0.5281
   22  -0.58850  -2.38767   3.48552  12    0.5272
   23   0.76779  -3.19470  -4.18429   2    0.0001
   24   1.56186  -3.50208  -1.89253   2    0.1931
   25   1.11870  -1.76440  -0.21323   2    0.0682
   26  -1.05810   1.01441  -4.48278   2    0.1469
   27  -0.97634   2.98833  -3.09307   2    0.2024
   28   1.02393   2.98382   3.06600   2    0.1979
   29   1.07821   1.02214   4.46717   2    0.1462
   30  -1.15845  -1.76403   0.23437   2    0.0651
   31  -1.52082  -3.51750   1.91300   2    0.1905
   32  -0.73207  -3.18223   4.20277   2    0.0051
    0  nslav-v
246.5  246.5 volu-u,volu-v
   36  nstr-u
    1    5   1.315  6443.1   N- C
    1    9   1.361  5350.1   N- C
    2    3   1.303  2000.0   N- N
    2   12   1.372  5099.4   N- C
    3   15   1.365  5265.9   N- C
    4   18   1.355  5492.5   N- C
    4   22   1.317  6387.3   N- C
    5    6   1.397  4725.6   C- C
    5   23   1.080  3600.0   C- H
    6    7   1.363  5443.6   C- C
    6   24   1.080  3600.0   C- H
    7    8   1.406  4539.5   C- C
    7   25   1.080  3600.0   C- H
    8    9   1.419  4262.6   C- C
    8   13   1.450  3619.1   C- C
    9   10   1.436  3906.5   C- C
   10   11   1.338  5966.7   C- C
   10   26   1.080  3600.0   C- H
   11   12   1.429  4058.4   C- C
   11   27   1.080  3600.0   C- H
   12   13   1.411  4428.7   C- C
   13   14   1.425  4133.8   C- C
   14   15   1.412  4409.6   C- C
   14   19   1.454  3535.5   C- C
   15   16   1.427  4107.1   C- C
   16   17   1.335  6037.2   C- C
   16   28   1.080  3600.0   C- H
   17   18   1.430  4035.4   C- C
   17   29   1.080  3600.0   C- H
   18   19   1.417  4307.3   C- C
   19   20   1.408  4503.6   C- C
   20   21   1.369  5317.3   C- C
   20   30   1.080  3600.0   C- H
   21   22   1.391  4850.7   C- C
   21   31   1.080  3600.0   C- H
   22   32   1.080  3600.0   C- H
   36  nstr-v
    1    5   1.321  6290.8   N- C
    1    9   1.362  5338.1   N- C
    2    3   1.302  2000.0   N- N
    2   12   1.373  5069.1   N- C
    3   15   1.371  5116.9   N- C
    4   18   1.363  5315.8   N- C
    4   22   1.317  6390.1   N- C
    5    6   1.388  4920.5   C- C
    5   23   1.080  3600.0   C- H
    6    7   1.368  5353.7   C- C
    6   24   1.080  3600.0   C- H
    7    8   1.408  4495.1   C- C
    7   25   1.080  3600.0   C- H
    8    9   1.415  4348.5   C- C
```

```
 8   13   1.452  3573.5   C- C
 9   10   1.432  4006.4   C- C
10   11   1.344  5850.6   C- C
10   26   1.080  3600.0   C- H
11   12   1.429  4066.2   C- C
11   27   1.080  3600.0   C- H
12   13   1.412  4420.7   C- C
13   14   1.427  4098.6   C- C
14   15   1.409  4491.0   C- C
14   19   1.448  3663.9   C- C
15   16   1.430  4043.1   C- C
16   17   1.340  5943.6   C- C
16   28   1.080  3600.0   C- H
17   18   1.428  4073.3   C- C
17   29   1.080  3600.0   C- H
18   19   1.417  4317.6   C- C
19   20   1.408  4494.7   C- C
20   21   1.366  5388.1   C- C
20   30   1.080  3600.0   C- H
21   22   1.389  4894.9   C- C
21   31   1.080  3600.0   C- H
22   32   1.080  3600.0   C- H
58 nbend-u
 1    5    6  124.00   646.0   N- C- C
 1    5   23  118.00   530.0   N- C- H
 1    9    8  123.00   636.7   N- C- C
 1    9   10  117.00   580.9   N- C- C
 2    3   15  120.00   608.8   N- N- C
 2   12   11  116.00   571.6   N- C- C
 2   12   13  124.00   646.0   N- C- C
 3    2   12  120.00   608.8   N- N- C
 3   15   14  124.00   646.0   N- C- C
 3   15   16  116.00   571.6   N- C- C
 4   18   17  116.00   571.6   N- C- C
 4   18   19  123.00   636.7   N- C- C
 4   22   21  124.00   646.0   N- C- C
 4   22   32  118.00   530.0   N- C- H
 5    1    9  118.00   590.2   C- N- C
 5    6    7  119.00   576.7   C- C- C
 5    6   24  121.00   492.5   C- C- H
 6    5   23  118.00   530.0   C- C- H
 6    7    8  120.00   583.8   C- C- C
 6    7   25  120.00   505.0   C- C- H
 7    6   24  121.00   492.5   C- C- H
 7    8    9  116.00   555.7   C- C- C
 7    8   13  124.00   611.8   C- C- C
 8    7   25  120.00   505.0   C- C- H
 8    9   10  120.00   583.8   C- C- C
 8   13   12  117.00   562.7   C- C- C
 8   13   14  127.00   632.9   C- C- C
 9    8   13  119.00   576.7   C- C- C
 9   10   11  121.00   590.8   C- C- C
 9   10   26  120.00   505.0   C- C- H
10   11   12  121.00   590.8   C- C- C
10   11   27  120.00   505.0   C- C- H
11   10   26  120.00   505.0   C- C- H
11   12   13  121.00   590.8   C- C- C
12   11   27  120.00   505.0   C- C- H
12   13   14  115.00   548.7   C- C- C
13   14   15  116.00   555.7   C- C- C
13   14   19  128.00   639.9   C- C- C
14   15   16  121.00   590.8   C- C- C
14   19   18  119.00   576.7   C- C- C
14   19   20  124.00   611.8   C- C- C
15   14   19  117.00   562.7   C- C- C
15   16   17  121.00   590.8   C- C- C
15   16   28  119.00   517.5   C- C- H
16   17   18  120.00   583.8   C- C- C
16   17   29  120.00   505.0   C- C- H
17   16   28  119.00   517.5   C- C- H
17   18   19  120.00   583.8   C- C- C
18    4   22  117.00   580.9   C- N- C
18   17   29  120.00   505.0   C- C- H
18   19   20  117.00   562.7   C- C- C
19   20   21  119.00   576.7   C- C- C
19   20   30  120.00   505.0   C- C- H
20   21   22  119.00   576.7   C- C- C
20   21   31  121.00   492.5   C- C- H
21   20   30  120.00   505.0   C- C- H
21   22   32  118.00   530.0   C- C- H
22   21   31  121.00   492.5   C- C- H
58 nbend-v
 1    5    6  124.00   646.0   N- C- C
 1    5   23  118.00   530.0   N- C- H
 1    9    8  123.00   636.7   N- C- C
 1    9   10  117.00   580.9   N- C- C
 2    3   15  120.00   608.8   N- N- C
 2   12   11  116.00   571.6   N- C- C
 2   12   13  123.00   636.7   N- C- C
 3    2   12  120.00   608.8   N- N- C
 3   15   14  123.00   636.7   N- C- C
 3   15   16  116.00   571.6   N- C- C
 4   18   17  117.00   580.9   N- C- C
 4   18   19  123.00   636.7   N- C- C
 4   22   21  124.00   646.0   N- C- C
 4   22   32  118.00   530.0   N- C- H
 5    1    9  118.00   590.2   C- N- C
 5    6    7  119.00   576.7   C- C- C
 5    6   24  121.00   492.5   C- C- H
 6    5   23  118.00   530.0   C- C- H
 6    7    8  120.00   583.8   C- C- C
 6    7   25  120.00   505.0   C- C- H
 7    6   24  121.00   492.5   C- C- H
 7    8    9  117.00   562.7   C- C- C
 7    8   13  123.00   604.8   C- C- C
 8    7   25  120.00   505.0   C- C- H
 8    9   10  120.00   583.8   C- C- C
 8   13   12  117.00   562.7   C- C- C
 8   13   14  127.00   632.9   C- C- C
 9    8   13  119.00   576.7   C- C- C
 9   10   11  121.00   590.8   C- C- C
 9   10   26  120.00   505.0   C- C- H
10   11   12  121.00   590.8   C- C- C
10   11   27  120.00   505.0   C- C- H
11   10   26  120.00   505.0   C- C- H
11   12   13  121.00   590.8   C- C- C
12   11   27  120.00   505.0   C- C- H
12   13   14  115.00   548.7   C- C- C
13   14   15  116.00   555.7   C- C- C
13   14   19  127.00   632.9   C- C- C
14   15   16  121.00   590.8   C- C- C
14   19   18  119.00   576.7   C- C- C
14   19   20  124.00   611.8   C- C- C
15   14   19  117.00   562.7   C- C- C
