Supporting Information

Dimerization of phenalenyls with embedded BNB/NBN bond

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Computational details

In this work, the M06-2X functional[1-3] was used to optimize the geometries and to perform the frequency calculations of the examined molecules, as implemented in the Gaussian 09 software[4]. All the molecules investigated here are listed in Figure S1. The geometry optimizations of monomer (1 and 2), hetero-dimer (1-2) and homo-dimers (12 and 22) with all real frequencies are obtained with a spin-restricted broken-symmetry (BS) M06-2X/6-31+G* method. Moreover, their important structural parameters were calculated at M06-2X/6-31+G* level, which are shown in Tables S1 for comparison.

In order to get insight into bond character of the system, the M06-2X method was employed to calculate the Wiberg bond indices (WBI) and the natural population analysis (NPA) in this work. Further, the interaction energy (E_{int}) was also calculated at M06-2X/6-31+G* level, to correct the basis set superposition error, the counterpoise (CP) procedure was used in calculations of interaction energy[5, 6]. The E_{int} can be expressed as the difference between the energy of dimer and the sum of energies of monomers by the following Equation:

$$\Delta E_{int}\,(AB) = E\,(AB)_{AB} - [E\,(A)_{AB} + E\,(B)_{AB}]$$

The Atoms in Molecules (AIM) method[7] was further utilized to analyze the mechanism of bonding interactions by means of the bond critical point (BCP) parameters. Chemical bonding was analyzed using the Localized molecular orbitals (LMOs) and the adaptive natural density partitioning (AdNDP) analysis[8]. The electron localization function (ELF) [9] analysis can describe the distribution character of electrons and constrain the situation by adjacent atoms. These bonding analysis strategies are all executed and presented using the Multiwfn 3.3.8 program[10].

In addition, in order to get insight into bonding character of dimer, the localized molecular orbital energy decomposition analysis (EDA) method[11-14] was employed at the M062X /DZP level by of theory by means of the energy decomposition scheme of the Amsterdam density functional (ADF) program [15-17].

1. Y. Zhao, N. E. Schultz and D. G. Truhlar, *J. Chem. Theory Comput.*, 2006, **2**, 364-382.
2. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.
3. K. E. Riley, M. Pitoňák, P. Jurečka and P. Hobza, *Chem. Rev.*, 2010, **110**, 5023-5063.
4. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Journal*, 2009.
5. S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553-566.
6. I. Alkorta and J. Elguero, *J. Phys. Chem. A*, 1999, **103**, 272-279.
7. P. Hobza, *Acc. Chem. Res.*, 2012, **45**, 663-672.
8. D. Y. Zubarev and A. I. Boldyrev, *Phys. Chem. Chem. Phys.*, 2008, **10**, 5207-5217.
9. B. Silvi and A. Savin, *Nature*, 1994, **371**, 683-686.
10. T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592.
11. C. Fonseca Guerra, J. G. Snijders, G. te Velde and E. J. Baerends, *Theor. Chem. Acc.*, 1998, **99**, 391-403.
12. G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders and T. Ziegler, 2001, **22**, 931-967.
13. S. Iwata and K. Morokuma, *J. Am. Chem. Soc.*, 1973, **95**, 7563-7575.
14. Z. Tang, Z. Jiang, H. Chen, P. Su and W. Wu, *J. Chem. Phys.*, 2019, **151**, 244106.
15. K. Morokuma, *J. Chem. Phys.*, 1971, **55**, 1236-1244.
16. T. Ziegler and A. Rauk, *Inorg. Chem.*, 1979, **18**, 1755-1759.
17. T. Ziegler and A. Rauk, *Inorg. Chem.*, 1979, **18**, 1558-1565.

