Design and Evaluation of Novel Energetic Materials Based on Tricyclo[3.1.1.1^{2,4}]

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Table S1. Cartesian XYZ Coordinates for the Optimized Structure of the Compound **Tecage** at the ωB97XD/def2-TZVP level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.967403	-0.808537	-0.000037
2	6	0	0.967269	-0.808688	0.000006
3	6	0	0.967403	0.808537	-0.000037
4	6	0	-0.967269	0.808688	0.000006
5	7	0	-0.000049	1.312033	-1.001040
6	7	0	0.000049	1.312572	1.001135
7	7	0	0.000049	-1.312033	-1.001040
8	7	0	-0.000049	-1.312572	1.001135
9	1	0	1.964760	1.248776	0.000270
10	1	0	-1.964760	-1.248776	0.000270
11	1	0	-1.964781	1.248577	-0.000765
12	1	0	1.964781	-1.248577	-0.000765
13	1	0	0.000237	-0.841977	-1.895368
14	1	0	0.000127	-0.842281	1.895387
15	1	0	-0.000127	0.842281	1.895387
16	1	0	-0.000237	0.841977	-1.895368

Table S2. Selected bond lengths and Mayer bond orders of the compound **Tecage**, which can determine nitro substitution sites.

Bond	Length（Å）	Mayer
C1-H10	1.0902	0.96410462
C2-H12	1.0902	0.96410536
C3-H9	1.0902	0.96410462
C4-H11	1.0902	0.96410536
N5-H16	1.0103	0.92297184
N6-H15	1.0104	0.92295416
N7-H13	1.0103	0.92297184
N8-H14	1.0104	0.92295416

The nitro group will substitute the **H16** atom.

Table S3. Cartesian XYZ Coordinates for the Optimized Structure of the Compound **Tec-1** at the ωB97XD/def2-TZVP level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.152795	-0.673229	-0.968893
2	6	0	-1.152795	-0.673229	0.968893
3	6	0	-0.443019	0.771802	0.986344
4	6	0	-0.443019	0.771802	-0.986344
5	7	0	0.661712	0.798402	0.000000
6	7	0	-1.202918	1.589704	0.000000
7	7	0	-0.491079	-1.552557	-0.000000
8	7	0	-2.268849	-0.619900	-0.000000
9	1	0	-0.244181	1.195050	1.966288
10	1	0	-1.350915	-1.058994	-1.967073
11	1	0	-0.244181	1.195050	-1.966288
12	1	0	-1.350915	-1.058995	1.967072
13	7	0	1.783250	0.011644	0.000000
14	8	0	2.250508	-0.263063	-1.086347
15	8	0	2.250508	-0.263063	1.086347
16	1	0	-0.813773	2.527351	0.000000
17	1	0	-2.740175	0.277193	-0.000000
18	1	0	0.510971	-1.641570	-0.000000

Table S4. Selected bond lengths and Mayer bond orders of the compound **Tec-1**, which can determine nitro substitution sites.

Bond	Length（Å）	Mayer
N5-N13	1.37	1.00078365
N6-H16	1.006	0.90403665
N7-H18	1.0152	0.91580049
N8-H17	1.0134	0.90590058

The nitro group will substitute the **H16** atom.

Table S5. Cartesian XYZ Coordinates for the Optimized Structure of the Compound **Tec-2** at the ωB97XD/def2-TZVP level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.776577	1.456060	0.968195
2	6	0	-0.776578	1.456060	-0.968195
3	6	0	0.176678	0.178650	-0.994435
4	6	0	0.176678	0.178650	0.994435
5	7	0	1.233003	0.512991	-0.000000
6	7	0	-0.282625	-0.814124	0.000000
7	7	0	-0.265004	2.449618	-0.000000
8	7	0	-1.836802	1.098116	-0.000000
9	1	0	0.496609	-0.182345	-1.964429
10	1	0	-1.061957	1.796774	1.960055
11	1	0	0.496609	-0.182344	1.964429
12	1	0	-1.061957	1.796773	-1.960055
13	7	0	2.339351	-0.377539	-0.000000
14	8	0	2.780635	-0.670959	1.079725
15	8	0	2.780634	-0.670960	-1.079725
16	1	0	-2.522547	1.844024	-0.000000
17	1	0	0.740828	2.584369	-0.000000
18	7	0	-1.544188	-1.400368	0.000000
19	8	0	-1.992817	-1.676206	-1.084065
20	8	0	-1.992817	-1.676206	1.084065

Table S6. Selected bond lengths and Mayer bond orders of the compound **Tec-2**, which can determine nitro substitution sites.

