

# Supporting Information

## Section 1: Coordinates of optimized structures

### B3N3

N 1.49024900 -0.29555500 -0.00000300  
N -1.00107000 -1.14281200 0.00000000  
N -0.48917200 1.43836200 -0.00000500  
B 0.72069700 0.82273500 0.00000800  
B -1.07284700 0.21277000 0.00000300  
B 0.35214100 -1.03549800 -0.00000100

### NH3

N 0.00000000 0.00000000 0.11493400  
H 0.00000000 0.94201500 -0.26818000  
H -0.81580900 -0.47100700 -0.26818000  
H 0.81580900 -0.47100700 -0.26818000

### NCH

N 0.00000000 0.00000000 0.65274100  
C 0.00000000 0.00000000 -0.49923300  
H 0.00000000 0.00000000 -1.57378700

### N2H2

N 0.58826600 0.18946200 -0.00001300  
N -0.58827800 -0.18946900 -0.00001300  
H 1.17549400 -0.66372400 0.00009300  
H -1.17540900 0.66376800 0.00009300

### BNH3-1

N -2.19981500 -0.00219100 0.00239800  
N 0.07106900 1.31788800 -0.00247700  
N 0.07461900 -1.31623300 -0.00237400  
B -1.21506600 0.93144700 0.00088900  
B -1.21126300 -0.93345800 0.00074200  
B 0.62777000 0.00188900 -0.00324400  
N 2.23390200 0.00330400 0.00062700  
H 2.57476700 0.95596300 -0.12574500  
H 2.58271400 -0.60545800 -0.73963200  
H 2.57688600 -0.36927600 0.88622200

### BNH3-2

N -1.31396300 1.31845700 -0.00000400  
N 0.00049700 -0.92929600 0.00000100  
N 1.31514800 1.31869100 0.00000400  
B -1.13096900 -0.09479600 -0.00001000  
B 0.00154000 1.58759800 -0.00000200  
B 1.13088300 -0.09562100 0.00001900  
N 2.53969400 -0.89989400 0.00001100  
H 2.34449100 -1.89967800 -0.00034300  
H 3.08425200 -0.64173200 0.82156900  
H 3.08457800 -0.64116200 -0.82115300  
N -2.54377300 -0.89347900 -0.00001800  
H -2.59849400 -1.49326000 -0.82153500  
H -3.30682900 -0.21811300 0.00000500  
H -2.59848300 -1.49331300 0.82146100

### BNH3-3

N 1.44216400 -0.39758400 0.00215600  
N -0.37682200 1.44807900 -0.00264100  
N -1.06564000 -1.05007000 -0.00240300  
B 0.91459500 0.89960100 0.00019600  
B 0.32148400 -1.24189500 0.00038800  
B -1.23641700 0.34268200 -0.00261300  
N 0.72701100 -2.83704800 0.00029500  
H -0.13349500 -3.38132500 -0.00377900  
H 1.28593000 -3.04937000 0.82382500  
H 1.29236600 -3.04675700 -0.81953200  
N -2.82070400 0.78858900 0.00067400  
H -2.86584100 1.79663700 -0.13558200  
H -3.24552300 0.53481000 0.88999000  
H -3.31849900 0.29157200 -0.73480700  
N 2.09383500 2.04780800 0.00018700  
H 2.99495100 1.57371600 -0.01132900  
H 2.00403900 2.63234200 0.82843500  
H 1.98886400 2.64800400 -0.81495200

### BNCH-1

N 0.25880100 1.31392500 0.00000500  
N 0.25879100 -1.31392100 0.00002000  
N 2.53275600 -0.00000700 0.00002400  
B -0.27902400 0.00000400 -0.00017800  
B 1.54655600 0.93278900 0.00009100  
B 1.54654900 -0.93279500 0.00010100  
N -1.88287900 0.00000900 -0.00006100  
C -3.02387900 0.00000600 -0.00000100  
H 4.09940400 -0.00006500 0.00002300

### BNCH-2

N -1.31333400 1.54733400 0.00015000  
N -0.00000500 -0.70066700 -0.00019200  
N 1.31334100 1.54732300 -0.00006000  
B -1.11236000 0.14524200 -0.00001400  
B 0.00000400 1.82342700 0.00016400  
B 1.11235700 0.14523200 -0.00027200  
N 2.52326400 -0.66007800 -0.00038700  
C 3.52021900 -1.21698700 -0.00044600  
H 4.45768900 -1.74128300 0.00104700  
N -2.52327300 -0.66005700 0.00036800  
C -3.52023000 -1.21696500 0.00058600  
H -4.45757500 -1.74149100 -0.00042700