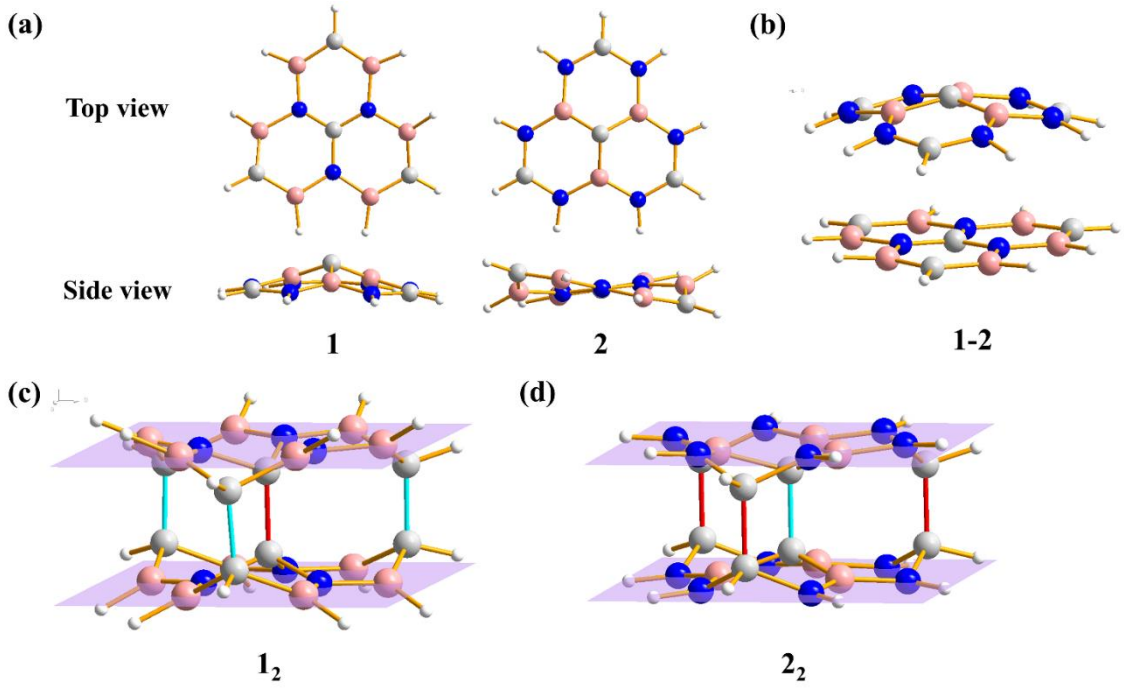
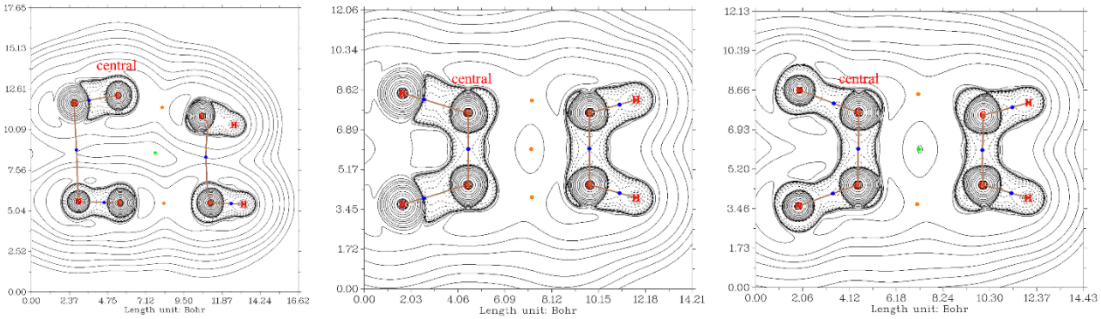


Figure S1. The structure of monomers(a) and hetro-dimer(b) and homo-dimers (c and d).



1-2 1_2 2_2

Figure S2. Laplacian plots of the electron density ($\nabla^2\rho$) of hetero-dimer(**1-2**) and homo-dimers (**1_2** and **2_2**). Solid and dashed lines correspond to the positive and negative regions of homo-diemrs.