15   16   17  121.00   590.8   C- C- C
15   16   28  120.00   505.0   C- C- H
16   17   18  120.00   583.8   C- C- C
16   17   29  120.00   505.0   C- C- H
17   16   28  120.00   505.0   C- C- H
17   18   19  120.00   583.8   C- C- C
18    4   22  117.00   580.9   C- N- C
18   17   29  120.00   505.0   C- C- H
18   19   20  116.00   555.7   C- C- C
19   20   21  120.00   583.8   C- C- C
19   20   30  120.00   505.0   C- C- H
20   21   22  119.00   576.7   C- C- C
20   21   31  120.00   505.0   C- C- H
21   20   30  120.00   505.0   C- C- H
21   22   32  118.00   530.0   C- C- H
22   21   31  120.00   505.0   C- C- H
46 ntors-u
 1    5    6    7  50.00   -1.0    1.0   N- C- C- C
 5    6    7    8  50.00   -1.0    1.0   C- C- C- C
 6    7    8    9  50.00   -1.0    1.0   C- C- C- C
 7    8    9    1  50.00   -1.0    1.0   C- C- C- N
 8    9    1    5  50.00   -1.0    1.0   C- C- N- C
 9    1    5    6  50.00   -1.0    1.0   C- N- C- C
 5    1    6   23 100.00   -1.0    1.0   C- N- C- H
 6    5    7   24 100.00   -1.0    1.0   C- C- C- H
 7    6    8   25 100.00   -1.0    1.0   C- C- C- H
 8    9   10   11  50.00   -1.0    1.0   C- C- C- C
 9   10   11   12  50.00   -1.0    1.0   C- C- C- C
10   11   12   13  50.00   -1.0    1.0   C- C- C- C
11   12   13    8  50.00   -1.0    1.0   C- C- C- C
12   13    8    9  50.00   -1.0    1.0   C- C- C- C
10    9   11   26 100.00   -1.0    1.0   C- C- C- H
11   10   12   27 100.00   -1.0    1.0   C- C- C- H
 2    3   15   14  50.00   -1.0    1.0   N- N- C- C
 3   15   14   13  50.00   -1.0    1.0   N- C- C- C
15   14   13   12  50.00   -1.0    1.0   C- C- C- C
12    2    3   15  50.00   -1.0    1.0   C- N- N- C
 2    3   13   12 100.00   -1.0    1.0   N- N- C- C
 3    2   14   15 100.00   -1.0    1.0   N- N- C- C
13   12    2    3  50.00   -1.0    1.0   C- C- N- N
14   15   16   17  50.00   -1.0    1.0   C- C- C- C
15   16   17   18  50.00   -1.0    1.0   C- C- C- C
16   17   18   19  50.00   -1.0    1.0   C- C- C- C
17   18   19   14  50.00   -1.0    1.0   C- C- C- C
18   19   14   15  50.00   -1.0    1.0   C- C- C- C
16   15   17   28 100.00   -1.0    1.0   C- C- C- H
17   16   18   29 100.00   -1.0    1.0   C- C- C- H
18   19   20   21  50.00   -1.0    1.0   C- C- C- C
19   20   21   22  50.00   -1.0    1.0   C- C- C- C
20   21   22    4  50.00   -1.0    1.0   C- C- C- N
21   22    4   18  50.00   -1.0    1.0   C- C- N- C
22    4   18   19  50.00   -1.0    1.0   C- N- C- C
20   19   21   30 100.00   -1.0    1.0   C- C- C- H
21   20   22   31 100.00   -1.0    1.0   C- C- C- H
```

```
 22   4  21  32 100.00   -1.0    1.0   C- N- C- H
  8   7   9  13 100.00   -1.0    1.0   C- C- C- C
  9   1   8  10 100.00   -1.0    1.0   C- N- C- C
 12   2  11  13 100.00   -1.0    1.0   C- N- C- C
 13   8  12  14 100.00   -1.0    1.0   C- C- C- C
 14  13  15  19 100.00   -1.0    1.0   C- C- C- C
 15   3  14  16 100.00   -1.0    1.0   C- N- C- C
 18   4  17  19 100.00   -1.0    1.0   C- N- C- C
 19  14  18  20 100.00   -1.0    1.0   C- C- C- C
  46  ntors-v
  1   5   6   7  50.00   -1.0    1.0   N- C- C- C
  5   6   7   8  50.00   -1.0    1.0   C- C- C- C
  6   7   8   9  50.00   -1.0    1.0   C- C- C- C
  7   8   9   1  50.00   -1.0    1.0   C- C- C- N
  8   9   1   5  50.00   -1.0    1.0   C- C- N- C
  9   1   5   6  50.00   -1.0    1.0   C- N- C- C
  5   1   6  23 100.00   -1.0    1.0   C- N- C- H
  6   5   7  24 100.00   -1.0    1.0   C- C- C- H
  7   6   8  25 100.00   -1.0    1.0   C- C- C- H
  8   9  10  11  50.00   -1.0    1.0   C- C- C- C
  9  10  11  12  50.00   -1.0    1.0   C- C- C- C
 10  11  12  13  50.00   -1.0    1.0   C- C- C- C
 11  12  13   8  50.00   -1.0    1.0   C- C- C- C
 12  13   8   9  50.00   -1.0    1.0   C- C- C- C
 10   9  11  26 100.00   -1.0    1.0   C- C- C- H
 11  10  12  27 100.00   -1.0    1.0   C- C- C- H
  2   3  15  14  50.00   -1.0    1.0   N- N- C- C
  3  15  14  13  50.00   -1.0    1.0   N- C- C- C
 15  14  13  12  50.00   -1.0    1.0   C- C- C- C
 12   2   3  15  50.00   -1.0    1.0   C- N- N- C
  2   3  13  12 100.00   -1.0    1.0   N- N- C- C
  3   2  14  15 100.00   -1.0    1.0   N- N- C- C
 13  12   2   3  50.00   -1.0    1.0   C- C- N- N
 14  15  16  17  50.00   -1.0    1.0   C- C- C- C
 15  16  17  18  50.00   -1.0    1.0   C- C- C- C
 16  17  18  19  50.00   -1.0    1.0   C- C- C- C
 17  18  19  14  50.00   -1.0    1.0   C- C- C- C
 18  19  14  15  50.00   -1.0    1.0   C- C- C- C
 16  15  17  28 100.00   -1.0    1.0   C- C- C- H
 17  16  18  29 100.00   -1.0    1.0   C- C- C- H
 18  19  20  21  50.00   -1.0    1.0   C- C- C- C
 19  20  21  22  50.00   -1.0    1.0   C- C- C- C
 20  21  22   4  50.00   -1.0    1.0   C- C- C- N
 21  22   4  18  50.00   -1.0    1.0   C- C- N- C
 22   4  18  19  50.00   -1.0    1.0   C- N- C- C
 20  19  21  30 100.00   -1.0    1.0   C- C- C- H
 21  20  22  31 100.00   -1.0    1.0   C- C- C- H
 22   4  21  32 100.00   -1.0    1.0   C- N- C- H
  8   7   9  13 100.00   -1.0    1.0   C- C- C- C
  9   1   8  10 100.00   -1.0    1.0   C- N- C- C
 12   2  11  13 100.00   -1.0    1.0   C- N- C- C
 13   8  12  14 100.00   -1.0    1.0   C- C- C- C
 14  13  15  19 100.00   -1.0    1.0   C- C- C- C
 15   3  14  16 100.00   -1.0    1.0   C- N- C- C
 18   4  17  19 100.00   -1.0    1.0   C- N- C- C
 19  14  18  20 100.00   -1.0    1.0   C- C- C- C
   4  nlist-u
7 20 7 30 25 30 25 20
   4  nlist-v
7 20 7 30 25 30 25 20
  0.410   235.0   650.0   77000.0
   0  nextr
```

Table S3. Steering parameters for the MD simulations (valid for both compounds). See MiCMoS user's manual for details. [1,2]

```
 [5] helicenes LJC
# n.steps irvel ipri ibox idistr  timestep Emolim  iengt ibias
   500000     0    0    1    0      0.001   0.0      0     0
# cutoffu cutoffv cutoffuv factin  ipots   ianh  inano
   16.0    16.0    16.0       0.7      1      0     0
#  N(T)   Tset Tstart  Trelax  itrel
   250   298   298    0.6      2
#  N(P)   Pset  comprs   ianis  ipr  ww   iextstr
   200    1.0   0.00      1      1   4.0    0
#  N(com)  nwbox   nwre  npri
     50    1000   1000   1000
```

Table S4. Comparison of the unit cells of the title compounds as predicted by MiCMoS MD simulations with the LJC force field [3] and the available single crystal X-ray data.

	DNH, MD	DNH (BOLMEV) [4]	Δ %	DNH(Expt, this work)	Δ %	TNH, MD	TNH(Expt, this work)	Δ %
a / Å	16.396(15)	15.7823(7)	3.9	15.8246(2)	3.6	14.49(2)	14.1140(1)	2.6
b / Å	8.700(8)	8.7508(4)	-0.6	8.7636(10)	-0.7	17.57(2)	17.5038(1)	0.4
c / Å	19.682(19)	19.8826(9)	-1.0	19.9202(3)	-1.2	10.86(1)	11.2428(1)	-3.4
α / deg	90.26(8)	90	0.3	90	0.3	89.87(8)	90	-0.1
β / deg	89.51(14)	90	-0.5	90	-0.5	106.22(14)	107.4440(1)	-1.1
γ / deg	90.19(9)	90	0.2	90	0.2	89.20(11)	90	-0.9
ρ / g·cm^{-3}	1.326(2)	1.356	-2.2	1.348	-1.6	1.414(2)	1.415	-0.1

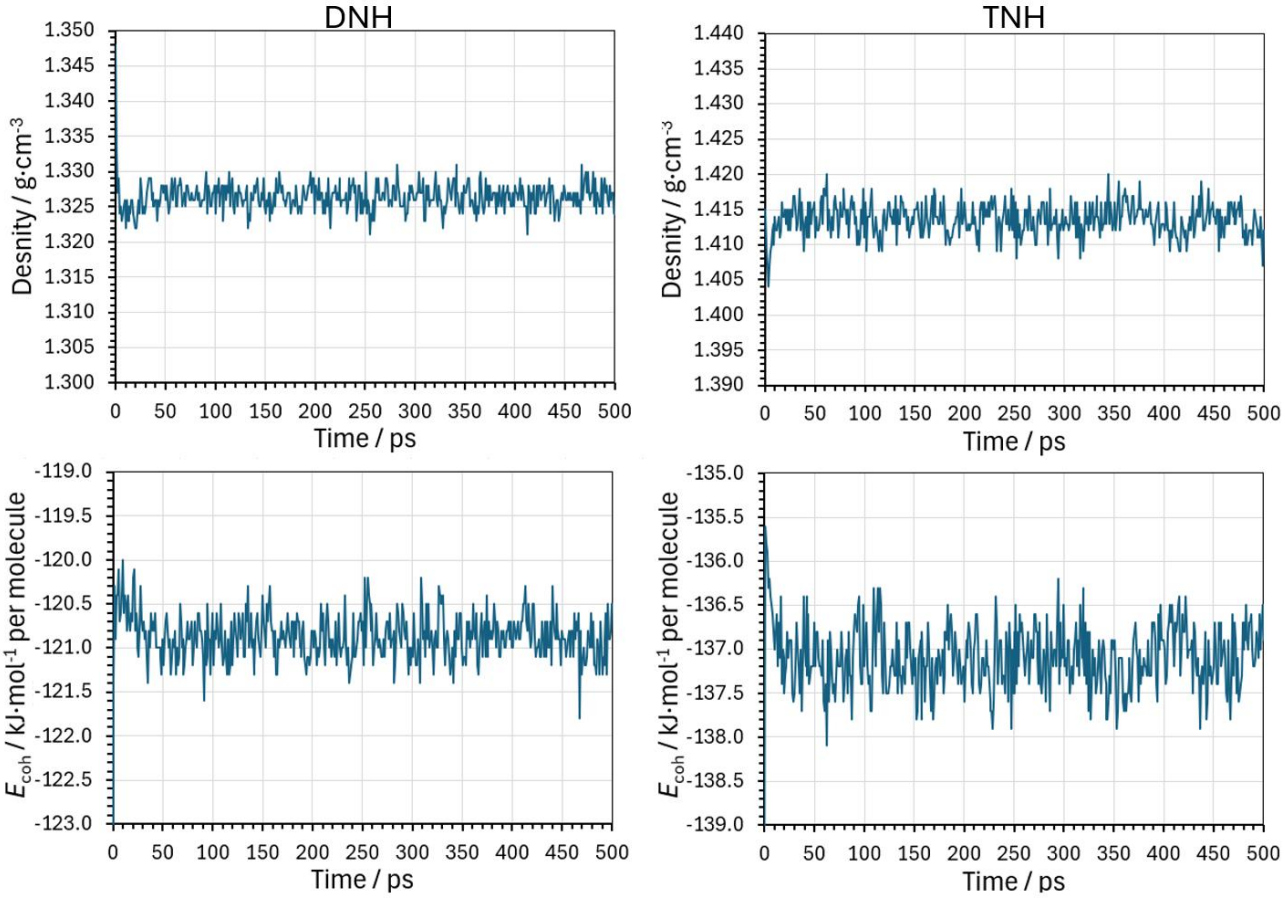


Figure S1. Convergence of crystal cohesive energies (kJ·mol^{-1} per molecule) and densities (g·cm^{-3}) in MiCMoS MD simulations.

