Electronic Supporting Information

Touching the density limits of energetic materials by molecular design

Yunlu Li,*[a,b] Xinzhong Wang,[a] Mei Xue*[c]

[a] Dr. Yunlu Li, Prof. Xinzhong Wang,
Department of Electronic Communication and Technology
Shenzhen Institute of Information Technology
2188 Longxiang Avenue, Longgang District, Shenzhen 518172 (P.R. China)
E-mail: liyunlu2014@163.com, 7520210114@bit.edu.cn

[b] Dr. Yunlu Li,
School of Materials and Energy
University of Electronic Science and Technology of China
2006 Xiyuan Avenue, High-tech Zone (West), Chengdu 610054 (P.R. China)

[c] Dr. Mei Xue,
School of Materials Science & Engineering
Beijing Institute of Technology
5 Zhongguan South Street, Haidian District, Beijing 100081 (P.R. China)

Contents

1. The Optimized Cartesian coordinates for the designed compounds.

We conducted geometry optimization and frequency analysis for RDX, β-HMX, ε-HNIW, ONC, and the designed molecules at the ωB97XD/def2-TZVP level[1,2] in the gas phase using the Gaussian 16 (A.03) program.[3] The optimized structures of all compounds demonstrate true local energy minima on the potential energy surface and do not exhibit any imaginary frequencies.

Table S1. Optimized Cartesian coordinates for CEM-1 at the ωB97XD/def2-TZVP level of theory

CEM-1 (charge=0, multiplicity=1)			
atom	*x*	*y*	*z*
C	-0.63754	0.40423	1.40602
C	-0.4119	-1.14695	1.24408
C	-0.56566	-0.17432	-0.80948
C	0.91116	0.62139	1.42203
C	1.13001	-0.91756	1.24483
C	1.01073	0.05179	-0.80894
H	1.41347	0.21714	-1.798
H	-1.00743	-0.13298	-1.79602
N	1.59812	-1.0845	-0.12429
N	1.36417	1.11519	0.13705
N	-1.09826	0.83637	0.10267
N	-0.80296	-1.43656	-0.11721
H	1.7286	-1.46515	1.95999
H	1.35022	1.14292	2.26295
H	-0.82694	-1.84063	1.96275
H	-1.23294	0.79674	2.21904
N	-2.02822	-2.08324	-0.34371
O	-2.48832	-1.97122	-1.44999
O	-2.46236	-2.7441	0.56642
N	-2.44925	1.2101	-0.05451
O	-2.86559	1.21103	-1.18188
O	-3.02741	1.55371	0.94383
N	1.08117	2.43193	-0.20594
O	0.97027	3.20745	0.71062
O	1.03482	2.67686	-1.38668
N	2.98732	-1.24546	-0.30717
O	3.42485	-0.91419	-1.37761
O	3.58742	-1.76406	0.59901

Table S2. Optimized Cartesian coordinates for CEM-2 at the ωB97XD/def2-TZVP level of theory

CEM-2 (charge=0, multiplicity=1)			
atom	*x*	*y*	*z*
C	1.11471	-0.07086	-1.05406
C	0.07096	-1.16486	-0.63651
C	0.54818	0.18786	1.13313
C	-0.05569	0.85791	-1.50715
C	-1.09298	-0.23003	-1.07505
C	-0.64699	1.14949	0.69504
H	-0.9916	1.78737	1.49645
H	0.83206	0.30321	2.16968
N	-1.67864	0.27962	0.15915
N	-0.28961	1.8885	-0.51901
N	1.62714	0.43974	0.20224
N	0.22707	-1.21128	0.78667
H	-1.8186	-0.6118	-1.77949
H	-0.04608	1.22055	-2.52659
H	1.88888	-0.32546	-1.76678
N	-0.79195	-1.83862	1.52726
O	-0.89153	-1.49178	2.67394
O	-1.41218	-2.69147	0.94962
N	2.91357	-0.02523	0.60832
O	3.1241	-0.01247	1.78875
O	3.66866	-0.31316	-0.27818
N	0.63767	2.92478	-0.41499
O	1.23896	3.19996	-1.42194
O	0.69892	3.47496	0.65582
N	-2.9739	0.85672	0.0568
O	-3.2563	1.66135	0.90166
O	-3.67142	0.43348	-0.82383
N	0.23725	-2.47368	-1.34058
O	-0.35646	-2.57709	-2.38854
O	1.0005	-3.26311	-0.85565