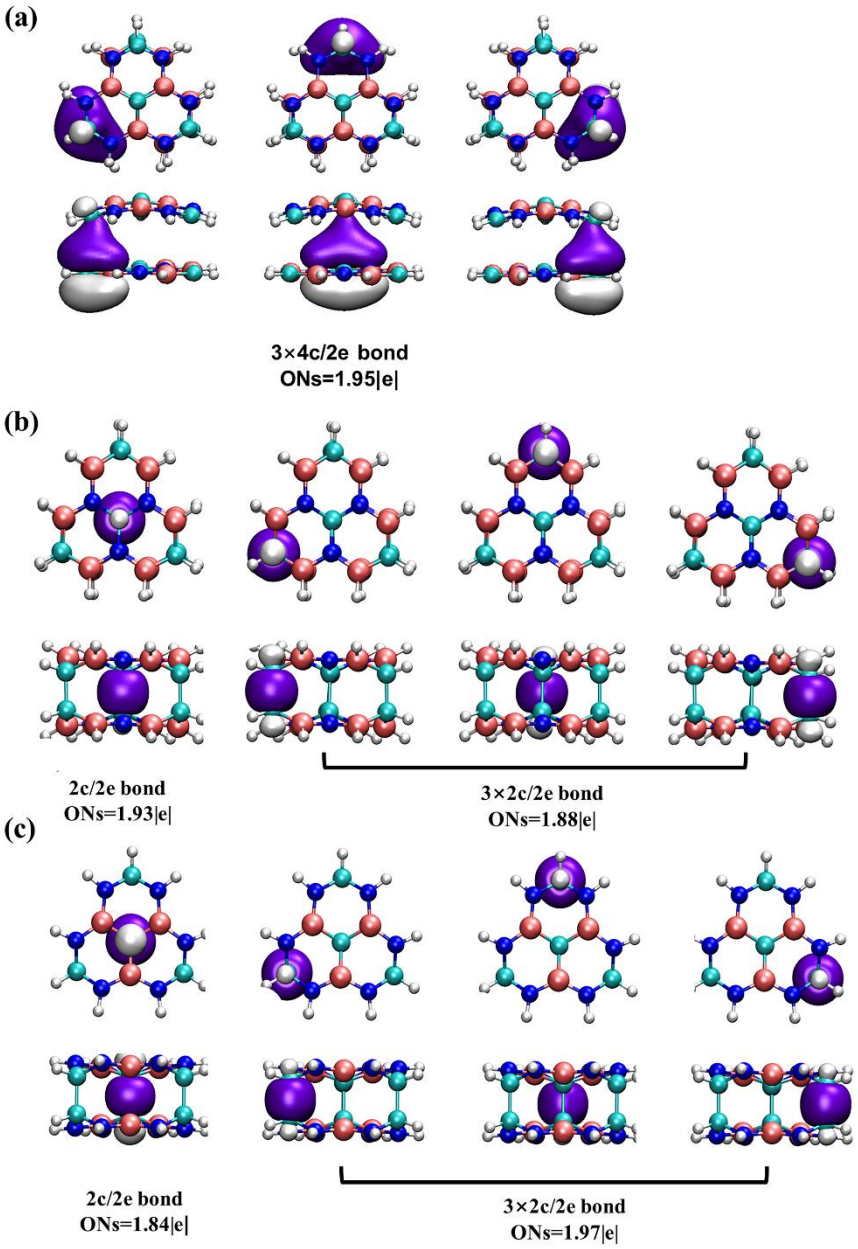


Figure S3. AdNDP bonding patterns of (a)**1-2**, (b)$\mathbf{1_2}$ and (c)$\mathbf{2_2}$. ON is the occupation number.