### BNCH-3

N -1.28267600 0.77394600 0.00013900  
N -0.02906200 -1.49793900 -0.00010600  
N 1.31159200 0.72366400 0.00023200  
B -1.10023800 -0.60717900 -0.00016100  
B 0.02428600 1.25617500 0.00044700  
B 1.07582300 -0.64935400 0.00000900  
N 2.49950900 -1.50831500 -0.00003300  
C 3.47831400 -2.09853800 -0.00007500  
H 4.39726900 -2.65249000 -0.00010700  
N 0.05659400 2.91880700 0.00000300  
C 0.07859500 4.06159400 -0.00038300  
H 0.09856400 5.13442100 0.00017600  
N -2.55598200 -1.41039200 -0.00007900  
C -3.55671000 -1.96264400 -0.00000800  
H -4.49620300 -2.48101700 0.00015800

### NHCN-1

N 0.03836200 -0.00245400 0.00303700  
N -2.23764700 1.31541900 -0.00082600  
N -2.24193900 -1.31287300 -0.00090700  
B -0.93527800 0.95069200 0.00087400  
B -0.93838200 -0.95240300 0.00079900  
B -2.57782200 0.00182400 -0.00172000  
C 3.31136000 -0.00050500 -0.00009500  
N 4.46409900 0.00049800 -0.00134200  
H 2.22912900 -0.00166400 0.00107500

### NHCN-2

N -1.31482500 0.36223400 0.00137100  
N 1.31470900 0.36202900 -0.00118200  
N 0.00011800 2.63700500 -0.00061000  
B -0.00008400 0.02366000 0.00020800  
B -0.94944900 1.67428600 0.00009400  
B 0.94953700 1.67413900 -0.00069600  
C -4.21990800 -1.21230400 0.00079700  
C 4.21996200 -1.21219100 -0.00026800  
N -5.24228500 -1.74407800 -0.00008200  
N 5.24223900 -1.74415600 0.00027200  
H 3.26190700 -0.71238300 -0.00057600  
H -3.26194600 -0.71231500 0.00098700

**NHCN-3**

N 0.54541600 1.41315500 0.00229500  
N -1.50097700 -0.23400500 -0.00139700  
N 0.94872400 -1.18262400 -0.00070400  
B -0.69206300 0.85580700 0.00063100  
B 1.08473000 0.16773500 0.00114400  
B -0.39952500 -1.02700600 -0.00158300  
C 1.75101400 4.52722400 0.00049800  
C 3.05069200 -3.77734100 -0.00016100  
C -4.80025700 -0.74876500 -0.00031700  
N 2.16977800 5.60073100 -0.00074100  
N 3.78050100 -4.66905600 -0.00000300  
N -5.93878100 -0.92634100 0.00039300  
H 2.36768400 -2.94148700 -0.00041100  
H -3.73374700 -0.58240700 -0.00077400  
H 1.35902600 3.52148600 0.00120400

**BNNH-1**

N 0.02602400 -1.17539200 -0.00090300  
N 0.52703100 1.41691600 -0.00127500  
N 2.50392100 -0.31420600 0.00126700  
B -0.25238400 0.22930300 -0.00132000  
B 1.36165400 -1.04581300 0.00033200  
B 1.71832800 0.79154200 0.00004800  
N -1.81383300 0.48252000 0.00124100  
N -2.65271300 -0.41291300 0.00015800  
H -2.18128600 1.44277700 0.00327900  
H -2.08971800 -1.29640900 -0.00199700

**BNNH-2**

N -1.43322600 1.28444500 -0.00030100  
N 0.26228800 -0.69200700 0.00085100  
N 1.14745700 1.76171700 0.00006000  
B -0.99222600 -0.07551900 0.00036800  
B -0.19570700 1.79670500 -0.00028100  
B 1.21868200 0.34694000 0.00065900  
N 2.69799900 -0.22958300 0.00012800  
N 2.94693000 -1.43228700 -0.00097400  
N -2.24309900 -1.05022400 0.00063800  
N -3.40990900 -0.66658400 -0.00080600  
H 3.51201000 0.39784400 0.00011800  
H 1.99500700 -1.87663300 -0.00077400  
H -2.10949800 -2.06889300 0.00099100  
H -3.33034900 0.37871000 -0.00124000

