Dissociative adsorption modes of TATB on Al (111) surface: A DFT investigation

Guo-zheng Zhao,*[a] Hui-li Li,[a] Jian-feng Jia,[a] Hai-shun Wu[a] and Ming Lu[b]

[a] *Key Laboratory of Magnetic Molecules, Magnetic Information Materials Ministry of Education, The School of Chemistry and Material Science, Shanxi Normal University, Linfen 041004, PR China;*

[b] *School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China*

1. The lattice parameters and coordinates of the Al (111) surface.

```
&CELL
    ABC 14.3437 14.3437    22.0269
    ALPHA_BETA_GAMMA    90.0    90.0    60.0
    PERIODIC XYZ
 &END CELL
&COORD
```

Al	5.7356821863	11.5948221664	2.3435609202
Al	5.7355326716	9.9386948660	0.0011546057
Al	8.6037072221	11.5953796210	2.3438495005
Al	8.6049719209	9.9392525955	0.0014433282
Al	11.4731464714	11.5959373505	2.3441382231
Al	11.4729969567	9.9398100501	0.0017319085
Al	14.3411715072	11.5964948051	2.3444268033
Al	14.3424362060	9.9403677796	0.0020206311
Al	17.2106107565	11.5970525346	2.3447155259
Al	17.2104612418	9.9409252342	0.0023092113
Al	4.3014455840	9.1095360088	2.3432721977
Al	4.3020030386	7.4538170606	0.0014433282
Al	7.1701775892	9.1105018155	2.3441382231
Al	7.1707353186	7.4539664379	0.0011546057
Al	10.0389098692	9.1106511928	2.3438495005

Al	10.0394673238	7.4549322446	0.0020206311
Al	12.9076418743	9.1116169996	2.3447155259
Al	12.9081996038	7.4550816219	0.0017319085
Al	15.7763741543	9.1117663769	2.3444268033
Al	15.7769316089	7.4560474287	0.0025979339
Al	2.8679158505	6.6254747334	2.3429836174
Al	2.8677663358	4.9693474330	0.0005773028
Al	5.7359408863	6.6260321880	2.3432721977
Al	5.7372055851	4.9699051625	0.0008660254
Al	8.6053801356	6.6265899175	2.3435609202
Al	8.6052306209	4.9704626171	0.0011546057
Al	11.4734051714	6.6271473721	2.3438495005
Al	11.4746698702	4.9710203466	0.0014433282
Al	14.3428444208	6.6277051015	2.3441382231
Al	14.3426949060	4.9715778012	0.0017319085
Al	1.4336792483	4.1401885757	2.3426948948
Al	1.4342367029	2.4844696275	0.0008660254
Al	4.3024112534	4.1411543825	2.3435609202
Al	4.3029689829	2.4846190048	0.0005773028
Al	7.1711435334	4.1413037598	2.3432721977
Al	7.1717009880	2.4855848116	0.0014433282
Al	10.0398755385	4.1422695666	2.3441382231
Al	10.0404332680	2.4857341889	0.0011546057
Al	12.9086078185	4.1424189439	2.3438495005
Al	12.9091652731	2.4866999957	0.0020206311
Al	0.0001495147	1.6561273004	2.3424063146
Al	0.0000000000	0.0000000000	0.0000000000
Al	2.8688815199	1.6570931071	2.3432723400
Al	2.8694392493	0.0005577295	0.0002887226
Al	5.7376137999	1.6572424845	2.3429836174

Al	5.7374642851	0.0011151841	0.0005773028
Al	8.6056388357	1.6577999390	2.3432721977
Al	8.6069035345	0.0016729135	0.0008660254
Al	11.4750780850	1.6583576685	2.3435609202
Al	11.4749285703	0.0022303681	0.0011546057
Al	7.1703973934	10.7666034893	4.5654585728
Al	5.7366820482	9.9387658989	6.9049178306
Al	10.0392768878	10.7671951047	4.5658076366
Al	8.6048613218	9.9391906796	6.9054911662
Al	12.9083751391	10.7671486734	4.5667295956
Al	11.4741295042	9.9391089983	6.9063119110
Al	15.7771389189	10.7671305321	4.5661389653
Al	14.3433584374	9.9387049730	6.9062774079
Al	18.6454439784	10.7670193462	4.5656021958
Al	17.2111913363	9.9392708898	6.9061190252
Al	5.7357130229	8.2819930928	4.5658983222
Al	4.3022812132	7.4539843979	6.9054934274
Al	8.6046955404	8.2823913571	4.5667322825
Al	7.1701123791	7.4541540137	6.9055889232
Al	11.4737396528	8.2826731883	4.5672082140
Al	10.0395201069	7.4541826218	6.9068650000
Al	14.3424213498	8.2823590726	4.5669285480
Al	12.9090041758	7.4538521788	6.9065313600
Al	17.2109367861	8.2824946168	4.5663989227
Al	15.7763615691	7.4541647485	6.9065733039
Al	4.3015947221	5.7977923796	4.5649842778
Al	2.8678623415	4.9704090964	6.9043383285
Al	7.1704927370	5.7983322042	4.5650764450
Al	5.7362480897	4.9708683076	6.9048979243
Al	10.0395495342	5.7984822083	4.5662051910