Section S2. Databank search

Table S5. Conquest [5] search of the Cambridge Structural Database (v5.46, last update: February 2025) looking for [5]helicene structures with possible heteroatom and/or substituents in positions 4,7,8 and 11. DIHEDRAL: angle between the least-squares planes describing the terminal aromatic rings. DIST_1-14: distance between atoms 1 and 14 (conventional numbering, see Tables S1 and S2 and Scheme 1 in the main text). Multiple molecules in the same asymmetric unit are referred to as "fragments".

CCDC refcode	Fragment	DIHEDRAL / deg	DIST_1-14 / Å	CCDC refcode	Fragment	DIHEDRAL / deg	DIST_1-14 / Å
SUFHOU	1	50.995	2.957	DBPHEN04	1	48.288	2.922
ABUMOB	1	46.110	2.950	DBPHEN04	2	50.173	2.950
ACIGIG	1	50.405	2.910	DBPHEN04	3	51.300	2.952
AVUKUA	1	40.829	2.823	DBPHEN05	1	51.941	2.957
AVUKUA	2	51.807	2.964	ECASAE	1	42.677	2.937
AVUKUA	3	54.844	2.969	EQEBUZ	1	53.911	2.966
AVUKUA	4	46.449	2.897	FATROL	1	43.348	2.904
AVUKUA	5	47.582	2.901	NAKLAN	1	51.126	2.964
AVUKUA	6	48.594	2.932	RIPVUK	1	50.537	2.974
AVULAH	1	53.810	2.991	SIFSAE	1	48.756	2.941
AVULAH	2	49.545	2.933	UFENOM	1	38.332	2.847
AVULEL	1	55.219	2.990	UTAHUU	1	53.096	2.969
AVULEL	2	49.120	2.906	WEVXUT	1	51.396	2.918
AVULIP	1	48.650	2.930	WEVXUT	2	51.023	2.935
AVULIP	2	55.410	2.985	WEVXUT	3	55.544	3.028
BOLMEV	1	48.045	2.915	WEVYAA	1	48.938	2.930
BUJGUL	1	52.950	2.952	WEVYAA	2	49.527	2.954
BUWROC	1	47.242	2.970	WEVYAA	3	50.197	2.959
BUWRUI	1	46.782	2.981	WEVYAA	4	48.496	2.950
DARXOK	1	56.430	2.976	WOFKIP	1	53.665	2.973
DBPHEN02	1	47.301	2.922	WOFKOV	1	46.541	2.888
DBPHEN03	1	50.549	2.954	XINLIS	1	60.164	3.058
DBPHEN03	2	48.874	2.925				

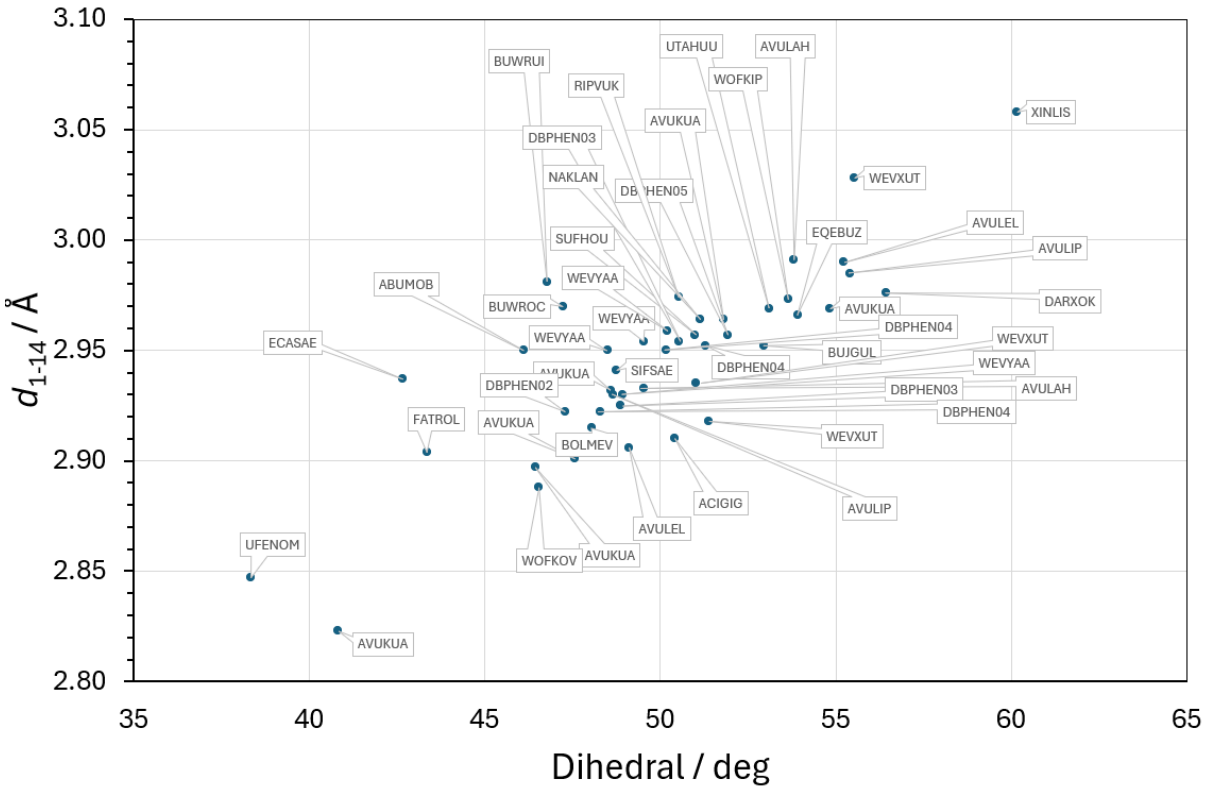
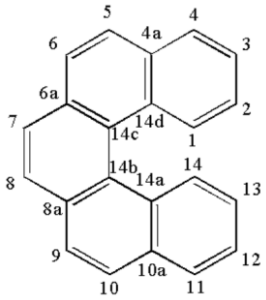


Figure S2. Scatterplot of geometrical data shown in Table S5 SI, i.e. distance 1-14 and dihedral angle between terminal aromatic rings of the [5]helicene structure. Refer to Tables S1 and S2 and to Scheme 1 in the main text for conventional atom numbering. Callouts highlight CCDC reference codes.

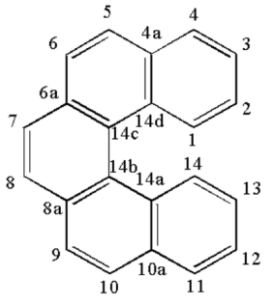
Section S3. Geometrical and structural analysis of title compounds

Table S6. Covalent bond distances for the two symmetry-independent molecules in the ASU of TNH, with the corresponding estimated standard deviations. Conventional labels refer to the scheme below (see also Scheme 1 in the main text). X-ray labels refer to numbering in Figure 1 (main text).