Bond	Length（Å）	Mayer
N5-N13	1.5076	0.96816385
N6-N18	1.0824	0.96289468
N7-H17	1.0828	0.90903422
N8-H16	1.0827	0.90462268

The nitro group will substitute the **H16** atom.

Table S7. Cartesian XYZ Coordinates for the Optimized Structure of the Compound **Tec-3** at the ωB97XD/def2-TZVP level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.017158	-1.333564	-0.989401
2	6	0	0.017158	-1.333564	0.989401
3	6	0	-0.328577	0.218309	0.998022
4	6	0	-0.328577	0.218309	-0.998022
5	7	0	0.604569	0.794371	0.000000
6	7	0	-1.382568	0.496743	-0.000000
7	7	0	1.084484	-1.605146	0.000000
8	7	0	-0.916916	-1.910985	0.000000
9	1	0	-0.395392	0.696338	1.967312
10	1	0	0.102863	-1.787146	-1.970286
11	1	0	-0.395392	0.696337	-1.967312
12	1	0	0.102863	-1.787146	1.970286
13	7	0	0.663323	2.216829	0.000000
14	8	0	0.726829	2.736997	-1.080424
15	8	0	0.726827	2.736998	1.080424
16	1	0	-0.821795	-2.919610	0.000000
17	7	0	-2.650573	-0.083810	-0.000000
18	8	0	-3.147025	-0.250870	1.084151
19	8	0	-3.147025	-0.250870	-1.084152
20	7	0	2.353238	-1.019094	0.000000
21	8	0	2.848633	-0.844756	1.084351
22	8	0	2.848633	-0.844757	-1.084351

Table S8. Cartesian XYZ Coordinates for the Optimized Structure of the Compound **Tec-4** at the ωB97XD/def2-TZVP level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.577504	-0.546456	1.000460
2	6	0	0.577504	-0.546455	-1.000460
3	6	0	-0.577610	0.547060	-1.000474
4	6	0	-0.577610	0.547060	1.000474
5	7	0	-1.539615	0.028416	0.000000
6	7	0	-0.283656	1.595429	-0.000000
7	7	0	0.283513	-1.594727	-0.000000
8	7	0	1.539602	-0.027798	0.000000
9	1	0	-0.955912	0.845515	-1.970107
10	1	0	0.955773	-0.844921	1.970102
11	1	0	-0.955912	0.845515	1.970107
12	1	0	0.955773	-0.844921	-1.970102
13	7	0	-2.804151	0.690246	0.000000
14	8	0	-3.282610	0.894633	1.080788
15	8	0	-3.282610	0.894632	-1.080788
16	7	0	0.858301	2.403173	-0.000000
17	8	0	1.255261	2.738557	-1.084846
18	8	0	1.255261	2.738557	1.084846
19	7	0	-0.857793	-2.403255	0.000000
20	8	0	-1.254533	-2.738920	-1.084853
21	8	0	-1.254533	-2.738920	1.084853
22	7	0	2.803695	-0.690509	0.000000
23	8	0	3.282024	-0.895224	1.080778
24	8	0	3.282024	-0.895224	-1.080778

Table S9. Selected bond lengths and Mayer bond orders of the compound **Tec-4**, which can determine nitro substitution sites.

Bond	Length（Å）	Mayer
C1-H10	1.0828	0.94232787
C2-H12	1.0828	0.94232787
C3-H9	1.0828	0.94234911
C4-H11	1.0828	0.94234912

The nitro group will substitute the **H9** atom.