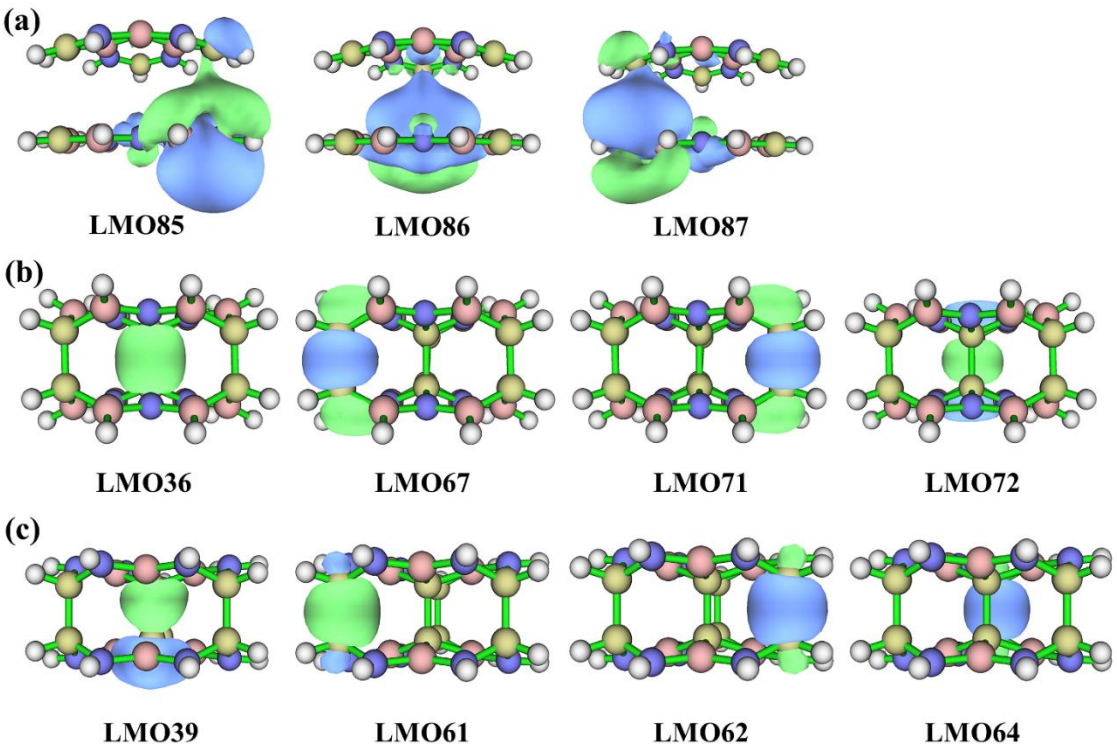


Figure S4. Localized molecular orbitals (LMOs) for the bonding of (a)**1-2**, (b)$\mathbf{1}_2$ and (c)$\mathbf{2}_2$.

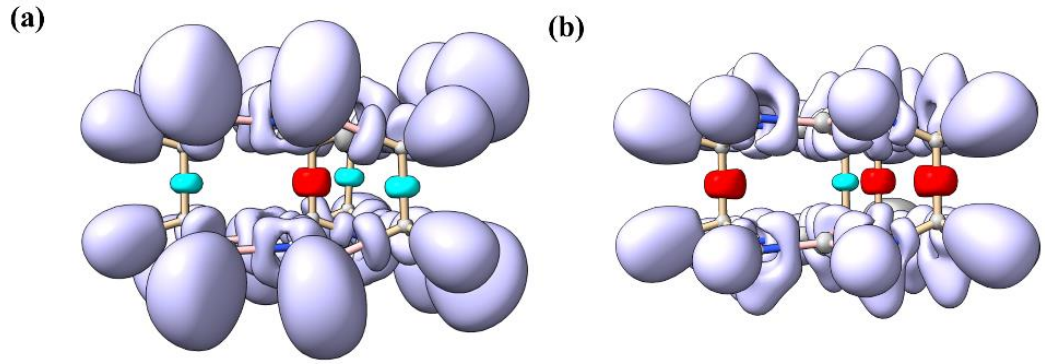


Figure S5. ELF basins plot (isosurface=0.80) of (a)**1**$_2$ and (b)**2**$_2$. the blue and red lobes correspond to the basins between carbon atoms.

Table S1. the NPA charge of molecules.

site	1	1-2(1)	1_2(1)	2	1-2(2)	2_2(2)
C	0.743	0.763	0.553	-1.347	-1.210	-1.054
γ	-2.491	-2.610	-2.892	2.749	2.916	3.134
C+γ	-1.748	-1.846	-2.339	1.401	1.706	2.080
α	3.467	3.186	4.462	-5.007	-4.832	-5.560
β	-2.247	-3.343	-2.765	0.485	1.278	0.377
Hβ	0.757	0.707	0.881	0.620	0.822	0.684
Hα	-0.229	-0.437	-0.238	2.499	2.758	2.418
outside	1.748	0.113	2.339	-1.401	0.026	-2.080
total	0	-1.733	0	0	1.733	0

Table S2. Topological properties of BCPs of various bonds in above mentioned dimers.