Molecule B (Figure 1, main text)						Molecule C (Figure 1, main text)					
Conventional labels		X-ray		d / Å	σ(d) / Å	Conventional labels		X-ray		d / Å	σ(d) / Å
11	12	N1	C1	1.3150	0.0019	11	12	N21	C21	1.3220	0.0020
11	10a	N1	C5	1.3624	0.0017	11	10a	N21	C25	1.3617	0.0017
8	7	N2	N3	1.3038	0.0017	8	7	N22	N23	1.3033	0.0019
8	8a	N2	C8	1.3720	0.0017	8	8a	N22	C28	1.3728	0.0017
7	6a	N3	C11	1.3645	0.0017	7	6a	N23	C31	1.3704	0.0017
4	3	N4	C18	1.3170	0.0020	4	3	N24	C38	1.3160	0.0019
4	4a	N4	C14	1.3560	0.0017	4	4a	N24	C34	1.3630	0.0017
12	13	C1	C2	1.3973	0.0019	12	13	C21	C22	1.3880	0.0020
13	14	C2	C3	1.3640	0.0016	13	14	C22	C23	1.3679	0.0016
14	14a	C3	C4	1.4068	0.0016	14	14a	C23	C24	1.4083	0.0016
14a	10a	C4	C5	1.4195	0.0016	14a	10a	C24	C25	1.4153	0.0016
14a	14b	C4	C9	1.4504	0.0016	14a	14b	C24	C29	1.4521	0.0015
10a	10	C5	C6	1.4345	0.0019	10a	10	C25	C26	1.4316	0.0019
10	9	C6	C7	1.3390	0.0020	10	9	C26	C27	1.3440	0.0020
9	8a	C7	C8	1.4284	0.0019	9	8a	C27	C28	1.4290	0.0020
8a	14b	C8	C9	1.4125	0.0016	8a	14b	C28	C29	1.4111	0.0015
14b	14c	C9	C10	1.4254	0.0016	14b	14c	C29	C30	1.4273	0.0016
14c	6a	C10	C11	1.4117	0.0015	14c	6a	C30	C31	1.4088	0.0015
14c	14d	C10	C15	1.4528	0.0016	14c	14d	C30	C35	1.4485	0.0015
6a	6	C11	C12	1.4266	0.0018	6a	6	C31	C32	1.4290	0.0020
6	5	C12	C13	1.3350	0.0020	6	5	C32	C33	1.3400	0.0020
5	4a	C13	C14	1.4306	0.0019	5	4a	C33	C34	1.4293	0.0019
4a	14d	C14	C15	1.4171	0.0016	4a	14d	C34	C35	1.4168	0.0016
14d	1	C15	C16	1.4084	0.0016	14d	1	C35	C36	1.4073	0.0016
1	2	C16	C17	1.3693	0.0018	1	2	C36	C37	1.3673	0.0016
2	3	C17	C18	1.3920	0.0020	2	3	C37	C38	1.3890	0.0020

Table S7. Same as Table S6 above, for DNH. The data of DNH are compared with the average from the two symmetry-independent molecules of TNH (Table S6 SI). The structural parameters are very similar in DNH and TNH, with significant differences in the region where nitrogen substitution in positions 7 and 8 takes place (entries highlighted in bold).



DNH, molecule A (Figure 1, main text)						TNH, average from molecules B and C in Table S6 SI					
Conventional labels		X-ray		d / Å	σ(d) / Å	Conventional labels		X-ray		d / Å	σ(d) / Å
11	12	N1	C1	1.3180	0.0020	11	12	N1	C1	1.3185	0.0014
11	10a	N1	C5	1.3601	0.0018	11	10a	N1	C5	1.3621	0.0012
8	**7**	**C19**	**C20**	**1.3510**	**0.0020**	**8**	**7**	**N2**	**N3**	**1.3036**	**0.0013**
8	**8a**	**C19**	**C8**	**1.4210**	**0.0020**	**8**	**8a**	**N2**	**C8**	**1.3724**	**0.0012**
7	**6a**	**C20**	**C11**	**1.4176**	**0.0018**	**7**	**6a**	**N3**	**C11**	**1.3675**	**0.0012**
4	3	N2	C18	1.3133	0.0017	4	3	N4	C18	1.3165	0.0014
4	4a	N2	C14	1.3634	0.0015	4	4a	N4	C14	1.3595	0.0012
12	13	C1	C2	1.3995	0.0019	12	13	C1	C2	1.3927	0.0014
13	14	C2	C3	1.3685	0.0016	13	14	C2	C3	1.3660	0.0011
14	14a	C3	C4	1.4069	0.0016	14	14a	C3	C4	1.4076	0.0011
14a	10a	C4	C5	1.4215	0.0015	14a	10a	C4	C5	1.4174	0.0011
14a	14b	C4	C9	1.4518	0.0016	14a	14b	C4	C9	1.4513	0.0011
10a	10	C5	C6	1.4250	0.0020	10a	10	C5	C6	1.4331	0.0013
10	9	C6	C7	1.3450	0.0020	10	9	C6	C7	1.3415	0.0014
9	8a	C7	C8	1.4290	0.0020	9	8a	C7	C8	1.4287	0.0014
8a	**14b**	**C8**	**C9**	**1.4144**	**0.0016**	**8a**	**14b**	**C8**	**C9**	**1.4118**	**0.0011**
14b	**14c**	**C9**	**C10**	**1.4438**	**0.0015**	**14b**	**14c**	**C9**	**C10**	**1.4264**	**0.0011**
14c	**6a**	**C10**	**C11**	**1.4156**	**0.0015**	**14c**	**6a**	**C10**	**C11**	**1.4103**	**0.0011**
14c	14d	C10	C15	1.4506	0.0015	14c	14d	C10	C15	1.4507	0.0011
6a	6	C11	C12	1.4258	0.0018	6a	6	C11	C12	1.4278	0.0013
6	5	C12	C13	1.3444	0.0019	6	5	C12	C13	1.3375	0.0014
5	4a	C13	C14	1.4225	0.0016	5	4a	C13	C14	1.4300	0.0013
4a	14d	C14	C15	1.4198	0.0014	4a	14d	C14	C15	1.4170	0.0011
14d	1	C15	C16	1.4110	0.0015	14d	1	C15	C16	1.4079	0.0011
1	2	C16	C17	1.3656	0.0015	1	2	C16	C17	1.3683	0.0012
2	3	C17	C18	1.3985	0.0016	2	3	C17	C18	1.3905	0.0014

Table S8. Analysis of stacking interactions, as performed with the aromatic analyser tool of Mercury. [6] Refer to Figure 3 in the main text to identify the centroids of the aromatic rings.

Centroids	Distance / Å	Relative orientation between ring normals / deg	Stacking interaction score [a]	Classification
DNH				
2-18	4.86	36.74	7.7	Strong
3-18	5.39	45.83	6.8	Moderate
1-19	5.32	0.00	6.6	Moderate
2-17	5.69	31.47	5.5	Moderate
2-16	5.90	29.35	4.7	Moderate
TNH				
1-6	4.10	22.79	9.2	Strong
2-5	4.10	22.79	9.2	Strong
1-4	4.44	26.45	8.5	Strong
2-3	3.99	22.56	8.1	Strong
2-4	5.25	3.80	6.5	Moderate
1-5	5.44	0.00	6.1	Moderate
2-6	6.38	0.00	3.7	Moderate

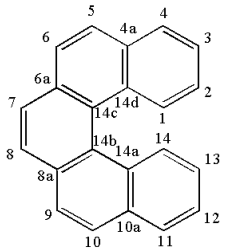
[a] This value is based on geometric descriptors of different π···π interactions. The "score" ranges from 0 to 10 and quantifies the similarity of the specific ring-ring geometry with highly stabilized benzene-benzene pairs, whose energies are computed by quantum chemical methods in the gas phase. A "score" higher than 7 marks allegedly "strong" stacking interactions, which are likely to be significantly stabilizing and potentially structure-directing. A "score" between 3 and 7 indicates that the strength is "moderate", which might imply still stabilizing interactions, with less-than-optimal geometries. Further contacts in this structure have scores below 3.0.

Table S9. Geometrical descriptors for relevant and CH···N hydrogen bonded contacts in DNH and TNH. See Figures 1 and 3 in the main text for more information.

D–H···A	$d_{D–H}$, Å	$d_{H···A}$, Å	$d_{D···A}$, Å	α_{DHA}, deg	Symmetry operation
DNH, $P2_1/c$					
C1–H1···N2	0.963(14)	2.476(14)	3.4270(18)	169.1(9)	x,1/2-y,-1/2+z
TNH, Pbca					
C1–H1···N22	0.973(12)	2.613(12)	3.5411(19)	159.4(5)	x,3/2-y,-1/2+z
C21-H21···N3	0.975(10)	2.586(11)	3.5054(19)	157.3(7)	x,1/2-y,1/2+z

Section S4. Packing energies

Table S10. Atomic CHelpG ESP charges from the fit against quantum electrostatic potential, as evaluated at the MP2/6-31G(p,d) level of theory on isolated molecules at their X-ray geometries.