**BNNH-3**

N 1.05180200 1.06199200 0.00083500  
N 0.39380600 -1.44134600 0.00004700  
N -1.44503200 0.38000900 0.00047500  
B 1.24074700 -0.33462500 0.00030300  
B -0.33012400 1.24213600 0.00079400  
B -0.91025800 -0.90684400 0.00021300  
N -1.98796000 -2.08518000 0.00004700  
N -1.68039300 -3.27484900 -0.00041100  
N 2.80006800 -0.67893700 -0.00023000  
N 3.67657300 0.18232900 -0.00079700  
N -0.81229800 2.76424300 0.00020500  
N -1.99678700 3.09143600 -0.00111100  
H -0.13649300 3.53796700 0.00122300  
H -2.49472200 2.16481000 -0.00154500  
H -2.99576300 -1.88576500 0.00007400  
H -0.62897200 -3.24442800 -0.00041100  
H 3.13125200 -1.65145500 -0.00015900  
H 3.12442800 1.07765500 -0.00060200

**NBNH-1**

N -1.10128900 -1.31282900 0.00025800  
N -1.09969200 1.31352400 0.00015200  
N 1.17194200 -0.00095400 -0.00022700  
B -1.64196200 0.00088100 0.00031700  
B 0.18261500 -0.93786400 0.00000000  
B 0.18382500 0.93713900 -0.00008000  
N 5.51356800 0.00058700 -0.00102900  
N -3.24217500 0.00074800 0.00062200  
C -4.38297000 -0.00031200 0.00083500  
H -5.45905300 -0.00134300 0.00094800  
C 4.36061100 -0.00058200 -0.00082400  
H 3.27434900 -0.00161500 -0.00062900

**NBNH-2**

N 0.00029700 -1.29400900 0.00010700  
N -1.31079200 0.94843800 -0.00002600  
N 1.31081700 0.94882200 -0.00034200  
B -1.12106600 -0.47286700 0.00014600  
B 1.12144500 -0.47250400 -0.00012400  
B -0.00004100 1.22567700 -0.00022200  
N 5.35283300 1.02440200 -0.00075000  
N 2.54554200 -1.21455700 -0.00020100  
N -2.54517300 -1.21506600 0.00041400  
N -5.35359200 1.02482400 0.00088900  
C 3.63258300 -1.56450500 -0.00027900  
H 4.66341400 -1.87482400 -0.00007800  
C -3.63224000 -1.56494500 0.00061800  
H -4.66310300 -1.87518300 0.00089800  
C -4.25139300 1.36954200 0.00050800  
H -3.16624200 1.56396500 0.00012200  
C 4.25087000 1.36987200 -0.00083300  
H 3.16580000 1.56476000 -0.00065400

**NBNH-3**

N -1.28803800 -0.73991200 0.00000000  
N 0.00266900 1.48527100 0.00000000  
N 1.28442900 -0.74502100 0.00000000  
B -1.11562200 0.64367000 0.00000000  
B 0.00000000 -1.28755700 0.00000000  
B 1.11490200 0.64435000 0.00000000  
N 5.22334100 -1.07173500 0.00000000  
N -0.08203400 -2.90650000 0.00000000  
N -3.53939100 -3.98939700 0.00000000  
N -2.47629600 1.52476700 0.00000000  
N 2.55791800 1.38189100 0.00000000  
N -1.68182800 5.06081500 0.00000000  
C -0.40509800 -4.00252000 0.00000000  
H -0.73011500 -5.02892300 0.00000000  
C -3.14364100 -2.90226700 0.00000000  
H -2.59501600 -1.90418600 0.00000000  
C -3.26385200 2.35264500 0.00000000  
H -3.99088900 3.14672500 0.00000000  
C 3.66860300 1.65020300 0.00000000  
H 4.71986400 1.88249600 0.00000000  
C -0.93979400 4.17317700 0.00000000  
H -0.35072600 3.19796900 0.00000000  
C 4.08381500 -1.27167300 0.00000000  
H 2.94490200 -1.29504300 0.00000000

**BN-1**

N 1.87442800 1.54048000 -0.00085100  
N 0.72219500 -0.85635800 -0.01738300  
N 3.29273500 -0.67768400 0.01324100  
B 0.73724200 0.73693800 -0.01028500  
B 2.82410900 0.60350000 0.00849200  
B 2.03889800 -1.12808600 0.00095200  
N -0.72200600 0.85575400 -0.00763200  
N -3.29253900 0.67802500 0.00931000  
N -1.87487400 -1.54030200 0.00191300  
B -0.73714300 -0.73716900 -0.00600200  
B -2.82426500 -0.60331600 0.00741600  
B -2.03875600 1.12825100 0.00138800