	BCPs	ρ	$\nabla^2\rho$	V	G	H	LOL	ELF
1_2	C_{β}-C_{β}	0.179	-0.272	-0.167	0.049	-0.117	0.768	0.916
	C_c-C_c	0.190	-0.332	-0.164	0.040	-0.123	0.817	0.952
2_2	C_{β}-C_{β}	0.204	-0.387	-0.181	0.042	-0.138	0.828	0.958
	C_c-C_c	0.170	-0.223	-0.162	0.053	-0.109	0.738	0.888
1-2	C_{β}-C_{β}	0.016	0.039	-0.007	0.008	0.001	0.255	0.105
	C_r-C_r	0.007	0.021	-0.004	0.004	0.0005	0.143	0.027

Table S3. The layer distances [Å] and Mayer bond order (MBO) of homo-dimer (1_2 and 2_2)

	C_C-C_C	C_β-C_β	MBO(c)	MBO(β)	ΔE_{int}
1_2	1.68	1.63	0.796	0.916	-414.8
2_2	1.65	1.65	0.919	0.843	-364.3

Table S4 Functional test for geometry optimization of dimers; basis set is 6-31+G (d).

	1-2		**1_2**		**2_2**	
	C_c-C_c	C_β- C_β	C_c-C_c	C_β- C	C_c-C_c	C_β- C
M06-2X	3.526	2.887	1.686	1.631	1.651	1.653
M06-2X-D3	3.529	2.888	1.685	1.631	1.652	1.653
CAM-B3LYP	3.668	2.915	1.670	1.633	1.655	1.651
ωB97XD	3.563	2.879	1.677	1.629	1.654	1.654

Table S5 Basis set test for geometry optimization of dimers with M06-2X method.

	1-2		**1_2**		**2_2**	
	C_c-C_c	C_B- C_B	C_c-C_c	C_B- C_B	C_c-C_c	C_B- C_B
6-31+G**	3.539	2.889	1.685	1.631	1.651	1.654
6-311+G*	3.541	2.871	1.686	1.633	1.654	1.652
6-311+G**	3.557	2.876	1.687	1.633	1.654	1.654

Cartesian coordinates of the optimized structures of monomers

(1) monomer 1

C	-1.44691100	2.51570400	0.35273100
C	0.02322000	0.00040000	0.00043100
C	-1.43099600	-2.52454500	-0.35325900
C	2.95708800	0.00774200	-0.00206100
H	4.04466300	0.01050900	-0.00386300
H	-1.94833900	3.44268300	0.61919900
H	-1.92657600	-3.45469000	-0.61958700
B	2.15879300	1.25979500	-0.25068100
H	2.58557700	2.33892900	-0.51556600
B	2.16576100	-1.24781500	0.25002500
H	2.59804400	-2.32451600	0.51614200
B	-0.03264500	2.46455300	-0.19211900
H	0.53025600	3.36376600	-0.72796500
B	-2.17863900	1.22300500	0.21190300
H	-3.35525500	1.07090900	0.26649500
B	-0.01901000	-2.46367200	0.19595400
H	0.54658800	-3.35772600	0.73764900
B	-2.17058700	-1.23600000	-0.21439900
H	-3.34800700	-1.09119200	-0.27126800
N	0.68912000	1.15900900	-0.17810300
N	0.69557400	-1.15413900	0.17984900
N	-1.37894100	-0.00398700	-0.00055900