	DNH	A (M)	TNH	B (P)	C (M)	Average B-C
Conventional numbering	Atom	Charge / *e*	Atom	Charge / *e*	Charge / *e*	Charge / *e*
1	C	0.17530	C	0.23339	0.22379	0.22859
2	C	-0.47540	C	-0.55325	-0.52661	-0.53993
3	C	0.45324	C	0.55523	0.52629	0.54076
4	N	-0.69809	N	-0.70309	-0.68582	-0.69445
5	C	-0.33511	C	-0.07246	-0.07160	-0.07203
6	C	-0.16632	C	-0.52230	-0.51252	-0.51741
7	C	-0.19083	N	-0.37089	-0.35739	-0.36414
8	C	-0.12884	N	-0.35704	-0.36647	-0.36175
9	C	-0.14506	C	-0.50030	-0.48263	-0.49146
10	C	-0.34107	C	-0.07822	-0.10190	-0.09006
11	N	-0.70098	N	-0.68281	-0.70061	-0.69171
12	C	0.45327	C	0.52715	0.54845	0.53780
13	C	-0.47243	C	-0.52807	-0.55586	-0.54196
14	C	0.18379	C	0.22335	0.25568	0.23952
10a	C	0.67956	C	0.47584	0.50141	0.48863
14a	C	-0.30838	C	-0.19925	-0.20081	-0.20003
14b	C	0.06164	C	-0.16469	-0.22214	-0.19341
14c	C	-0.04446	C	-0.24899	-0.16887	-0.20893
14d	C	-0.27222	C	-0.16609	-0.19067	-0.17838
4a	C	0.67381	C	0.48087	0.47377	0.47732
6a	C	0.14185	C	0.73965	0.70094	0.72030
8a	C	0.06004	C	0.69646	0.70733	0.70189
1	H	0.07107	H	0.06819	0.06327	0.06573
2	H	0.17778	H	0.19309	0.18920	0.19114
3	H	0.01900	H	0.00011	0.00728	0.00370
5	H	0.17004	H	0.14689	0.14317	0.14503
6	H	0.14020	H	0.20242	0.20263	0.20252
7	H	0.12600	-	-	-	-
8	H	0.11777	-	-	-	-
9	H	0.13864	H	0.19792	0.19570	0.19681
10	H	0.17120	H	0.14620	0.15135	0.14877
12	H	0.02023	H	0.00507	0.00305	0.00406
13	H	0.17428	H	0.19054	0.19347	0.19200
14	H	0.07049	H	0.06507	0.05710	0.06109

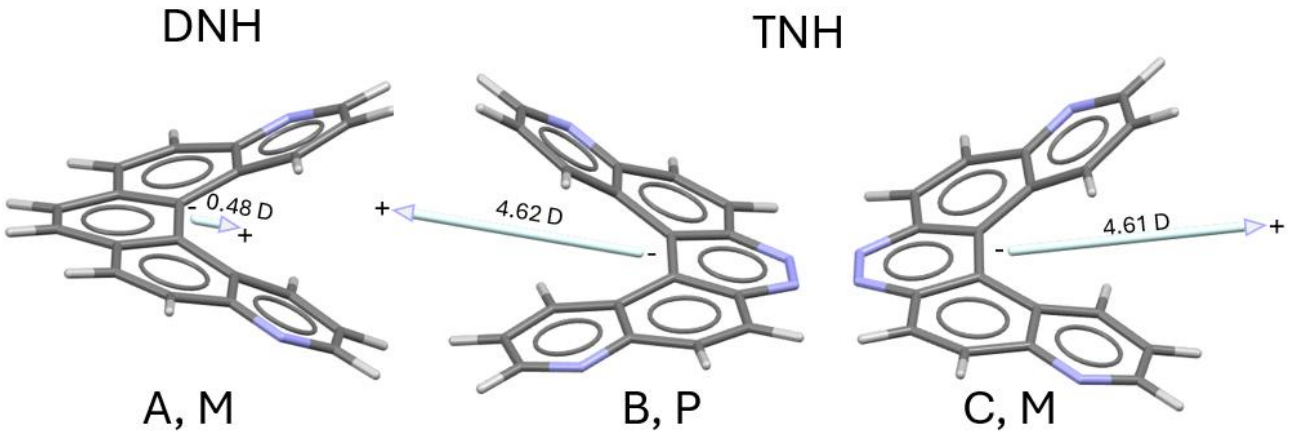


Figure S3. Dipole moments, as computed at the MP2/6-31G(p,d) level of theory for isolated symmetry-independent molecules in DNH and TNH. The length of the vectors corresponds to the dipole vector module in units of debye (D), where 1 D = $3.336 \cdot 10^{-30}$ C·m. The origin is arbitrarily set at the centre of mass coordinates.

Table S11. Molecule-molecule interaction energies (kJ·mol^{-1}) for DNH, as computed on the static experimental X-ray structure by PIXEL. In bold: hydrogen-bonded molecules (see also Table S9).

Symmetry matrix representation[a]									Translations			d_{COM}	E_c	E_{pol}	E_{disp}	E_{rep}	E_{tot}	Molecules[b]
Heterochiral pairs																		
-1	0	0	0	1	0	0	0	-1	0	0.5	0.5	7.368	-6.6	-4.2	-36.3	23.3	-23.8	A...A
-1	0	0	0	-1	0	0	0	-1	0	0	0	9.826	-3.6	-1.3	-13.6	6.8	-11.6	A...A
-1	0	0	0	1	0	0	0	1	-1	-0.5	0	5.964	-10.8	-5.1	-50.5	27.7	-38.7	A...A
-1	0	0	0	-1	0	0	0	1	-1	1	-0.5	10.865	1.5	-0.4	-5.8	1.3	-3.5	A...A
-1	0	0	0	-1	0	0	0	1	-1	1	0.5	10.865	1.5	-0.4	-5.8	1.3	-3.5	A...A
-1	0	0	0	1	0	0	0	-1	0	-0.5	0.5	7.368	-6.6	-4.2	-36.3	23.3	-23.8	A...A
-1	0	0	0	-1	0	0	0	-1	0	1	0	6.884	-7.4	-6.3	-42.9	17.7	-38.8	A...A
1	**0**	**0**	**0**	**-1**	**0**	**0**	**0**	**1**	**0**	**0.5**	**-0.5**	**10.347**	**-3.9**	**-1.3**	**-12.1**	**4.6**	**-12.9**	**A...A**
1	**0**	**0**	**0**	**-1**	**0**	**0**	**0**	**1**	**0**	**0.5**	**0.5**	**10.347**	**-3.9**	**-1.3**	**-12.1**	**4.6**	**-12.9**	**A...A**
1	0	0	0	-1	0	0	0	1	0	1.5	-0.5	11.607	-14.6	-5.8	-13.8	19	-15.2	A...A
1	0	0	0	-1	0	0	0	1	0	1.5	0.5	11.607	-14.6	-5.8	-13.8	19	-15.2	A...A
-1	0	0	0	1	0	0	0	1	-1	0.5	0	5.964	-10.8	-5.1	-50.5	27.6	-38.7	A...A
Homochiral pairs																		
1	0	0	0	1	0	0	0	1	0	-1	0	8.764	-4.3	-2.1	-23.1	11.6	-17.9	A...A
1	0	0	0	1	0	0	0	1	0	1	0	8.764	-4.3	-2.1	-23.1	11.6	-17.9	A...A

[a] The first 9 entries give the rotation matrix, written per rows. The next 3 entries give the *a*, *b*, *c* components of the translation vector in fractional coordinates.
[b] See Figure 1 in the main text for label meaning.

Table S12. Molecule-molecule interaction energies (kJ·mol^{-1}) for TNH (heterochiral pairs), as computed on the static experimental X-ray structure by PIXEL.

Symmetry matrix representation[a]									Translations			d_{COM}	E_c	E_{pol}	E_{disp}	E_{rep}	E_{tot}	Molecules[b]
-1	0	0	0	-1	0	0	0	-1	0	0	0	4.986	-16.6	-6.6	-64.6	31.9	-55.9	B...B
-1	0	0	0	1	0	0	0	-1	0	-0.5	-0.5	10.065	-4.7	-2	-7.9	2.6	-12	B...B
-1	0	0	0	1	0	0	0	-1	0	0.5	-0.5	10.065	-4.7	-2	-7.9	2.6	-12	B...B
-1	0	0	0	-1	0	0	0	-1	0	0	-1	10.348	-6.8	-3.1	-19.2	11.9	-17.2	B...B
1	0	0	0	-1	0	0	0	1	0	0.5	-0.5	7.966	-11.5	-7.2	-40.4	27.4	-31.8	B...B
1	0	0	0	-1	0	0	0	1	0	0.5	0.5	7.966	-11.5	-7.2	-40.4	27.4	-31.8	B...B
1	0	0	0	1	0	0	0	1	0	0	0	5.093	-14	-5.8	-59.8	28.6	-51.1	B...C
1	0	0	0	1	0	0	0	1	0	0	1	10.789	-1.7	-0.7	-9.5	3	-8.9	B...C
1	0	0	0	1	0	0	0	1	0	0	-1	10.789	-1.7	-0.7	-9.5	3	-8.9	C...B
1	0	0	0	-1	0	0	0	1	0	-0.5	-0.5	7.549	-16.1	-9.2	-47.1	33.6	-38.9	C...C
-1	0	0	0	1	0	0	0	-1	-1	-0.5	-0.5	10.065	-9.2	-4.1	-12.5	9.9	-16	C...C
-1	0	0	0	1	0	0	0	-1	-1	0.5	-0.5	10.065	-9.2	-4.1	-12.5	9.9	-16	C...C
-1	0	0	0	-1	0	0	0	-1	-1	0	-1	5.264	-12.5	-5.1	-55.3	22.4	-50.4	C...C
-1	0	0	0	-1	0	0	0	-1	-1	0	0	10.607	-2.9	-1.2	-12	5.9	-10.2	C...C
1	0	0	0	-1	0	0	0	1	0	-0.5	0.5	7.549	-16.1	-9.2	-47.1	33.6	-38.9	C...C

[a] The first 9 entries give the rotation matrix, written per rows. The next 3 entries give the *a*, *b*, *c* components of the translation vector in fractional coordinates.
[b] See Figure 1 in the main text for the labelling.

Table S13. Molecule-molecule interaction energies (kJ·mol^{-1}) for TNH (homochiral pairs), as computed on the static experimental X-ray structure by PIXEL. In bold: hydrogen-bonded molecules (see also Table S9).

Symmetry matrix representation[a]									Translations			d_{COM}	E_c	E_{pol}	E_{disp}	E_{rep}	E_{tot}	Molecules[b]
1	0	0	0	1	0	0	0	1	0	0	-1	11.243	0.6	-0.3	-4.5	0.4	-3.8	B...B
1	0	0	0	1	0	0	0	1	0	0	1	11.243	0.6	-0.3	-4.5	0.4	-3.8	B...B
-1	0	0	0	1	0	0	0	-1	-1	0.5	-0.5	8.816	-3.3	-1.4	-13.7	7.7	-10.6	B...C
-1	0	0	0	1	0	0	0	-1	0	0.5	-0.5	8.886	-0.7	-0.9	-8.6	2.3	-7.9	B...C
-1	0	0	0	-1	0	0	0	-1	-1	0	0	10.262	1.4	-0.8	-7.8	2.2	-5	B...C
-1	0	0	0	-1	0	0	0	-1	0	0	-1	10.26	0.9	-1.1	-10	4.6	-5.6	B...C
1	**0**	**0**	**0**	**-1**	**0**	**0**	**0**	**1**	**0**	**-0.5**	**0.5**	**9.966**	**-12.7**	**-5.1**	**-13.8**	**13.5**	**-18**	**B...C**
1	0	0	0	-1	0	0	0	1	0	0.5	0.5	10.484	-5.8	-3.6	-10.7	9.4	-10.7	B...C
1	**0**	**0**	**0**	**-1**	**0**	**0**	**0**	**1**	**0**	**-0.5**	**-0.5**	**9.966**	**-12.7**	**-5.1**	**-13.8**	**13.6**	**-18**	**C...B**
-1	0	0	0	1	0	0	0	-1	-1	-0.5	-0.5	8.816	-3.3	-1.4	-13.7	7.7	-10.6	C...B
-1	0	0	0	1	0	0	0	-1	0	-0.5	-0.5	8.886	-0.7	-0.9	-8.6	2.3	-7.9	C...B
-1	0	0	0	-1	0	0	0	-1	-1	0	0	10.262	1.4	-0.8	-7.8	2.2	-5	C...B
-1	0	0	0	-1	0	0	0	-1	0	0	-1	10.26	0.9	-1.1	-10	4.6	-5.6	C...B
1	**0**	**0**	**0**	**-1**	**0**	**0**	**0**	**1**	**0**	**0.5**	**-0.5**	**10.484**	**-5.8**	**-3.6**	**-10.7**	**9.3**	**-10.8**	**C...B**

[a] The first 9 entries give the rotation matrix, written per rows. The next 3 entries give the *a*, *b*, *c* components of the translation vector in fractional coordinates.