Table S10. Cartesian XYZ Coordinates for the Optimized Structure of the Compound **Tec-5** at the ωB97XD/def2-TZVP level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.590884	-0.456726	0.464554
2	6	0	0.246106	-0.057164	-1.438257
3	6	0	-1.058201	0.759299	-1.038083
4	6	0	-0.703841	0.376816	0.893862
5	7	0	-1.724039	-0.125622	-0.053307
6	7	0	-0.766349	1.629476	0.117802
7	7	0	0.322471	-1.327049	-0.672921
8	7	0	1.274673	0.445101	-0.494812
9	1	0	0.498789	-0.083867	-2.490422
10	7	0	-3.065030	0.252845	0.272841
11	8	0	-3.365588	0.143405	1.427374
12	8	0	-3.754018	0.559873	-0.658705
13	7	0	0.195996	2.652373	0.120346
14	8	0	0.331610	3.223978	-0.930390
15	8	0	0.701545	2.888104	1.181319
16	7	0	-0.687761	-2.319433	-0.696653
17	8	0	-1.173507	-2.510117	-1.777582
18	8	0	-0.875999	-2.898405	0.335009
19	7	0	2.627722	0.105915	-0.859906
20	8	0	3.374257	-0.058166	0.058394
21	8	0	2.862842	0.125227	-2.033762
22	1	0	-0.919469	0.394408	1.954688
23	1	0	-1.645750	1.155342	-1.856796
24	7	0	1.364234	-1.013741	1.632729
25	8	0	1.846295	-2.100845	1.498294
26	8	0	1.405477	-0.285340	2.592202

Table S11. Selected bond lengths and Mayer bond orders of the compound **Tec-5**, which can determine nitro substitution sites.

Bond	Length（Å）	Mayer
C1-N24	1.5076	0.858163
C2-H9	1.0824	0.93871364
C3-H23	1.0828	0.9447788
C4-H22	1.0827	0.94784466

The nitro group will substitute the **H9** atom.

Table S12. Cartesian XYZ Coordinates for the Optimized Structure of the Compound **Tec-6** at the ωB97XD/def2-TZVP level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.365572	-0.269814	-0.977040
2	6	0	0.365572	-0.269813	0.977040
3	6	0	-0.986178	0.585816	1.001252
4	6	0	-0.986178	0.585814	-1.001253
5	7	0	-0.898976	1.661472	-0.000001
6	7	0	-1.817355	-0.120353	0.000000
7	7	0	1.214230	0.461096	-0.000000
8	7	0	0.311444	-1.355882	0.000001
9	7	0	0.040268	2.712251	-0.000002
10	8	0	0.349532	3.119647	-1.085201
11	8	0	0.349531	3.119649	1.085196
12	7	0	-3.199088	0.266067	-0.000000
13	8	0	-3.702501	0.366689	1.081606
14	8	0	-3.702501	0.366687	-1.081608
15	7	0	2.639400	0.182685	0.000000
16	8	0	3.142855	0.143526	1.080541
17	8	0	3.142855	0.143521	-1.080540
18	7	0	-0.717139	-2.357473	0.000001
19	8	0	-1.051971	-2.735152	-1.083599
20	8	0	-1.051971	-2.735151	1.083602
21	1	0	-1.389651	0.797170	-1.983501
22	1	0	-1.389651	0.797173	1.983499
23	7	0	0.909108	-0.583710	-2.352502
24	8	0	1.393226	-1.664864	-2.511430
25	8	0	0.774460	0.309934	-3.148767
26	7	0	0.909108	-0.583706	2.352504
27	8	0	1.393226	-1.664860	2.511433
28	8	0	0.774457	0.309938	3.148768

Table S13. Selected bond lengths and Mayer bond orders of the compound **Tec-6**, which can determine nitro substitution sites.

Bond	Length（Å）	Mayer
C1-N23	1.5119	0.85160686
C2-N26	1.5119	0.85160693
C3-H22	1.0827	0.95100829
C4-H21	1.0827	0.9510084

The nitro group will substitute the **H21** atom.