Al	8.6052283304	4.9706347652	6.9052911830
Al	12.9084106383	5.7982143991	4.5654607432
Al	11.4747643862	4.9704586711	6.9054678562
Al	15.7767749327	5.7983892528	4.5650723800
Al	14.3423710608	4.9708921428	6.9052527706
Al	2.8678490022	3.3136596801	4.5648458312
Al	1.4339251251	2.4861480211	6.9045113991
Al	5.7368698321	3.3140025304	4.5655747405
Al	4.3017503154	2.4863644145	6.9046673465
Al	8.6058554868	3.3141163809	4.5658718573
Al	7.1713162667	2.4864791156	6.9057277970
Al	11.4745992698	3.3139838252	4.5656732118
Al	10.0404751284	2.4860232626	6.9051175157
Al	14.3430440255	3.3139819409	4.5650573770
Al	12.9082638556	2.4864335236	6.9054096734
Al	1.4326992871	0.8294109992	4.5652929264
Al	-0.0010559846	0.0010196330	6.9044259215
Al	4.3016977482	0.8298966851	4.5658024449
Al	2.8671477058	0.0014213025	6.9049485995
Al	7.1706674834	0.8300728987	4.5664187438
Al	5.7362491837	0.0012093662	6.9055345893
Al	10.0394009623	0.8298734254	4.5657267795
Al	8.6059129310	0.0010436741	6.9053894258
Al	12.9078863400	0.8299835200	4.5655298802
Al	11.4732410254	0.0013646939	6.9052889470

&END COORD

2. Computational details.

All of the calculations were conducted in the QuickStep module of CP2K software package on the basis of density functional theory (DFT) with the gradient corrected functional of a revised

Perdew-Burke-Ernzerhof (PBEsol). Quickstep is based on a mixed Gaussian and plane waves method (GPW), in which a dual basis of atom-centered Gaussian orbitals and plane waves can interpret the wave functions and the electronic density, respectively.

Table 1 The configurations for the CP2K calculations

Parameter	Value
Method	Mixed Gaussian and Plan-wave (GPW)
Functional	PBEsol
Dispersive interaction	DRSLL
Pseudo-potential	Goedecker -Teter-Hutter (GTH)
Gaussian-type basis set sets	DZVP-MOLOPT-SR-GTH
Plane-wave cut-off	600 Ry
k-points sampling	Gamma-point only
Electron density convergence criteria	1.0×10^{-7} a.u.
Convergence criteria for geometry optimization	Maximum force 4.5×10^{-5} a.u. RMS force 3.0×10^{-5} a.u. Maximum coordinate change 3.0×10^{-4} a.u. RMS coordinate change 1.5×10^{-4} a.u.

In order to build the Al (111) surface, a 4 × 4 × 4 supercell of Al was optimized with lattice parameters $a = b = c = 4.057$ Å, which matches well with the reported values ($a = b = c = 4.050$ Å) [1]. A 5 × 5 slab was constructed on the basis of the optimized Al cell, which ensures that the distance between TATB and its period replica is larger than 7 Å. Four Al layers were included and the vacuum region along *c* was larger than 15 Å. In the following optimizing process, we fixed the lattice parameters of the supercell and froze the last two Al layers. Aimed at finding the most stable TATB/Al (111) configuration, many kinds of adsorption site were analyzed. Equation (1) shows the adsorption energy of TATB on Al (111) surface:

$$E_{ads} = E[\text{TATB/Al}] - E[\text{TATB}] - E[\text{Al}] \qquad (1)$$

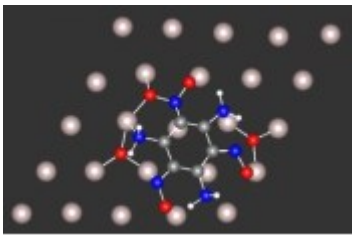
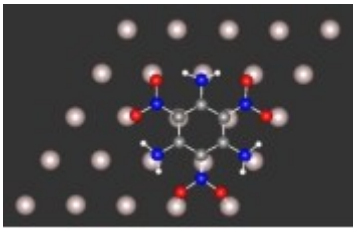
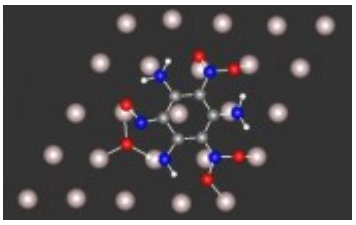
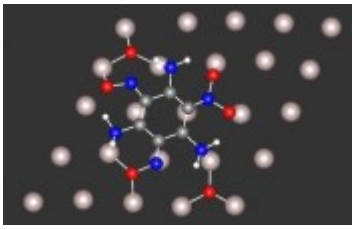
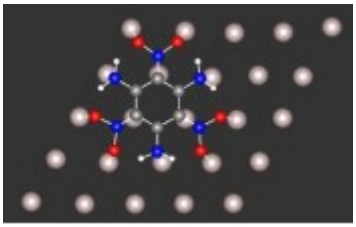
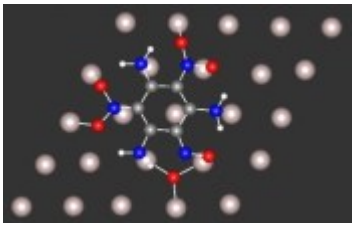
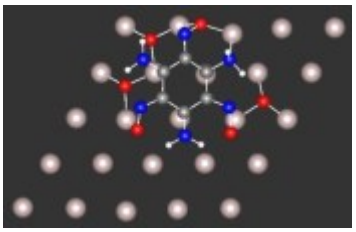
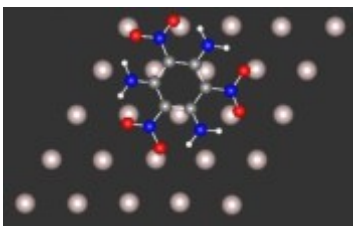
where, each term in Equations (1) is defined as follows: E[TATB/Al], the total energy of TATB/Al (111) surface; E[TATB], the energy of the isolated TATB molecule; E[Al], the relaxed Al (111) surface without any adsorbed molecules. The counterpoise correction method [2] was used to correct the basis set errors.