[b] See Figure 1 in the main text for label meaning.

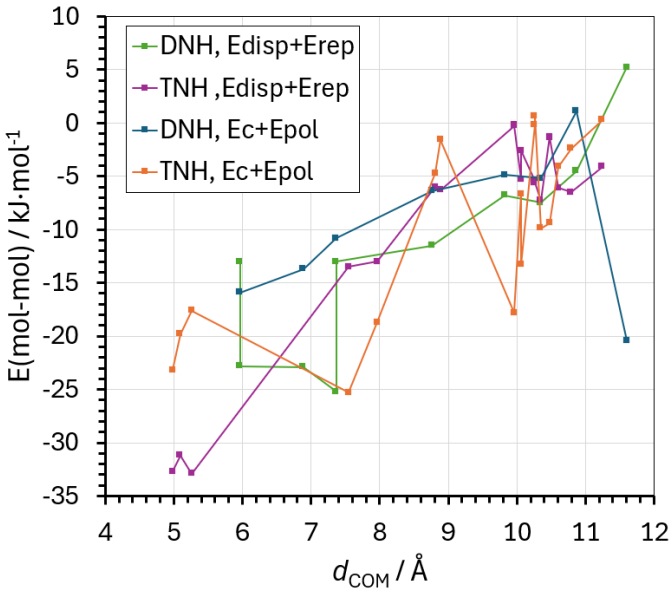


Figure S4. Dispersive and Coulomb/polarization energy contributions for molecule-molecule interactions as a function of the centre of mass distance, as retrieved from PIXEL calculations on the experimental structures. See Figure 3 in the main text for total molecule-molecule energies.

Section S4. Crystal structure prediction of homochiral systems

Table S14. Input parameters (file *.sci*) for the SC-MC algorithm applied to the title compounds. [7] See the SC-MC users' manual for details. [8]

DNH:

```
title = CSP_diaza
molname = diaza5helicene
molcode = diaza

seeds
   maxseed = 200

spacegroup = 4 19

forcefield
   ff = ljc

mc
   temp = 298
   pre_n_cyc = 1000
   pre_print_traj = 500
   pre_print = 500
   n_cyc = 10000
   print_traj = 1000
   print = 1000
```

TNH:

```
title = CSP_tetraaza
molname = tetraaza5helicene
molcode = tetraaza

seeds
   maxseed = 200

spacegroup = 4 19

forcefield
   ff = ljc

mc
   temp = 298
   pre_n_cyc = 1000
   pre_print_traj = 500
   pre_print = 500
   n_cyc = 10000
   print_traj = 1000
   print = 1000
```

Table S15. First 20 unique SC-MC predictions for DNH, ranked in increasing order of cohesive energies (E_{coh}), for space groups (Sg) 4 ($P2_1$) and 19 ($P2_12_12_1$). Measure units are kJ·mol^{-1} per molecule, Å, deg, Å^3 and g·cm^{-3}.

Sg	E_{coh}	*a*	*b*	*c*	α	β	γ	volume	density	C_{pack}
4	-112.77	4.3719	12.013	14.3541	90	98.4826	90	745.6305	1.2486	0.6796
4	-112.503	10.9343	13.1931	5.2431	90	94.9676	90	753.5129	1.2356	0.6725
4	-110.434	4.5701	10.1195	16.5509	90	98.3803	90	757.2602	1.2295	0.6692
4	-109.351	4.5821	12.9085	13.1767	90	97.6136	90	772.5086	1.2052	0.656
4	-107.371	10.4474	15.9545	4.4698	90	99.0616	90	735.7471	1.2654	0.6888
4	-107.332	8.6572	19.3356	4.618	90	99.3663	90	762.7084	1.2207	0.6644
4	-106.318	8.6009	20.4603	4.3287	90	101.7902	90	745.6787	1.2486	0.6796
4	-105.537	7.6871	11.9619	8.7053	90	103.6527	90	777.8628	1.1969	0.6515
4	-105.422	5.124	9.8184	15.8327	90	102.2909	90	778.2733	1.1963	0.6511
4	-104.269	10.8494	15.9687	4.5907	90	103.5974	90	773.049	1.2044	0.6555
4	-102.277	11.4867	6.4405	11.0913	90	105.0469	90	792.3957	1.175	0.6395
4	-102.238	6.9475	13.2724	8.6754	90	94.6298	90	797.3452	1.1677	0.6356
4	-101.078	8.5948	7.9173	11.6461	90	103.2178	90	771.4927	1.2068	0.6568
4	-100.201	5.6793	13.3913	10.9715	90	102.4163	90	814.8977	1.1425	0.6219
4	-99.8436	12.0555	16.0362	4.3732	90	95.5594	90	841.477	1.1064	0.6022
4	-99.6935	12.0465	6.6425	10.1255	90	95.6474	90	806.2938	1.1547	0.6285
4	-99.5382	10.8815	8.3812	8.7499	90	104.4488	90	772.7507	1.2048	0.6558
4	-99.012	12.2209	5.5896	11.854	90	96.2174	90	804.9812	1.1566	0.6295
4	-98.9152	8.3711	11.5176	8.3838	90	95.1445	90	805.0615	1.1565	0.6295
4	-98.8558	5.0796	18.1378	8.5185	90	100.1583	90	772.5244	1.2052	0.656
19	-114.573	18.2126	18.7168	4.2991	90	90	90	1465.47	1.2706	0.6916
19	-114.362	12.6054	7.4962	15.423	90	90	90	1457.373	1.2777	0.6954
19	-113.359	8.547	14.1112	13.1812	90	90	90	1589.765	1.1713	0.6375
19	-113.199	19.059	9.4188	8.3725	90	90	90	1502.973	1.2389	0.6743
19	-112.932	12.3361	8.1253	15.1954	90	90	90	1523.112	1.2225	0.6654
19	-111.445	15.5264	10.9588	8.9462	90	90	90	1522.2	1.2233	0.6658
19	-110.881	8.3456	19.6363	9.0814	90	90	90	1488.24	1.2512	0.681
19	-110.791	17.1122	10.2277	8.6518	90	90	90	1514.242	1.2297	0.6693
19	-107.989	5.3784	31.8455	9.0632	90	90	90	1552.326	1.1995	0.6529
19	-107.691	9.0196	21.8133	7.6099	90	90	90	1497.225	1.2437	0.6769
19	-107.438	9.2243	17.6035	9.5212	90	90	90	1546.051	1.2044	0.6555
19	-107.289	13.5373	11.0406	10.4808	90	90	90	1566.46	1.1887	0.647
19	-107.251	10.4874	13.3803	11.1207	90	90	90	1560.513	1.1932	0.6495
19	-107.128	7.8707	17.0594	11.5665	90	90	90	1553.024	1.199	0.6526
19	-106.811	14.0338	16.5377	6.7152	90	90	90	1558.525	1.1948	0.6503
19	-106.079	19.1394	17.6325	4.4276	90	90	90	1494.208	1.2462	0.6783
19	-105.783	13.09	12.6723	9.1879	90	90	90	1524.089	1.2217	0.665
19	-105.621	10.7252	9.8247	15.1004	90	90	90	1591.164	1.1702	0.637
19	-105.46	7.6035	14.3778	14.8171	90	90	90	1619.845	1.1495	0.6257
19	-105.429	19.8556	13.2574	5.8183	90	90	90	1531.568	1.2158	0.6617

Table S16. First 20 unique SC-MC predictions for TNH, ranked in increasing order of cohesive energies (E_{coh}), for space groups (Sg) 4 ($P2_1$) and 19 ($P2_12_12_1$). Measure units are kJ·mol^{-1} per molecule, Å, deg, Å^3 and g·cm^{-3}.