Table S14. Cartesian XYZ Coordinates for the Optimized Structure of the Compound **Tec-7** at the ωB97XD/def2-TZVP level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.098748	0.819319	-0.116377
2	6	0	-0.185774	-0.743863	0.625323
3	6	0	1.148719	-0.340725	-0.212691
4	6	0	0.197361	1.235316	-0.939872
5	7	0	0.798653	0.040430	-1.571417
6	7	0	1.269364	1.109907	0.072724
7	7	0	-1.243680	-0.628865	-0.409741
8	7	0	-0.776643	0.432540	1.255293
9	7	0	0.125162	-0.780609	-2.527782
10	8	0	-0.562541	-0.167374	-3.293504
11	8	0	0.387229	-1.944428	-2.490847
12	7	0	2.505256	1.762857	-0.327172
13	8	0	3.509447	1.208523	-0.001805
14	8	0	2.355808	2.823783	-0.856248
15	7	0	-2.559607	-1.206180	-0.125105
16	8	0	-2.576233	-2.171136	0.572119
17	8	0	-3.442300	-0.675276	-0.724020
18	7	0	-0.098186	1.327645	2.159618
19	8	0	-0.398492	2.478776	2.015201
20	8	0	0.605220	0.809696	2.966872
21	1	0	0.119778	2.149044	-1.514856
22	7	0	-2.285086	1.738793	-0.317952
23	8	0	-3.040694	1.844575	0.603099
24	8	0	-2.330627	2.267921	-1.397919
25	7	0	-0.088502	-2.039779	1.394411
26	8	0	-0.368360	-2.010380	2.552619
27	8	0	0.265260	-2.966955	0.712827
28	7	0	2.354360	-1.205510	0.049120
29	8	0	2.954530	-1.605434	-0.902202
30	8	0	2.579657	-1.370783	1.220379

Table S15. Cartesian XYZ Coordinates for the Optimized Structure of the Compound **Tec-8** at the ωB97XD/def2-TZVP level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.753352	-0.981297	-0.295662
2	6	0	-0.754464	0.980369	-0.295696
3	6	0	0.753352	0.981291	0.295663
4	6	0	0.754482	-0.980395	0.295666
5	7	0	0.888838	0.000518	1.368942
6	7	0	1.438422	0.000829	-0.583377
7	7	0	-1.438428	-0.000814	0.583342
8	7	0	-0.888823	-0.000557	-1.368982
9	7	0	0.089208	0.000027	2.580136
10	8	0	-0.154748	-1.083766	3.011687
11	8	0	-0.156282	1.083520	3.011565
12	7	0	2.914159	0.001700	-0.543142
13	8	0	3.413682	1.080252	-0.581951
14	8	0	3.414973	-1.076262	-0.581953
15	7	0	-2.914129	-0.001604	0.543260
16	8	0	-3.414906	1.076384	0.582137
17	8	0	-3.413780	-1.080108	0.582124
18	7	0	-0.089172	-0.000104	-2.580200
19	8	0	0.156349	-1.083608	-3.011564
20	8	0	0.154731	1.083676	-3.011792
21	7	0	-1.388940	-2.347232	-0.444098
22	8	0	-1.932445	-2.580576	-1.479905
23	8	0	-1.278529	-3.034111	0.536458
24	7	0	-1.391608	2.345616	-0.444136
25	8	0	-1.935421	2.578346	-1.479915
26	8	0	-1.281960	3.032598	0.536443
27	7	0	1.388915	2.347232	0.444087
28	8	0	1.932089	2.580740	1.480026
29	8	0	1.278806	3.033961	-0.536611
30	7	0	1.391598	-2.345644	0.444086
31	8	0	1.282319	-3.032454	-0.536659
32	8	0	1.935075	-2.578538	1.480002