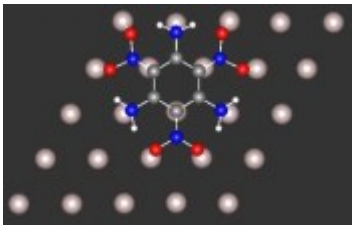
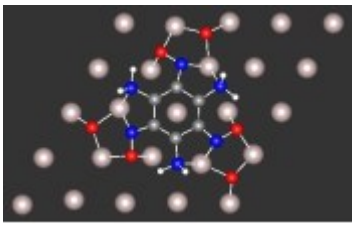
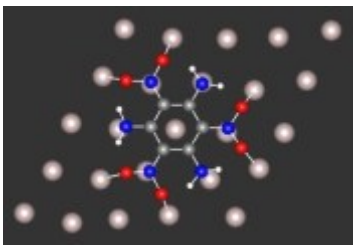
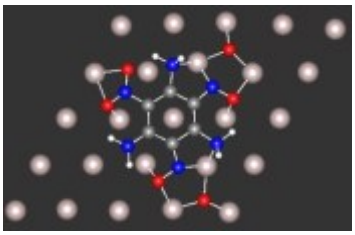
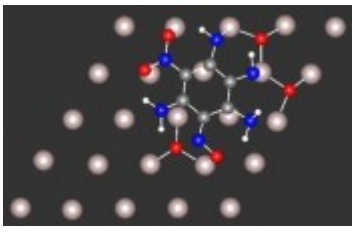
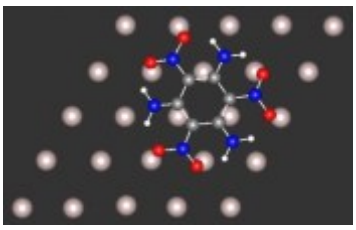
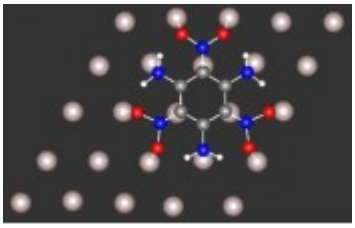
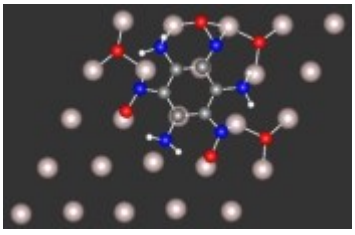
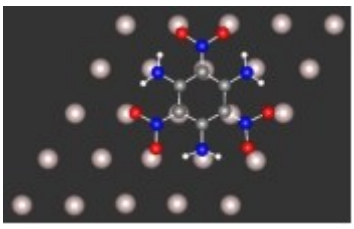
Reference

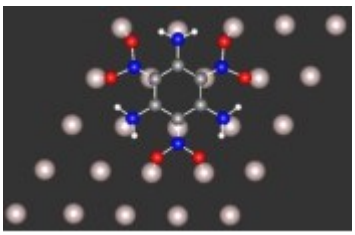
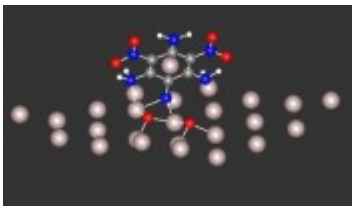
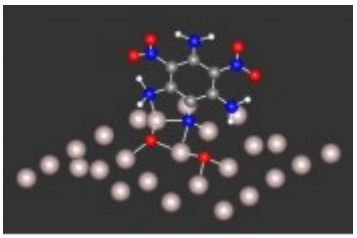
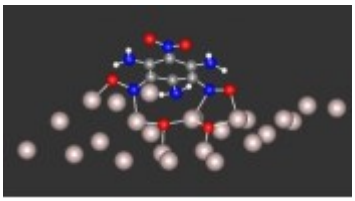
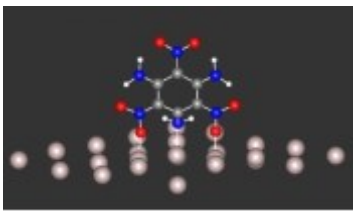
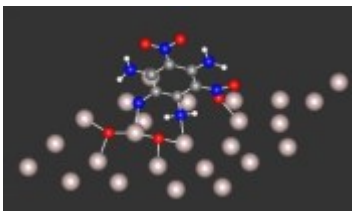
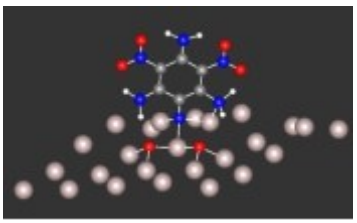
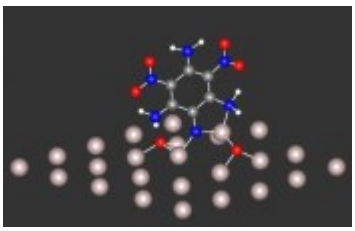
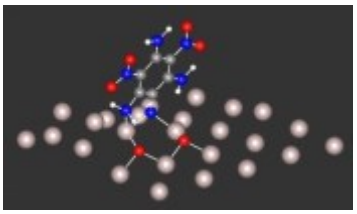
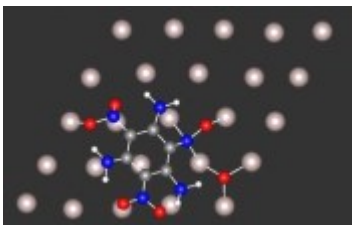
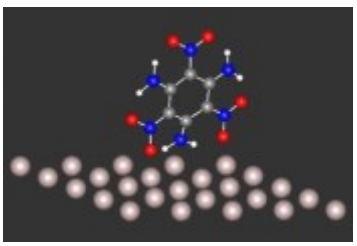
[1] A. S. Cooper, Acta Cryst., 1962, 15: 578-582