(2) monomer 2

C	0.05887400	2.81231800	0.00000000
C	-0.68856400	0.00009600	0.00000000
C	0.06220000	-1.40580300	2.43455300
C	0.06220000	-1.40580300	-2.43455300
H	0.23951300	-1.93930200	-3.35944500
H	0.23643400	3.87991000	0.00000000
H	0.23951300	-1.93930200	3.35944500
B	-0.20145700	0.70729500	-1.22436500
B	-0.20345300	-1.41362200	0.00000000
B	-0.20145700	0.70729500	1.22436500
N	0.09090700	-0.04473300	-2.44288800
H	0.26412800	0.37367300	-3.34846300
N	0.08855700	-2.09411000	-1.26003100
H	0.26084700	-3.08760200	-1.35041700
N	0.08855700	-2.09411000	1.26003100
H	0.26084700	-3.08760200	1.35041700
N	0.09090700	-0.04473300	2.44288800
H	0.26412800	0.37367300	3.34846300
N	0.08985900	2.13821700	1.18321800

H	0.26382300	2.71281800	1.99845900
N	0.08985900	2.13821700	-1.18321800
H	0.26382300	2.71281800	-1.99845900

Cartesian coordinates of the optimized structures of dimers

(1) hetero-dimer (1-2)

C	1.52722800	2.60726800	0.00000000
C	1.93873500	-0.21448400	0.00000000
C	1.14863800	-1.53236500	2.39791100
C	1.14863800	-1.53236500	-2.39791100
H	0.80114000	-2.02188900	-3.29816700
H	1.33289100	3.67103300	0.00000000
H	0.80114000	-2.02188900	3.29816700
B	1.74829700	0.52936700	-1.25058000
B	1.55255300	-1.62926800	0.00000000
B	1.74829700	0.52936700	1.25058000
N	1.47162700	-0.23956900	-2.47265400
H	1.18094900	0.19028400	-3.34704800
N	1.29002300	-2.27242700	-1.29628200
H	0.88176300	-3.19906700	-1.38641900
N	1.29002300	-2.27242700	1.29628200
H	0.88176300	-3.19906700	1.38641900
N	1.47162700	-0.23956900	2.47265400
H	1.18094900	0.19028400	3.34704800
N	1.67756100	1.99544600	1.17760400
H	1.40841500	2.57977200	1.96485600
N	1.67756100	1.99544600	-1.17760400
H	1.40841500	2.57977200	-1.96485600
C	-1.28395000	3.14598300	0.00000000
C	-1.56512600	0.18319500	0.00000000
C	-1.72338800	-1.29972100	2.57797600
C	-1.72338800	-1.29972100	-2.57797600
H	-1.83277600	-1.83740600	-3.52125400
H	-1.22464900	4.23564300	0.00000000
H	-1.83277600	-1.83740600	3.52125400
B	-1.60825900	0.17049000	-2.50985500
H	-1.50288700	0.90895100	-3.45414300
B	-1.75233700	-1.97462000	-1.26697200
H	-1.76463700	-3.16683900	-1.09380800
B	-1.38338400	2.35561700	-1.24267900
H	-1.29074900	2.79322200	-2.35998500
B	-1.38338400	2.35561700	1.24267900
H	-1.29074900	2.79322200	2.35998500
B	-1.75233700	-1.97462000	1.26697200
H	-1.76463700	-3.16683900	1.09380800
B	-1.60825900	0.17049000	2.50985500
H	-1.50288700	0.90895100	3.45414300
N	-1.50289200	0.86607000	-1.18961200