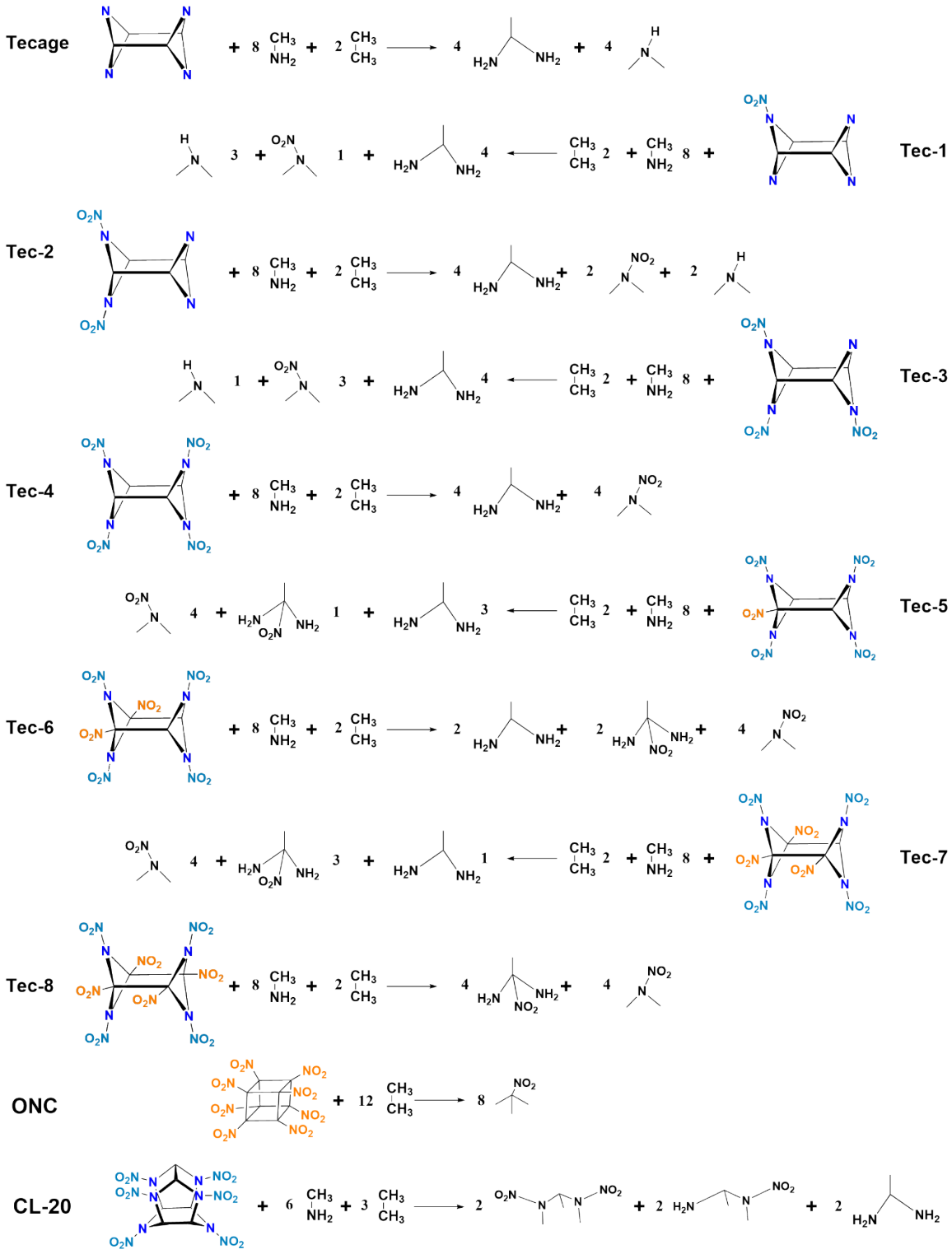

Figure S1. The cage Strain is calculated using the isomeric reaction.

Table S16. The theoretical densities calculated using Eq. (1) were compared with the experimental densities.

Compound	M_w/V_m (g/cm³)	ν	σ_{tot}^2 (kcal/mol)²	Theoretical Density (g/cm³)	Experimental Density (g/cm³)	Absolute Error
TEX	1.93	0.18	146.04	1.89	2.00[1]	0.11
PATN	2.01	0.07	180.79	1.92	1.98[2]	0.06
TAOTN	1.99	0.09	171.68	1.91	1.97[2]	0.05
HNA	1.89	0.10	147.61	1.82	1.76[3]	0.06
HNHAA	2.06	0.06	152.48	1.96	2.02[4]	0.06
ONOP	1.93	0.04	261.08	1.85	1.85[5]	0.00
A1	1.76	0.23	97.60	1.72	1.68[6]	0.04
B1	1.91	0.10	219.33	1.86	1.88[7]	0.02
B2	1.87	0.14	215.36	1.84	1.86[7]	0.02
C1	1.73	0.18	84.52	1.67	1.61[8]	0.06

Mean Absolute Error (MAE): 0.0483 g/cm³.

The results in Table 16 demonstrate that the mean absolute error (MAE) of the theoretical densities calculated using Eq. 1 is 0.0483 g/cm³, indicating high predictive accuracy. Therefore, we conclude that the predictive accuracy of Eq. 1 is sufficiently robust to support performance evaluations across all compounds in this study.