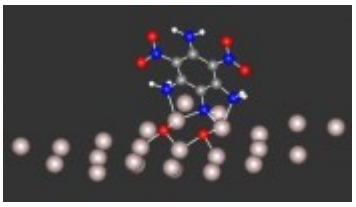
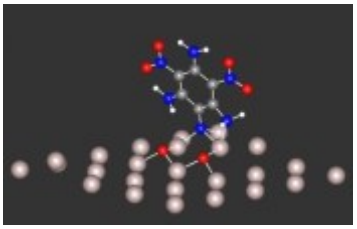
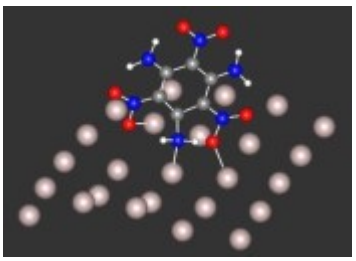
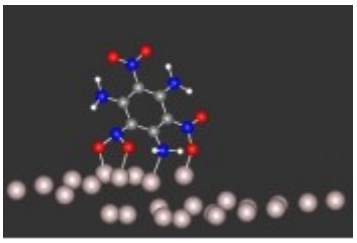
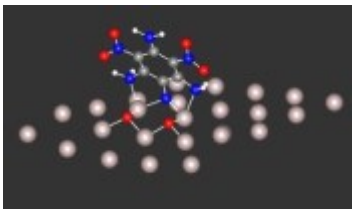
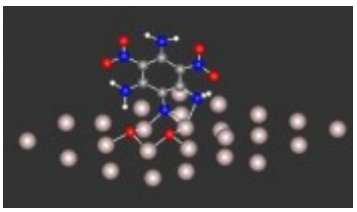
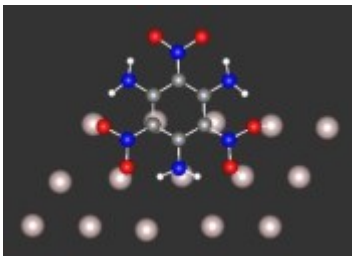
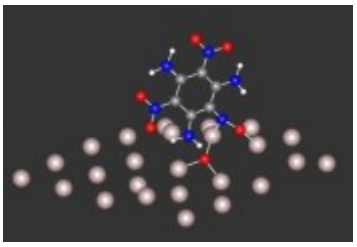
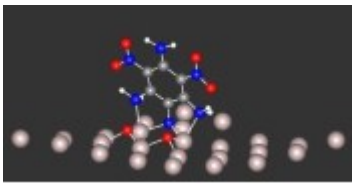
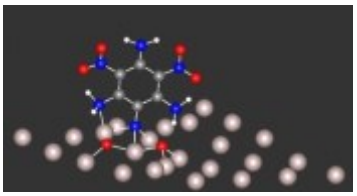
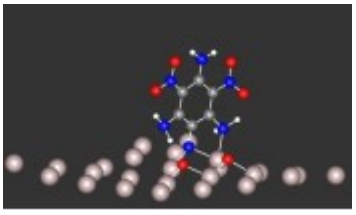
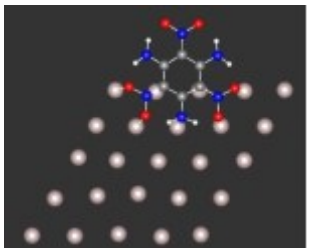
[2] S. F. Boys, F. Bernardi, Mol. Phys., 1970, 19: 553-566.