## Section 2: Tables

**Table S1.** Selected geometrical parameters of the  $B_3N_3$  molecule in the optimized monomer and the complexes

Parameter	B3N3	BNH3-1	BNH3-2	BNH3-3	BNCH-1	BNCH-2	BNCH-3	NCHN-1	NCHN-2	NCHN-3	NBNH-1	NBNH-2	NBNH-3
B1-N1 (Å)	1.36	1.43	1.41	1.40	1.42	1.40	1.39	1.36	1.36	1.36	1.42	1.39	1.40
N1-B2 (Å)	1.36	1.34	1.42	1.40	1.34	1.40	1.39	1.36	1.36	1.36	1.34	1.39	1.39
B2-N2 (Å)	1.36	1.36	1.41	1.40	1.36	1.42	1.39	1.35	1.36	1.36	1.36	1.43	1.40
N2-B3 (Å)	1.36	1.36	1.34	1.40	1.36	1.34	1.39	1.35	1.36	1.36	1.36	1.34	1.39
B3-N3 (Å)	1.36	1.34	1.34	1.40	1.34	1.34	1.39	1.36	1.35	1.36	1.34	1.34	1.40
N3-B1 (Å)	1.36	1.43	1.42	1.40	1.42	1.42	1.39	1.36	1.35	1.36	1.42	1.43	1.39
∠B1-N1-B2 (°)	88.5	96.2	107.2	104.9	95.8	105.5	102.8	88.6	88.9	89.2	96.1	107.5	105.9
∠N1-B2-N2 (°)	151.5	153.3	133.8	135.1	153.1	135.4	137.3	151.2	151.1	150.8	152.8	133.8	134.1
∠B2-N2-B3 (°)	88.5	86.8	94.1	104.9	86.8	93.7	102.8	88.9	88.9	89.2	86.9	94.3	105.9
∠N2-B3-N3 (°)	151.5	153.3	156.9	135.1	153.1	156.2	137.3	151.1	150.9	150.8	152.8	156.1	134.1
∠B3-N3-B1 (°)	88.5	96.2	94.1	104.9	95.8	93.7	102.8	88.9	89.2	89.2	96.1	94.3	105.9
∠N3-B1-N1 (°)	151.5	134.3	133.8	135.1	135.5	135.4	137.3	151.2	150.9	150.8	135.2	133.8	134.1

Parameter	BNNH-1	BNNH-2	BNNH-3
B1-N1 (Å)	1.43	1.41	1.41
N1-B2 (Å)	1.34	1.40	1.39
B2-N2 (Å)	1.36	1.43	1.41
N2-B3 (Å)	1.36	1.34	1.39
B3-N3 (Å)	1.34	1.34	1.41
N3-B1 (Å)	1.42	1.42	1.39
∠B1-N1-B2 (°)	95.7	106.5	105.1
∠N1-B2-N2 (°)	152.9	134.1	134.8
∠B2-N2-B3 (°)	87.2	94.5	105.1
∠N2-B3-N3 (°)	153.1	156.0	134.8
∠B3-N3-B1 (°)	95.6	94.4	105.1
∠N3-B1-N1 (°)	135.5	134.5	134.8

**Table S2:** The magnitude of the atomic charge on the  $B_3N_3$  and the probe molecules after complex formation.

Complex	$B_3N_3$	Probe Molecules
BNH3-1	-0.12 e	0.12 e (NH3)
BNH3-2	-0.19 e	0.19 e (2x NH3)
BNH3-3	-0.24 e	0.24 e (2x NH3)
BNCH-1	-0.04 e	0.04 e (NCH)
BNCH-2	-0.04 e	0.04 e (2x NCH)
BNCH-3	-0.03 e	0.03 e (3x NCH)
NCHN-1	0.02 e	-0.02 (HCN)
NCHN-2	0.03 e	-0.03 (2x HCN)
NCHN-3	0.04 e	-0.04 (3x HCN)
NBNH-1	-0.02 e	0.04 (NCH) and -0.02 (HCN)
NBNH-2	-0.02 e	0.06 (NCH) and -0.02 (HCN)
NBNH-3	0.15 e	0.09 (2xNCH) and -0.24 (2xHCN)
BNHN-1	-0.04 e	0.04 e (N2H2)
BNHN-2	-0.03 e	0.03 e (2XN2H2)
BNHN-3	0.02 e	-0.02 e (3xN2H2)