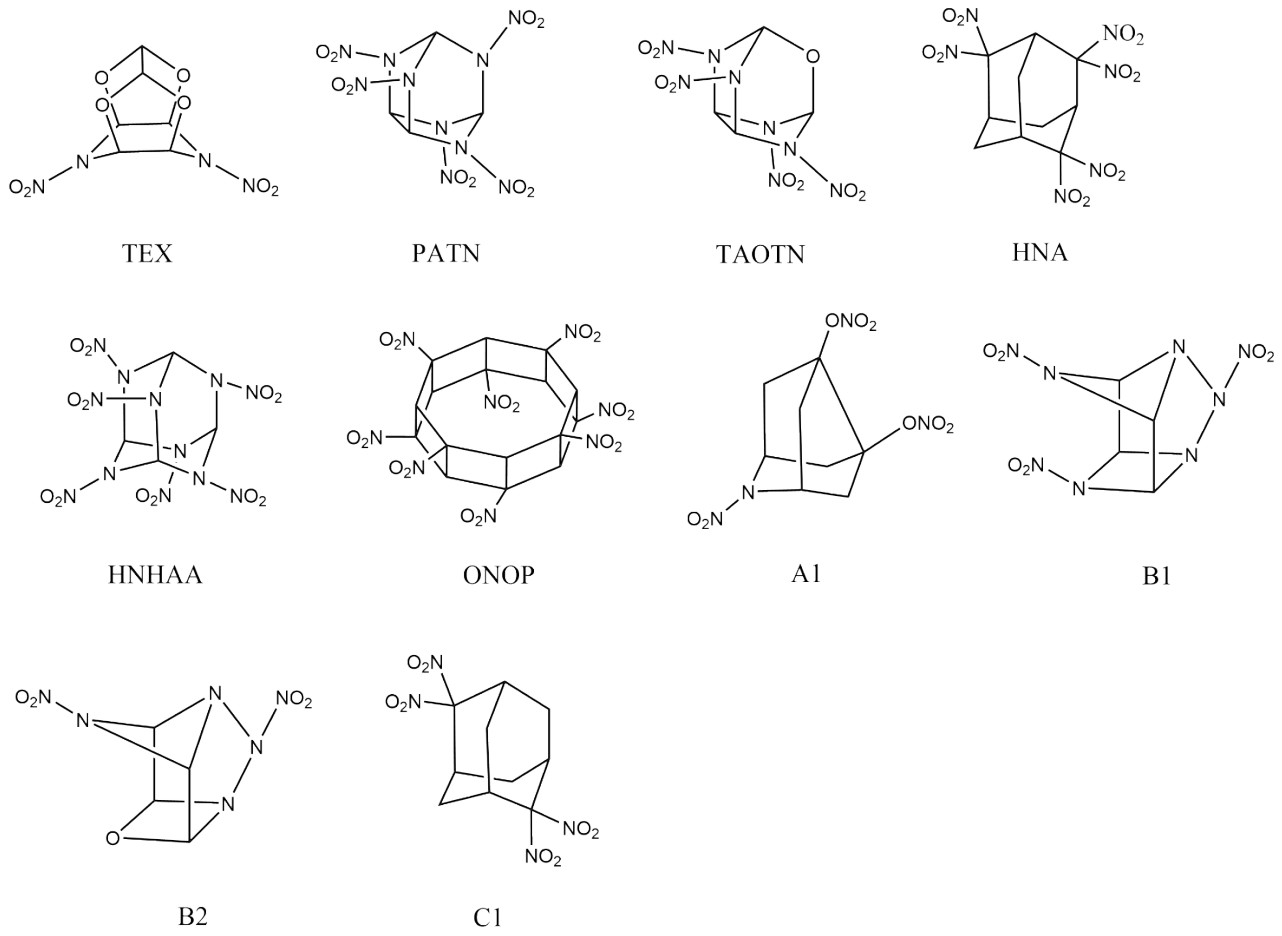

Figure S2. The compounds listed in Table 16.

Table S17. The heats of formation (HOF) values determined using isodesmic reactions were compared with experimental values.

Compound	Theoretical HOF (kJ/mol)	Experimental HOF (kJ/mol)	Absolute Error
RDX	175.64	192.17[9]	16.53
HMX	267.35	263.70[10]	3.65
DHT	979.06	1033.45[11]	54.39
DAAT	867.76	861.90[12]	5.86
BTT	921.65	935.96[12]	14.31
TATB	16.47	28.42[13]	11.95
D1	344.26	326.77[9]	17.49
D2	340.66	324.26[9]	16.40
D3	468.44	447.27[9]	21.17
E1	-105.44	-129.41[14]	23.97
E2	-46.44	-41.84[14]	4.60

Mean Absolute Error (MAE): 13.48 kJ/mol

It can be seen from the table that the maximum absolute error of the predicted HOF and the experimental value is 23.97 kJ/mol, the minimum is 3.65 kJ/mol, and the average absolute error is 13.48 kJ/mol, which is very small and within the acceptable range. We have listed only 11 N-hetero-energetic compounds here, which cannot represent all of them, but can at least show that the HOF calculated by isodesmic reaction is valuable for reference.