Sg	E_{coh}	*a*	*b*	*c*	α	β	γ	volume	density	C_{pack}
4	-117.267	8.3358	21.4022	4.2397	90	103.6331	90	735.0605	1.2755	0.6707
4	-113	11.2923	7.2323	9.6403	90	99.2664	90	777.0454	1.2066	0.6345
4	-112.212	17.1816	4.943	8.9439	90	95.2803	90	756.3792	1.2396	0.6518
4	-111.969	11.4177	10.0224	6.4481	90	93.7516	90	736.2854	1.2734	0.6696
4	-111.477	9.5959	7.2487	11.6883	90	103.994	90	788.8894	1.1885	0.625
4	-109.455	8.0677	9.0807	10.6502	90	103.021	90	760.1782	1.2334	0.6486
4	-108.977	23.3677	4.3292	8.2242	90	94.6697	90	829.2338	1.1307	0.5945
4	-106.86	9.3008	7.3099	11.7665	90	100.8438	90	785.6946	1.1933	0.6275
4	-106.711	6.2184	15.0788	8.2819	90	89.7305	90	776.5535	1.2074	0.6349
4	-106.199	9.3593	7.1547	11.9929	90	97.981	90	795.2983	1.1789	0.6199
4	-106.153	21.0169	9.0045	4.0729	90	92.4903	90	770.0615	1.2176	0.6402
4	-103.915	10.2235	13.2612	5.4775	90	90.2092	90	742.6106	1.2626	0.6639
4	-102.895	8.758	11.1155	8.0953	90	94.3377	90	785.8092	1.1932	0.6274
4	-102.76	9.4331	10.708	8.0281	90	102.2267	90	792.5279	1.183	0.6221
4	-102.281	12.2649	9.659	7.1024	90	104.4277	90	814.8604	1.1506	0.605
4	-102.07	4.775	16.3327	9.8208	90	96.24	90	761.3666	1.2315	0.6475
4	-101.982	9.7288	10.661	8.0562	90	101.3983	90	819.099	1.1447	0.6019
4	-101.214	11.1905	17.6804	4.0658	90	100.6818	90	790.4937	1.1861	0.6237
4	-101.115	13.2316	4.4386	13.5333	90	97.1291	90	788.6697	1.1888	0.6251
4	-100.95	10.8762	7.3378	9.9295	90	103.2383	90	771.3895	1.2155	0.6391
19	-129.685	6.98	17.6286	11.6302	90	90	90	1431.071	1.3103	0.689
19	-125.068	15.6976	17.0702	5.4167	90	90	90	1451.474	1.2919	0.6793
19	-124.763	9.7875	14.0167	10.5951	90	90	90	1453.525	1.2901	0.6784
19	-124.124	20.4946	16.8558	4.1326	90	90	90	1427.634	1.3135	0.6907
19	-123.439	4.3557	17.2676	18.603	90	90	90	1399.184	1.3402	0.7047
19	-122.95	8.6248	14.6421	11.7474	90	90	90	1483.523	1.264	0.6647
19	-122.918	9.4153	8.2547	19.1712	90	90	90	1489.992	1.2585	0.6618
19	-122.683	8.2279	15.2737	11.8479	90	90	90	1488.94	1.2594	0.6622
19	-121.952	8.8583	19.1913	8.6266	90	90	90	1466.549	1.2786	0.6724
19	-121.913	12.7159	16.4342	7.1375	90	90	90	1491.564	1.2572	0.6611
19	-120.708	16.7222	14.7019	5.9574	90	90	90	1464.627	1.2803	0.6732
19	-118.874	6.0559	18.6395	12.8052	90	90	90	1445.427	1.2973	0.6822
19	-118.77	14.8111	10.0416	10.079	90	90	90	1499.013	1.2509	0.6578
19	-117.854	13.2271	7.9729	13.5729	90	90	90	1431.384	1.31	0.6889
19	-117.796	8.5173	18.6657	9.4394	90	90	90	1500.698	1.2495	0.6571
19	-117.779	18.0124	9.5182	8.8569	90	90	90	1518.469	1.2349	0.6494
19	-117.506	8.705	8.3093	20.416	90	90	90	1476.738	1.2698	0.6677
19	-117.347	14.9246	11.153	9.1076	90	90	90	1516.01	1.2369	0.6504
19	-117.33	12.6666	8.1185	14.4218	90	90	90	1483.045	1.2644	0.6649
19	-117.211	11.6182	11.6499	11.4078	90	90	90	1544.049	1.2145	0.6386

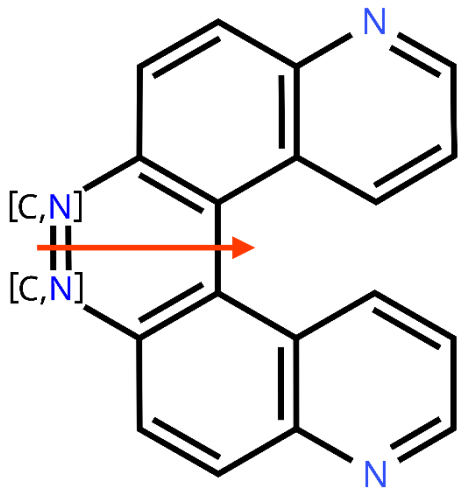


Figure S7. Reference vectors employed to compute rotational correlation functions in MD simulations of the top-ranked predicted structures (see text and MiCMoS users' manual [1]).

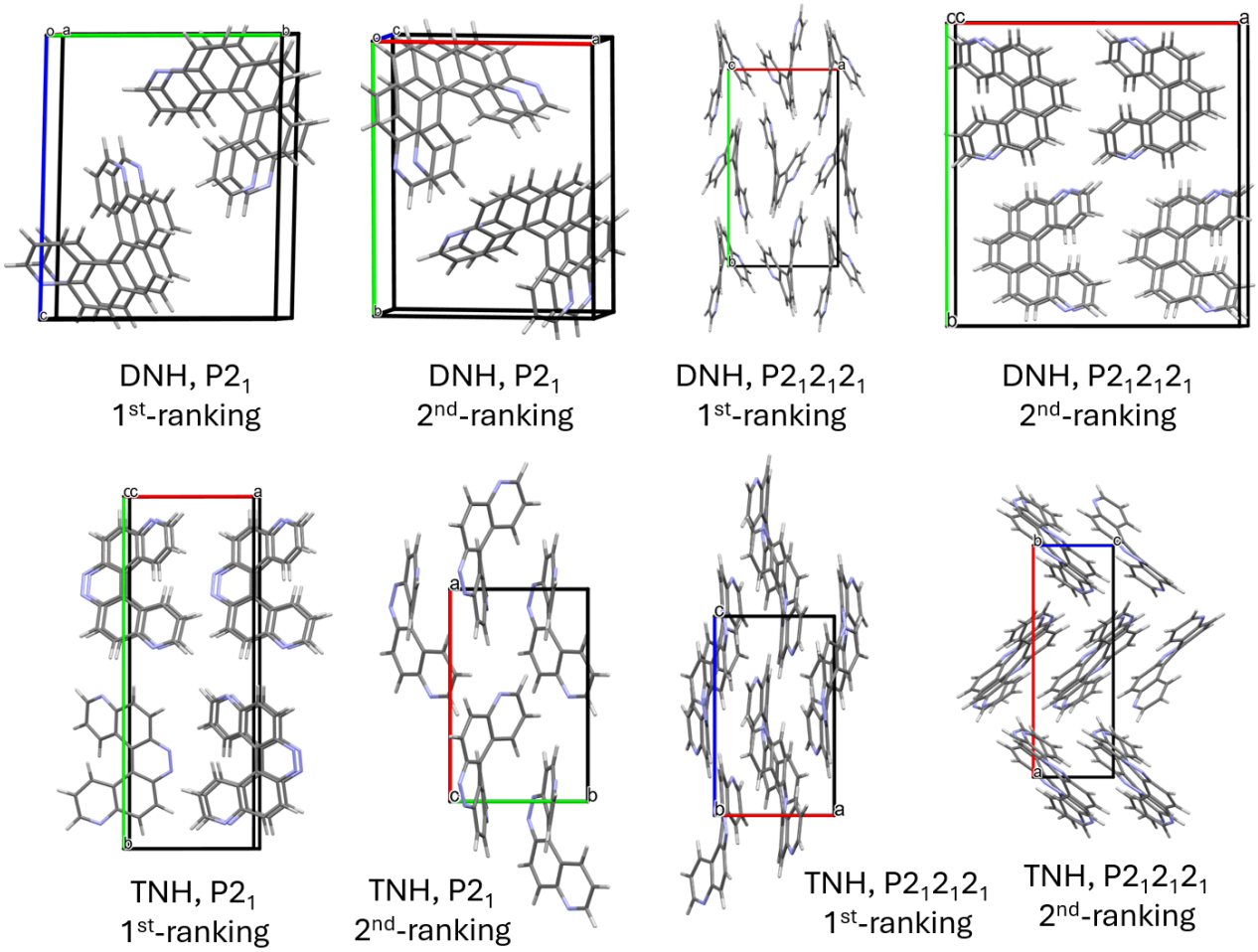


Figure S8. First-ranking DNH and TNH structures predicted in $P2_1$ and $P2_12_12_1$ space groups, showing the setup of different stacking motifs.

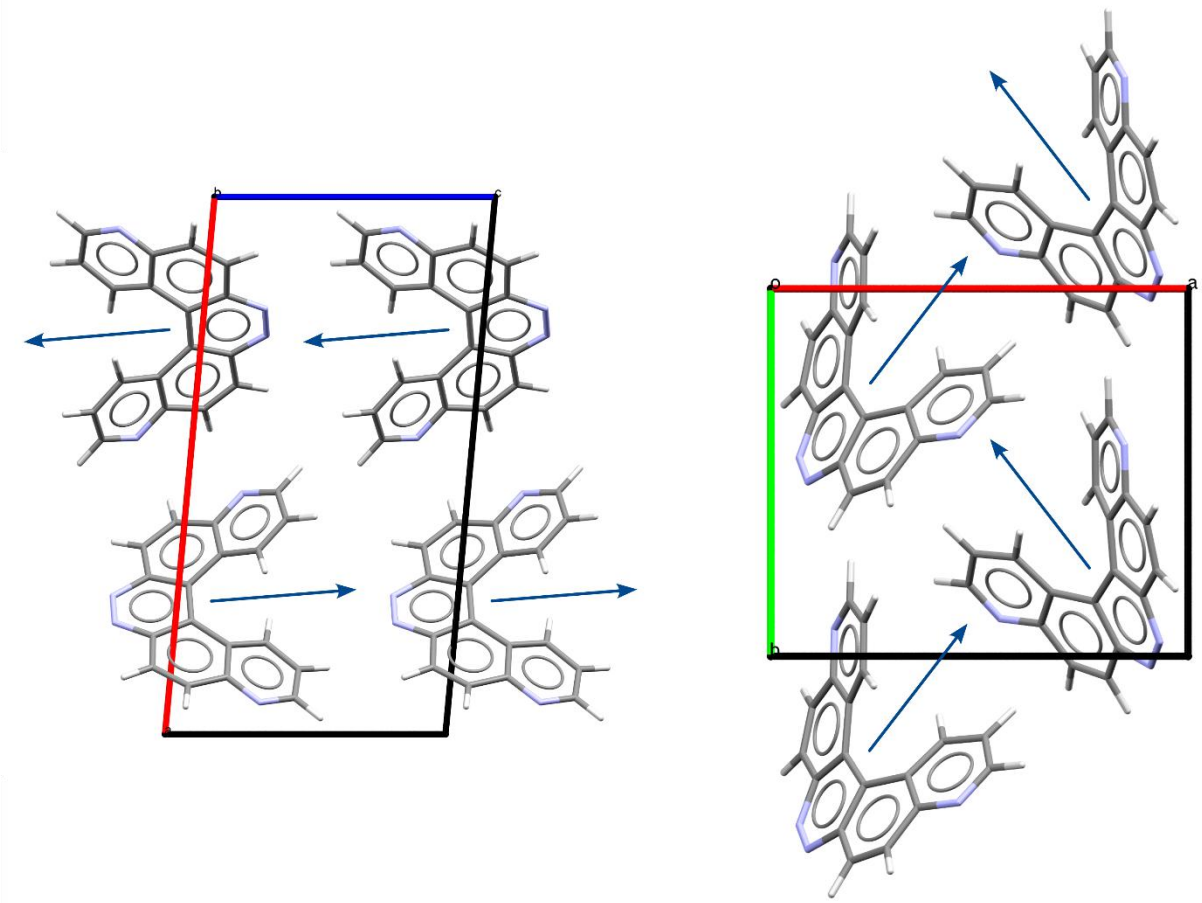


Figure S9. Example of predicted structures for TNH in the monoclinic polar space group $P2_1$ (n. 4) illustrating qualitatively the buildup of total cell dipole moment. The arrows represent molecular dipole moments. See Tables S15-S16 above for information on the corresponding cell edges and energies. (a): 4th-rank predicted structure. The dipoles are roughly orthogonal to the *b* cell axis and result in an antiparallel packing with no significant components left along the polar axis. Seven out of the first 10 top-ranked predictions show analogue arrangements. (b) 5th-rank prediction. Here the components along *b* are significant, resulting in a ~7 D large net cell dipole moment.