N	-1.65562900	-1.18613600	0.00000000
N	-1.50289200	0.86607000	1.18961200

(2) homo-dimer 1_2

C	-1.41613100	2.54202400	0.81466000
C	-0.00015800	-0.00093400	0.84296000
C	-1.49399000	-2.49770800	0.81447900
C	2.90895400	-0.04423300	0.81394100
H	3.95859100	-0.07496400	1.10740800
H	-1.91434700	3.46613200	1.10857300
H	-2.04521500	-3.39160900	1.10704900
B	2.14636200	1.18203400	1.42511600
H	2.67076100	2.12879300	1.92382100
B	2.10440100	-1.25678600	1.39795600
H	2.60017100	-2.21509100	1.90398100
B	0.03588500	2.45031000	1.40042500
H	0.61774900	3.35725600	1.90910900
B	-2.09847200	1.26747100	1.42234700
H	-3.18271300	1.24714200	1.91570200
B	-0.04922000	-2.45149400	1.42301600
H	0.51056700	-3.38039000	1.91646600
B	-2.14103800	-1.19491300	1.39944200
H	-3.21765000	-1.14462100	1.90778300
N	0.71215000	1.18373500	1.34676600
N	0.66919300	-1.21002600	1.34575300
N	-1.38271000	0.02462400	1.34476000
C	-1.50067900	2.49341100	-0.81379300
C	0.00075500	0.00010700	-0.84308300
C	-1.40972500	-2.54464500	-0.81425600
C	2.90985600	0.05294400	-0.81435100
H	3.95950500	0.08642100	-1.10687300
H	-2.05470700	3.38536000	-1.10724800
H	-1.90520100	-3.47036400	-1.10795600
B	2.10221400	1.26288700	-1.39886800
H	2.59461000	2.22182700	-1.90675300
B	2.15090500	-1.17663100	-1.42366100
H	2.67781600	-2.12372800	-1.91868200
B	-0.05580400	2.45126100	-1.42235500
H	0.50061800	3.38174400	-1.91649900
B	-2.14345100	1.18868000	-1.40009800
H	-3.21939800	1.13546800	-1.90932200
B	0.04269600	-2.45031200	-1.39879300
H	0.62708600	-3.35725200	-1.90444700
B	-2.09405500	-1.27285800	-1.42460500
H	-3.17718000	-1.25567100	-1.92107200

N	0.66669700	1.21206000	-1.34476400
N	0.71662800	-1.18200000	-1.34624600
N	-1.38145100	-0.02846400	-1.34683900

(3) homo-dimer 2_2

C	-0.35561500	-2.77221600	-0.82668000
C	-0.00052400	-0.00011400	-0.82626200
C	-2.22310200	1.69423100	-0.82674700
C	2.57924500	1.07801500	-0.82682100
H	3.55292400	1.48467900	-1.12321300
H	-0.49004400	-3.81894100	-1.12259500
H	-3.06230600	2.33393800	-1.12280500
H	3.33615400	-0.76467200	-1.47377000
H	1.79900000	2.91251100	-1.46977500
B	1.19515800	-0.91085300	-1.27026800
H	1.62318000	-3.01389400	-1.46987700
B	0.19146700	1.49056600	-1.27008900
N	0.90535100	-2.30519800	-1.39350200
N	-1.45788300	-2.00210200	-1.39270700
B	1.19538700	-0.91063800	1.27021500
H	-2.32977700	-2.50818400	-1.47544900
H	-1.00541900	3.27218400	-1.47116900
B	-1.38714000	-0.57958500	-1.27129200
H	-3.42186500	0.10340100	-1.47440500
N	-2.44919400	0.36913100	-1.39371000
N	-1.00464800	2.26370500	-1.39242300
N	1.54417900	1.93654500	-1.39320500
N	2.46251300	-0.26141100	-1.39314100
C	-0.35522000	-2.77236600	0.82652400
C	-0.00055900	-0.00022300	0.82622800
C	-2.22337300	1.69380700	0.82682500
C	2.57906300	1.07831500	0.82689800
H	3.55251100	1.48548400	1.12334300
H	-0.48905800	-3.81919900	1.12232800
H	-3.06294000	2.33301700	1.12293000
H	3.33621300	-0.76480500	1.47193700
H	1.79888600	2.91229300	1.47198900
H	1.62296300	-3.01397300	1.47217000
H	-2.32991000	-2.50837400	1.47308800
H	-1.00543300	3.27210000	1.46924700
H	-3.42180300	0.10333800	1.47657800
B	0.19099900	1.49047400	1.27021100
B	-1.38700600	-0.58014200	1.27118200

N	0.90585600	-2.30500800	1.39266300
N	2.46263200	-0.26093700	1.39382200
N	1.54358400	1.93671900	1.39261000
N	-1.00529600	2.26340200	1.39331700
N	-2.44921300	0.36833600	1.39289200
N	-1.45746600	-2.00271200	1.39336500