Table S3. Optimized Cartesian coordinates for CEM-3 at the ωB97XD/def2-TZVP level of theory

CEM-3 (charge=0, multiplicity=1)			
atom	*x*	*y*	*z*
C	-1.01236	-0.64394	-1.23172
C	-0.9894	0.68095	-0.38715
C	-0.90897	-1.14801	0.96677
C	0.54125	-0.62542	-1.34308
C	0.58822	0.69816	-0.50492
C	0.6749	-1.11983	0.86943
H	1.15968	-1.63688	1.68768
H	-1.27277	-1.6805	1.83431
N	1.05764	0.30631	0.82039
N	1.0334	-1.63775	-0.4433
N	-1.39711	-1.67092	-0.28998
N	-1.42214	0.23069	0.89579
H	0.98675	-0.63837	-2.32912
H	-1.58364	-0.65047	-2.15148
N	-1.20617	1.06306	2.0203
O	-1.16335	0.49005	3.07631
O	-1.14587	2.23804	1.80065
N	-2.76419	-2.06468	-0.2972
O	-3.18101	-2.52117	0.73087
O	-3.33319	-1.96396	-1.34967
N	2.34652	-2.12377	-0.63294
O	2.75261	-2.11483	-1.76181
O	2.89025	-2.55898	0.34868
N	2.45745	0.48016	1.14924
O	2.7464	0.09141	2.24051
O	3.15672	1.00345	0.32817
N	-1.81018	1.77797	-0.99507
O	-1.31704	2.28583	-1.97509
O	-2.89613	1.98161	-0.53412
N	1.21526	1.93723	-1.07934
O	1.13899	2.91982	-0.39224
O	1.69847	1.83208	-2.17385

Table S4. Optimized Cartesian coordinates for CEM-4 at the ωB97XD/def2-TZVP level of theory

CEM-4 (charge=0, multiplicity=1)			
atom	*x*	*y*	*z*
C	0.99085	0.18428	-0.9979
C	0.18131	-1.10129	-0.60596
C	1.35708	-0.34009	1.18066
C	-0.21647	1.08655	-0.62072
C	-1.05427	-0.19241	-0.22449
C	0.11547	0.56356	1.57661
H	0.12959	0.86498	2.6149
H	2.03187	-0.52661	2.00441
N	-1.09662	-0.17367	1.23531
N	-0.01497	1.70818	0.6596
N	1.97948	0.31723	0.05048
N	0.87862	-1.57428	0.54318
H	1.37592	0.26733	-2.00743
N	0.24975	-2.53391	1.3758
O	0.62565	-2.53975	2.51737
O	-0.53692	-3.25758	0.83863
N	3.30791	-0.11713	-0.26573
O	3.97642	-0.44927	0.67073
O	3.61878	-0.03818	-1.41932
N	0.98884	2.70338	0.75008
O	1.2475	3.28684	-0.26539
O	1.4298	2.88316	1.85246
N	-2.25774	0.44989	1.87141
O	-2.11314	0.65645	3.0387
O	-3.2157	0.63945	1.18718
N	0.07898	-2.08763	-1.73694
O	-0.73827	-1.81281	-2.58
O	0.87519	-2.98187	-1.74731
N	-2.36406	-0.55841	-0.88702
O	-2.82544	-1.60128	-0.51524
O	-2.782	0.1916	-1.72069
N	-0.75877	2.01857	-1.67638
O	-1.52974	2.85261	-1.29774
O	-0.37225	1.8113	-2.79683

Table S5. Optimized Cartesian coordinates for CEM-5 at the ωB97XD/def2-TZVP level of theory