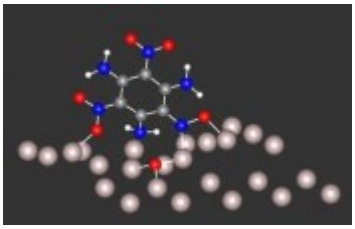
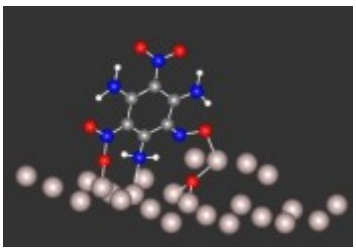
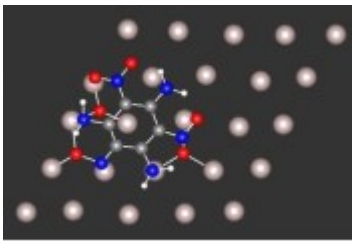
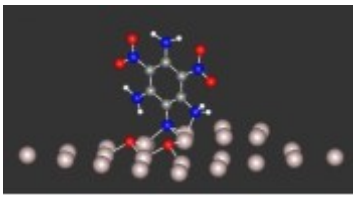
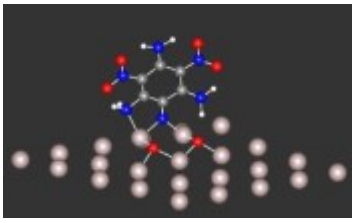
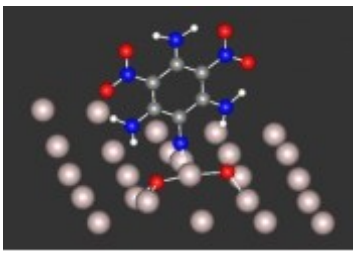
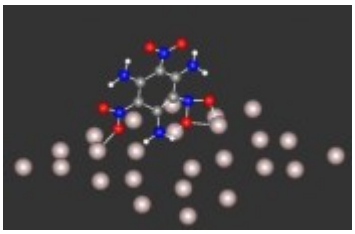
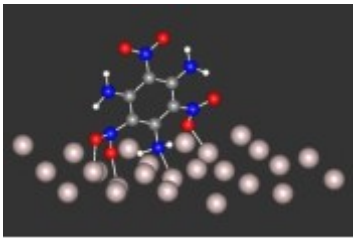
3. The structure and relative energies (E_{rel}, eV) of the considered TATB/Al (111).

No.	Structure	E_{rel}	No.	Structure	E_{rel}
The center of the benzene ring above a bridge site between the second layer of Al					
1P		0.00	1P-1		5.45
1P-2		3.43			
The center of the benzene ring above a bridge site between the third layer of Al					
2P		0.00	2P-1		5.53
2P-2		4.14			
The center of the benzene ring above an fcc site					
3P		0.00	3P-1		7.53

3P-2		6.48			
The center of the benzene ring above an on-top site					
4P		0.00	4P-1		10.86
4P-2		3.96			
The center of the benzene ring above an hcp site					
5P		0.00	5P-1		9.08
5P-2		7.28			
The center of the benzene ring above a bridge site between the first layer of Al					
6P		0.00	6P-1		8.50

6P-2		8.12			
The C–C symmetric axis of the benzene ring above an on-top site					
1V		0.00	1V-1		0.57
1V-2		0.51	1V-3		8.62
The C–C symmetric axis of the benzene ring above a bridge site between the second layer of Al					
2V		0.00	2V-1		0.47
2V-2		1.24	2V-3		0.29
2V-4		0.89	2V-5		10.88
The C–C symmetric axis of the benzene ring above an fcc site					

3V		0.00	3V-1		0.71
3V-2		7.77	3V-3		7.41
The C–C symmetric axis of the benzene ring above an hcp site					
4V		0.00	4V-1		0.71
4V-2		2.38	4V-3		5.98
The C–C symmetric axis of the benzene ring above a bridge site between the third layer of Al					
5V		0.00	5V-1		1.07
5V-2		0.52	5V-3		2.45

5V-4		5.17	5V-5		5.64
The C–C symmetric axis of the benzene ring above a bridge site between the first layer of Al					
6V		0.00	6V-1		1.28
6V-2		1.98	6V-3		2.68
6V-4		9.00	6V-5		8.91

4. The bond lengths (Å) of the considered TATB/Al (111).

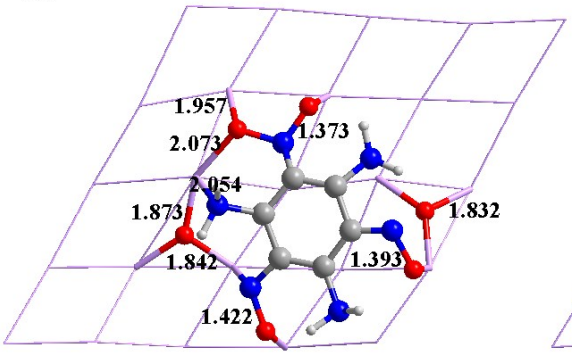
Geometries	P	1P	2P	3P	4P	5P	6P
C1-N1	1.414	1.325	1.447	1.324	1.374	1.323	1.365
C2-N2	1.327	1.425	1.43	1.413	1.448	1.484	1.443
C3-N3	1.414	1.444	1.327	1.333	1.375	1.348	1.368
C4-N4	1.327	1.488	1.461	1.486	1.448	1.414	1.453
C5-N5	1.415	1.362	1.379	1.338	1.374	1.399	1.362
C6-N6	1.327	1.463	1.463	1.379	1.450	1.369	1.485
N2-H21	1.043	1.051	1.034	1.033	1.041	1.049	1.045
N2-H22	1.043	1.032	1.048	1.036	1.036	1.041	1.040

N4-H41	1.042	1.039	1.036	1.040	1.036	1.034	1.049
N4-H42	1.042	1.035	1.065	1.053	1.041	2.124	1.036
N6-H61	1.042	1.034	1.044	1.033	1.036	1.033	1.039
N6-H62	1.042	1.046	1.040	1.030	1.041	1.032	1.034