Table S17: Dipole moments (Debye) of the top ranked $P2_1$ structures for DNH and TNH best predictions after MD thermalization. Estimates come from classical LJC force field and "Structure No." stands for the cardinal number of the prediction in each set.

DNH			TNH[a]		
Rank	Structure No.	Cell dipole	Rank	Structure No.	Cell dipole
1	179	0.065	1	63	1.611
2	81	0.296	2	$P2_12_12_1$	0
3	22	0.354	3	$P2_12_12_1$	0
4	12	0.910	4	$P2_12_12_1$	0

[a] Only the top-ranking prediction for TNH is monoclinic $P2_1$. Structures 2-4 are all $P2_12_12_1$ (apolar)

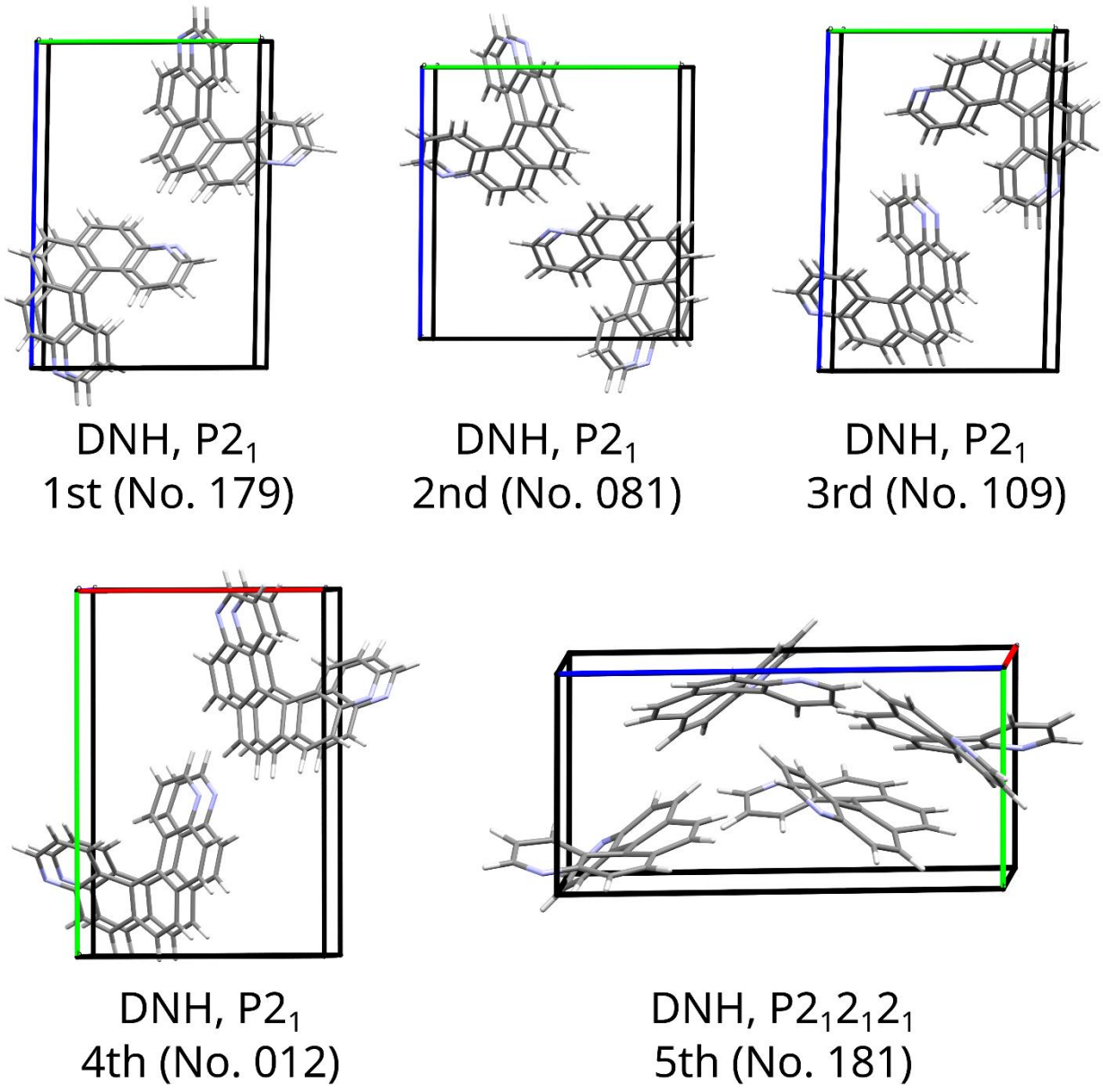


Figure S10. Crystal packing of top-ranking predictions of DNH after MD thermalization.

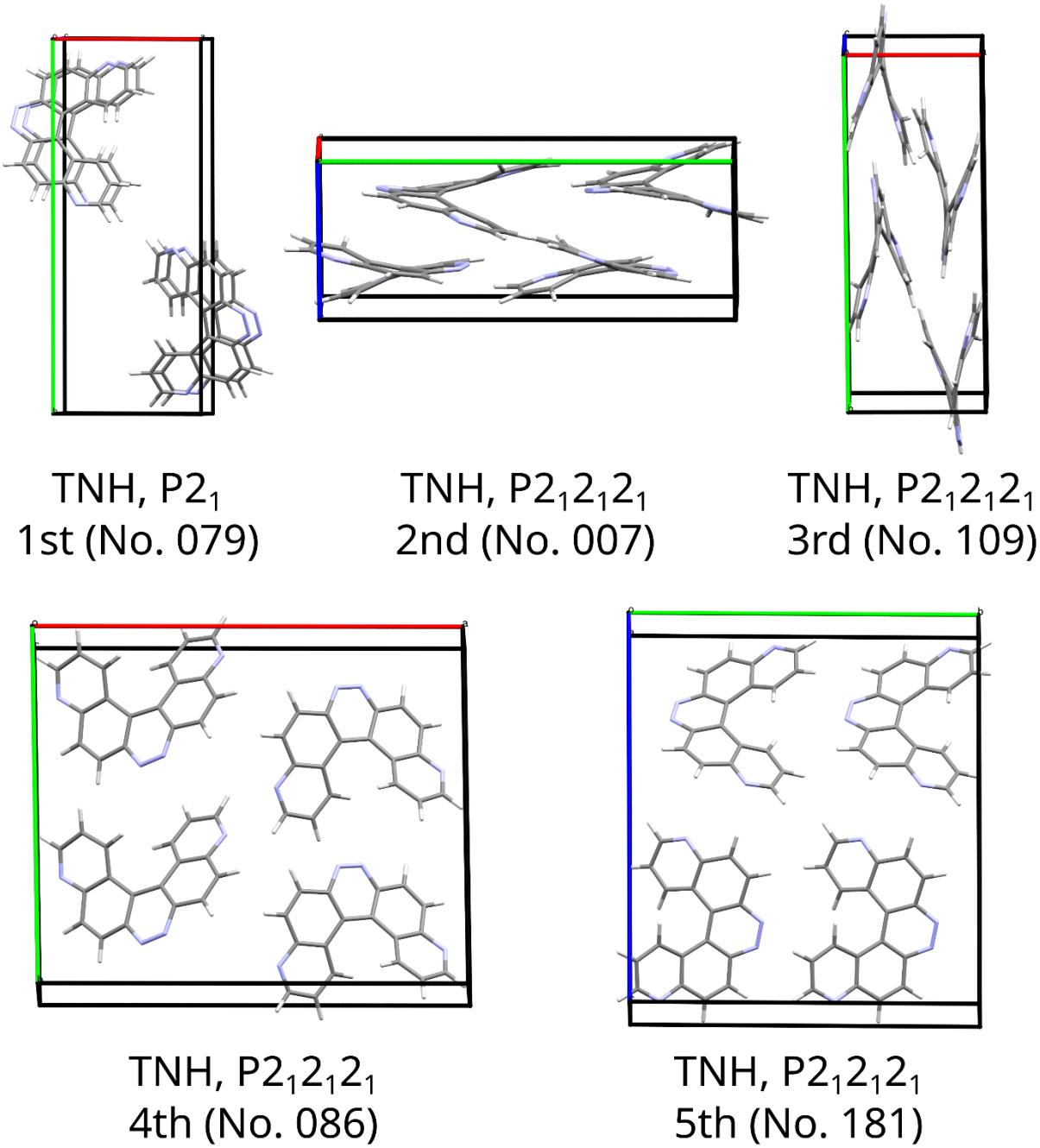


Figure S11. Crystal packing of top-ranking predictions of TNH after MD thermalization.

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