**Table S3:** The magnitude of  $|\mu|$  of the interacting atoms after complex formation.

Complex	$ \mu $ (of interacting atom in $B_3N_3$ )	$ \mu $ (of interacting atom of probe molecule)	$ \Delta\mu $
BNH3-1	0.83 a.u. (B)	1.15 a.u. (N)	0.32
BNH3-2	0.80 a.u. (B)	1.06 a.u. (N)	0.26
BNH3-3	0.73 a.u. (B)	0.96 a.u. (N)	0.23
BNCH-1	0.71 a.u. (B)	1.48 a.u. (N)	0.77
BNCH-2	0.67 a.u. (B)	1.38 a.u. (N)	0.71
BNCH-3	0.59 a.u. (B)	1.28 a.u. (N)	0.69
NCHN-1	1.51 a.u. (N)	0.11 a.u. (H)	1.40
NCHN-2	1.47 a.u. (N)	0.10 a.u. (H)	1.37
NCHN-3	1.43 a.u. (N)	0.09 a.u. (H)	1.34
NBNH-1	0.72 a.u. (B)	1.52 a.u. (N)	0.80
	1.61 a.u. (N)	0.13 a.u. (H)	1.48

<b>NBNH-2</b>	0.62 a.u. (B)	1.23 a.u. (N)	0.61
	1.53 a.u. (N)	0.05 a.u. (H)	1.48
<b>NBNH-3</b>	1.17 a.u. (B)	0.57 a.u. (N)	0.60
	1.50 a.u. (N)	0.13 a.u. (H)	1.37
<b>BNHN-1</b>	0.56 a.u. (B)	0.82 a.u. (N)	0.26
	1.36 a.u. (N)	0.19 a.u. (H)	1.17
<b>BNHN-2</b>	0.53 a.u. (B)	0.74 a.u. (N)	0.21
	1.41 a.u. (N)	0.19 a.u. (H)	1.22
<b>BNHN-3</b>	0.48 a.u. (B)	0.67 a.u. (N)	0.19
	1.40 a.u. (N)	0.17 a.u. (H)	1.23

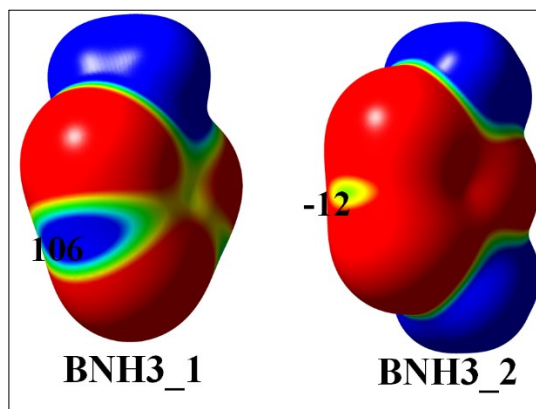
**Table S4.** Results of localized molecular orbital energy decomposition analysis. Total energy is divided into electrostatics (EL), polarization (POL), dispersion (DISP) and exchange-repulsion (EX-REP). All values in kJ/mol.

Parameter	BNH3-1	BNH3-2	BNH3-3	BNCH-1	BNCH-2	BNCH-3	NCHN-1	NCHN-2	NCHN-3	BNNH-1	BNNH-2	BNNH-3
Electrostatic (EL)	-428.4	-830.2	-1190.2	-280.0	-533.8	-732.5	-22.3	-40.3	-54.1	-422.0	-838.6	-1246.8
Polarization (POL)	-396.7	-735.2	-1001.8	-343.0	-623.4	-806.0	-11.3	-19.2	-24.1	-413.0	-797.4	-1145.5
Dispersion (DISP)	-89.0	-174.6	-256.8	-76.1	-149.2	-216.6	-10.6	-19.5	-26.9	-99.6	-199.6	-300.8
Exchange-Repulsion (EX-REP)	673.2	1308.4	1889.3	562.9	1076.8	1488.8	26.4	49.3	63.8	690.6	1370.7	2043.3
Total	-240.9	-431.6	-559.5	-136.2	-229.7	-266.3	-17.8	-29.7	-41.3	-244.1	-464.9	-649.8