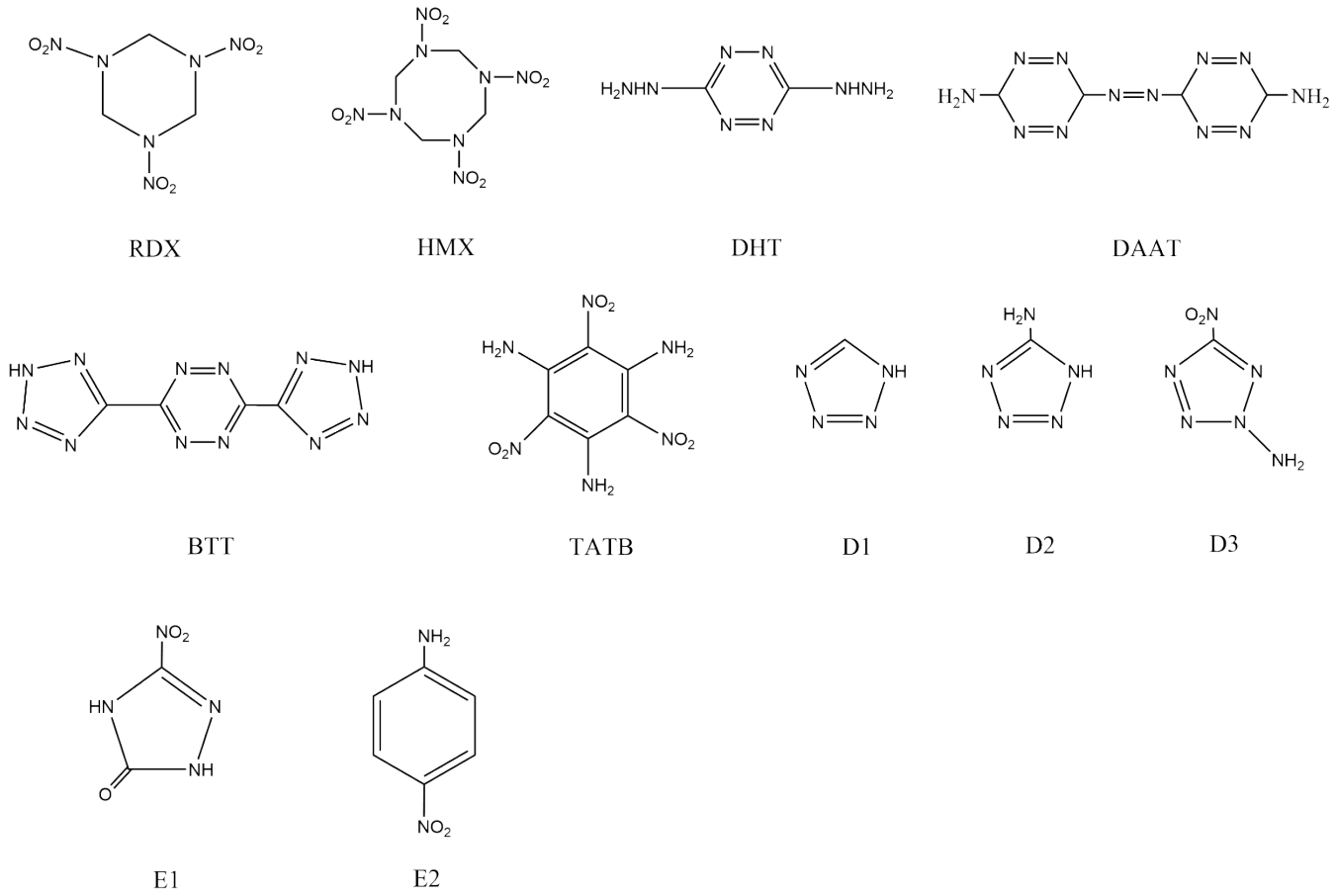

Figure S3. The compounds listed in Table 17.

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