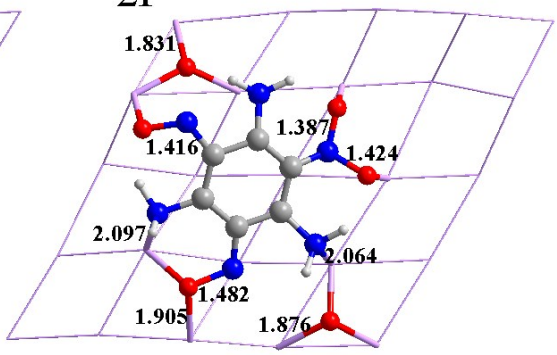
Geometries	V	1V	2V	3V	4V	5V	6V
C1-N1	1.416	1.408	1.386	1.410	1.414	1.411	1.407
C2-N2	1.328	1.436	1.414	1.428	1.422	1.419	1.437
C3-N3	1.415	1.413	1.376	1.414	1.415	1.412	1.352
C4-N4	1.329	1.333	1.335	1.332	1.333	1.332	1.346
C5-N5	1.415	1.409	1.415	1.414	1.417	1.408	1.415
C6-N6	1.328	1.426	1.337	1.431	1.423	1.420	1.442
N2-H21	1.043	1.041	1.053	1.053	1.046	1.056	1.035
N2-H22	1.043	1.069	1.047	1.051	1.066	1.065	1.068
N4-H41	1.043	1.039	1.038	1.040	1.039	1.039	1.033
N4-H42	1.043	1.041	1.037	1.039	1.038	1.039	1.040
N6-H61	1.043	1.056	1.033	1.061	1.062	1.062	1.032
N6-H62	1.043	1.075	1.031	1.053	1.049	1.051	1.069

5. Optimized adsorption configurations of TATB/Al (111) marked by bond lengths (unit: Å): 1P, 2P, 3P, 4P, 5P, and 6P denote the center of the benzene ring above a bridge site between the second layer of Al, a bridge site between the third layer of Al, an fcc site, an on-top site, an hcp site, and a bridge site between the first layer of Al, respectively. 1V, 2V, 3V, 4V, 5V, and 6V denote the C–C symmetric axis of the benzene ring above an on-top site, a bridge site between the second layer of Al, an fcc site, an hcp site, a bridge site between the third layer of Al, and the first layer of Al, respectively.