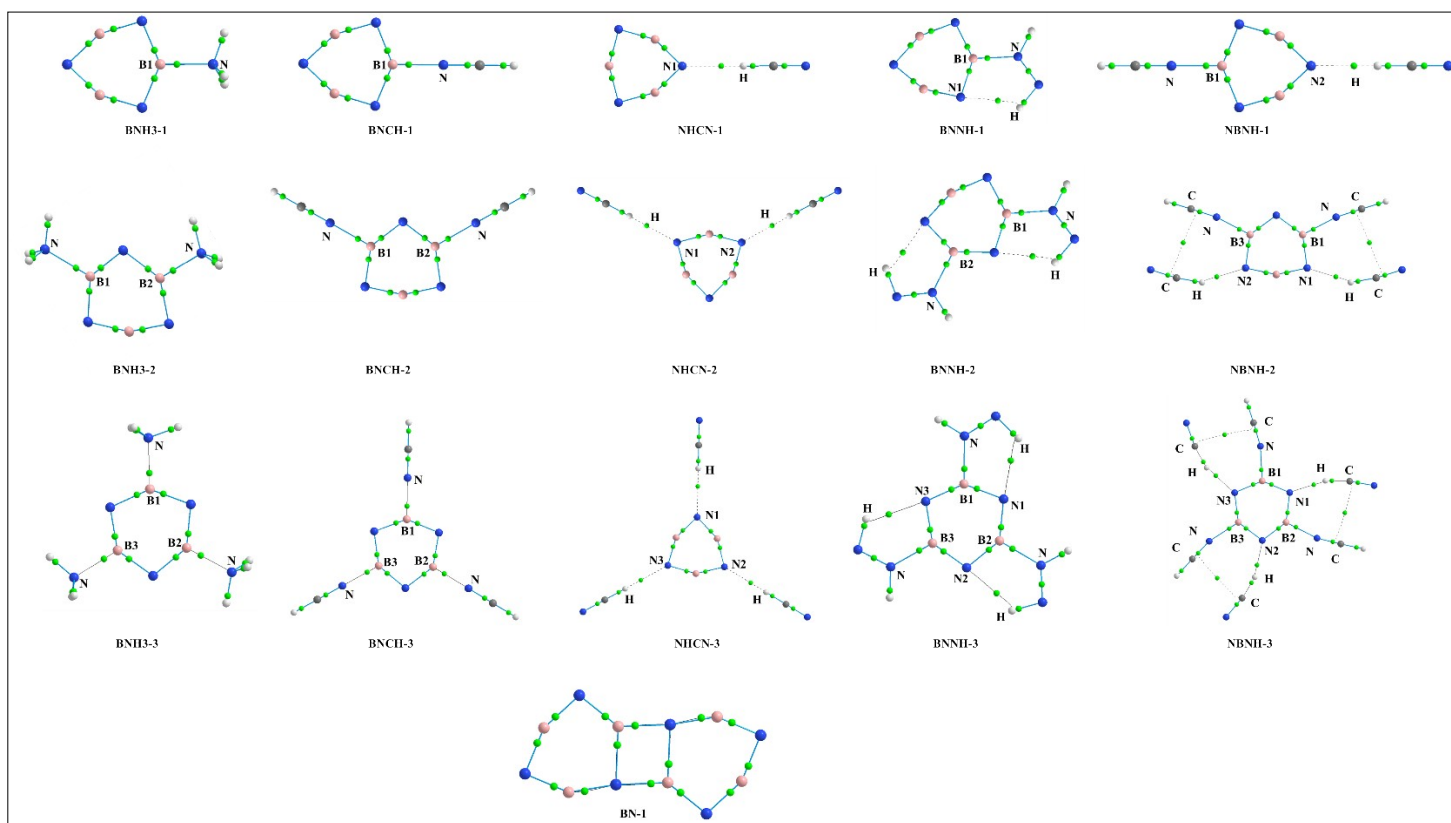
**Table S5.** Topological parameters for the  $C(\pi)\cdots C(\pi)$  interaction observed in NBNH-2 and NBNH-3

Complex	$C(\pi)\cdots C(\pi)$ (Å)	$\rho^a$ ( $e/\text{Å}^3$ )	$\nabla^2\rho^a$ ( $e/\text{Å}^5$ )	$ V /G^a$
NBNH-2	3.00	0.07	0.81	0.72
NBNH-3	2.95	0.06	0.89	0.73

### Section 3: Figures



**Figure S1.** The electrostatic potential map of BNH3-1 and BNH3-2. The ESP maps were drawn on 0.001 au electron density isosurface. All values are in kJ/mol.



**Figure S2.** Molecular graphs representing the existence of B...N triel bond and H...N bond critical point.