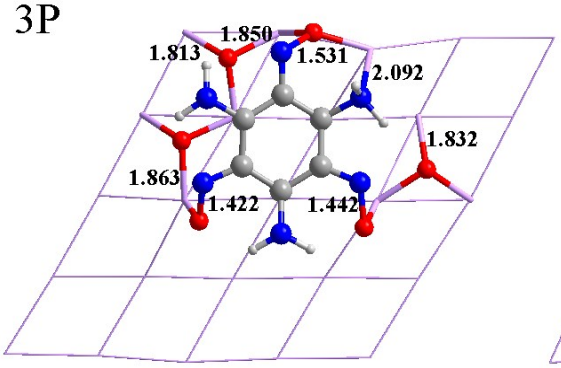
1P



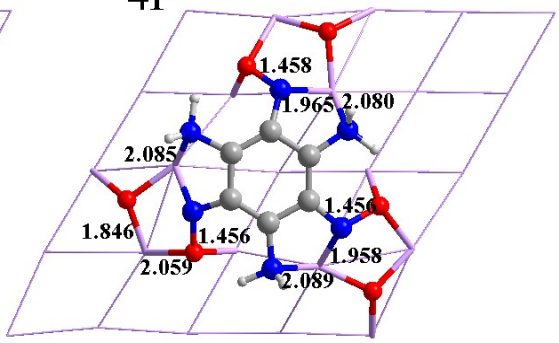
2P



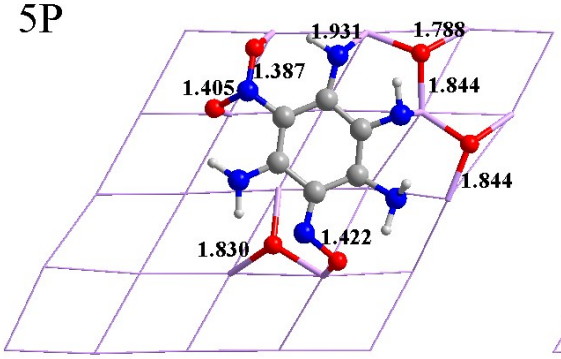
3P



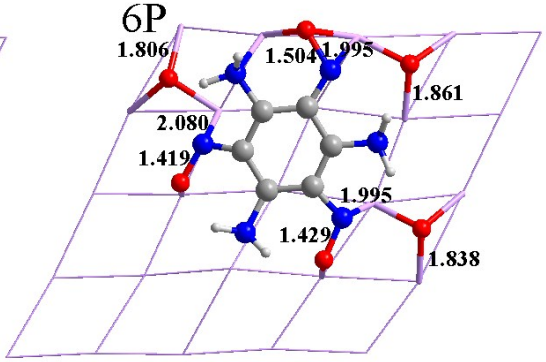
4P



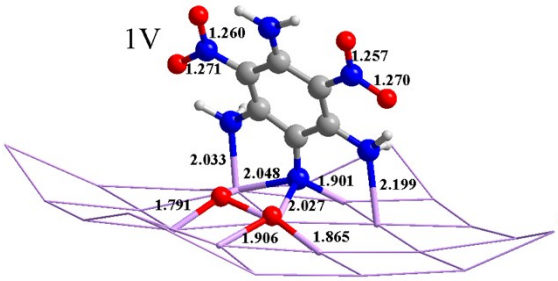
5P



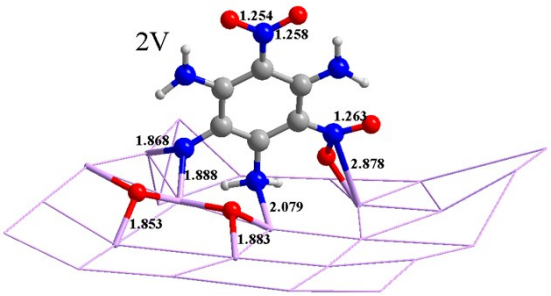
6P



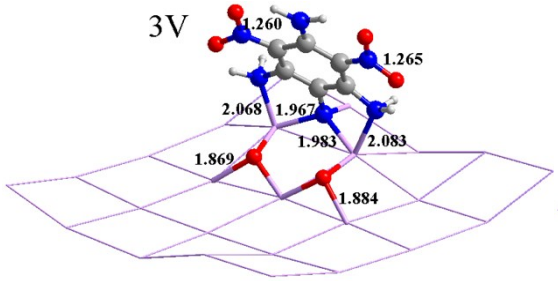
1V



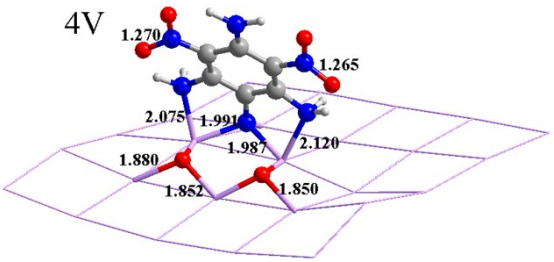
2V

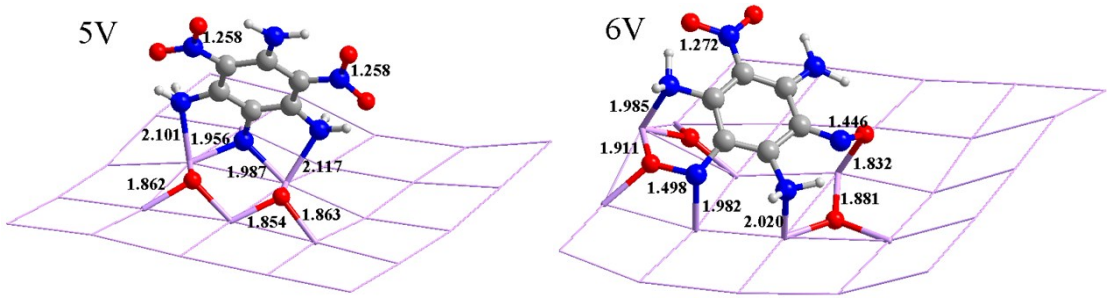


3V

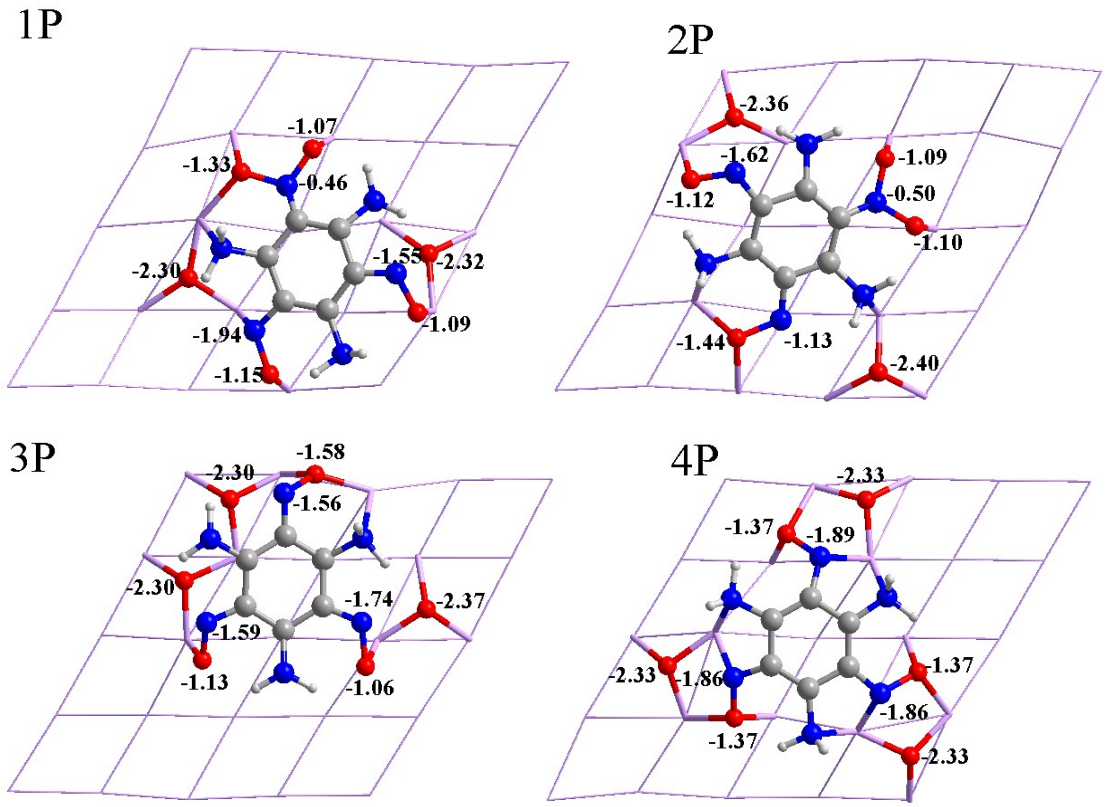


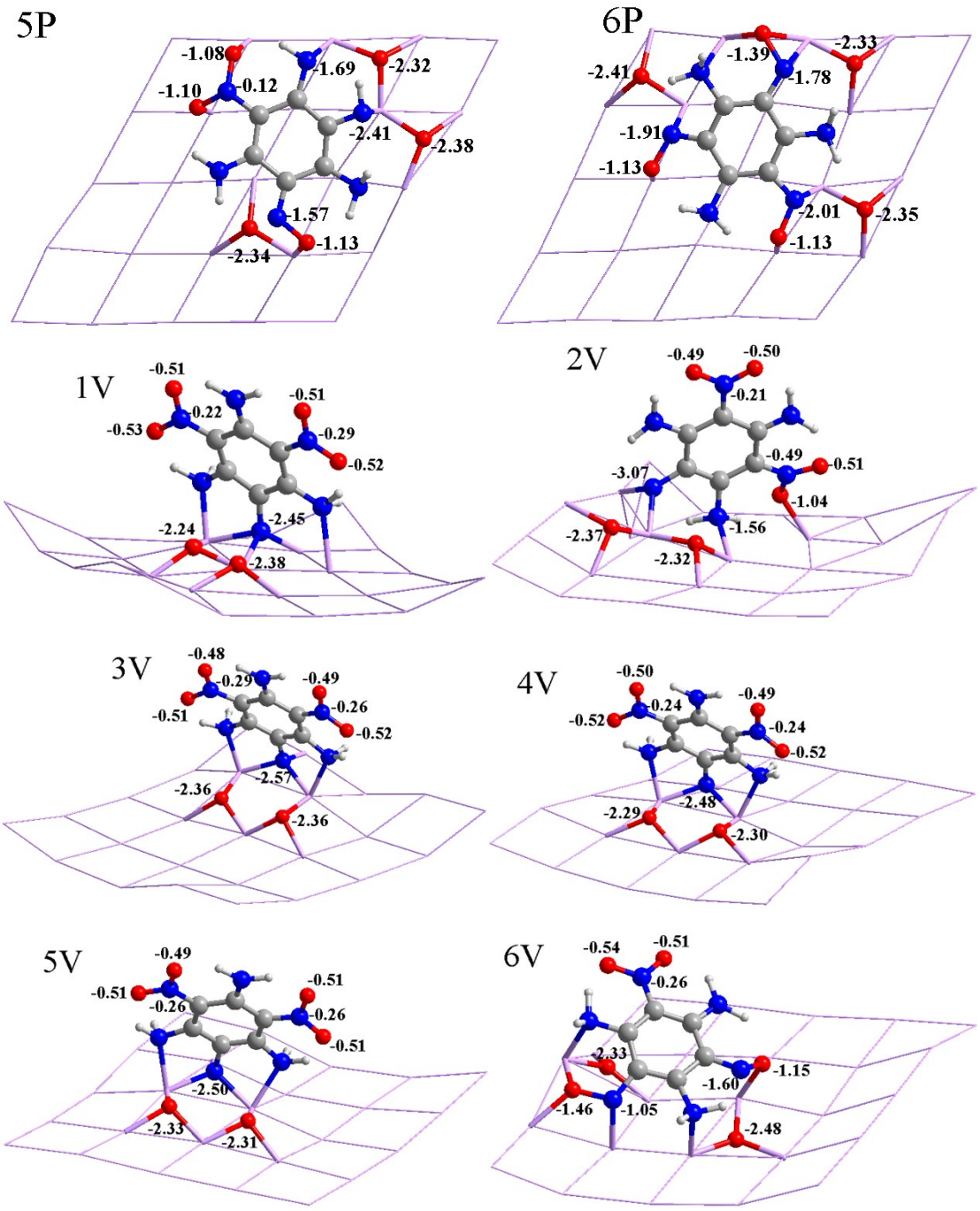
4V





6. Optimized adsorption configurations of TATB/Al (111) marked by Bader charges (unit: *e*): 1P, 2P, 3P, 4P, 5P, and 6P denote the center of the benzene ring above a bridge site between the second layer of Al, a bridge site between the third layer of Al, an fcc site, an on-top site, an hcp site, and a bridge site between the first layer of Al, respectively. 1V, 2V, 3V, 4V, 5V, and 6V denote the C–C symmetric axis of the benzene ring above an on-top site, a bridge site between the second layer of Al, an fcc site, an hcp site, a bridge site between the third layer of Al, and the first layer of Al, respectively. Negative sign means getting electrons.




5P
-1.08
-1.10
-0.12
-1.69
-2.32
-2.41
-2.38
-1.57
-1.13
-2.34
6P
-2.41
-1.39
-2.33
-1.78
-1.91
-1.13
-2.01
-2.35
-1.13
1V
-0.51
-0.53
0.22
-0.51
-0.29
-0.52
-2.24
-2.45
-2.38
2V
-0.49
-0.50
-0.21
-0.49
0.51
-3.07
-1.04
-2.37
-1.56
-2.32
3V
-0.48
-0.29
-0.49
-0.51
-0.26
-0.52
-2.36
-2.57
-2.36
4V
-0.50
-0.24
-0.49
-0.52
-0.24
-0.52
-2.48
-2.29
-2.30
5V
-0.49
-0.51
-0.51
-0.26
-0.26
-0.51
-2.50
-2.33
-2.31
6V
-0.54
-0.51
-0.26
-2.33
-1.15
-1.60
-1.46
-1.05
-2.48