CEM-5 (charge=0, multiplicity=1)			
atom	*x*	*y*	*z*
C	-1.10402	0.16627	0.4312
C	-0.17053	-1.10768	0.4353
C	-0.63673	-0.45959	-1.70157
C	0.17051	1.10768	0.43538
C	1.10399	-0.16627	0.43119
C	0.63673	0.45973	-1.70153
H	0.9788	0.70864	-2.69696
H	-0.9788	-0.70844	-2.69702
N	1.6609	-0.21778	-0.9162
N	0.40633	1.64495	-0.86891
N	-1.66093	0.21783	-0.91619
N	-0.40633	-1.64486	-0.86903
N	0.49054	-2.62483	-1.37228
O	0.53271	-2.70068	-2.56997
O	1.05249	-3.29041	-0.55292
N	-2.95264	-0.45093	-1.13386
O	-3.26222	-0.51435	-2.28442
O	-3.54793	-0.82101	-0.16986
N	-0.49051	2.62498	-1.37211
O	-1.05246	3.29052	-0.55272
O	-0.53265	2.70091	-2.5698
N	2.95266	0.45087	-1.1338
O	3.26206	0.51477	-2.28439
O	3.54819	0.82042	-0.16973
N	-0.39074	-2.12864	1.54148
O	0.26773	-1.98679	2.53339
O	-1.23697	-2.9433	1.3168
N	2.12845	-0.44435	1.51663
O	2.79257	-1.42159	1.3198
O	2.15052	0.30482	2.4489
N	0.39068	2.12854	1.54166
O	1.23711	2.94307	1.31719
O	-0.26801	1.98677	2.53342
N	-2.12842	0.44432	1.51668
O	-2.1503	-0.30474	2.44906
O	-2.79279	1.42136	1.31973

Table S6. Optimized Cartesian coordinates for RDX at the ωB97XD/def2-TZVP level of theory

RDX (charge=0, multiplicity=1)			
atom	*x*	*y*	*z*
C	0.967103	-0.986793	0.213879
N	1.378162	0.354408	-0.175428
N	-0.382185	-1.370734	-0.175398
H	1.676792	-1.711226	-0.185443
H	1.018707	-1.039492	1.306107
C	0.371028	1.330882	0.213993
C	-1.338188	-0.344043	0.213921
N	-0.995915	1.016241	-0.175552
H	0.643498	2.307824	-0.185091
H	0.390764	1.401657	1.306246
H	-2.320502	-0.596608	-0.185151
H	-1.409486	-0.362262	1.306210
H	-0.423910	-1.520220	-1.176351
H	-1.104854	1.127488	-1.176371
H	1.528899	0.393152	-1.176278

Table S7. Optimized Cartesian coordinates for β-HMX at the ωB97XD/def2-TZVP level of theory

β-HMX (charge=0, multiplicity=1)			
atom	*x*	*y*	*z*
O	1.942030	-2.343179	-0.339851
N	0.743228	-2.290774	-0.191089
O	-0.082640	-3.033562	-0.667948
N	0.271889	-1.251122	0.584561
C	1.235726	-0.339050	1.169419
C	-1.131551	-1.194920	0.867705
N	1.865851	0.537314	0.215330
H	0.684672	0.246352	1.904117
H	2.035252	-0.876346	1.672380
N	-1.865853	-0.537288	-0.215338
H	-1.527061	-2.197774	0.998447
H	-1.263081	-0.646492	1.801035
N	3.223186	0.429587	0.016687
C	1.131550	1.194937	-0.867719
N	-3.223187	-0.429564	-0.016694
C	-1.235729	0.339072	-1.169431
O	3.877692	-0.124974	0.865461
O	3.643797	0.950484	-0.995005
N	-0.271889	1.251145	-0.584578
H	1.527063	2.197788	-0.998471
H	1.263079	0.646500	-1.801044
O	-3.877701	0.124953	-0.865490
O	-3.643803	-0.950514	0.994969
H	-0.684677	-0.246332	-1.904128
H	-2.035256	0.876368	-1.672390
N	-0.743226	2.290800	0.191069
O	-1.942019	2.343141	0.339923
O	0.082651	3.033525	0.668011

Table S8. Optimized Cartesian coordinates for HNIW at the ωB97XD/def2-TZVP level of theory

HNIW (charge=0, multiplicity=1)			
atom	*x*	*y*	*z*
C	0.000100	1.450883	0.483513
H	0.000295	2.491959	0.781746
N	-1.144837	1.126174	-0.352671
C	0.000138	0.490111	1.750081
N	1.144756	1.126064	-0.352850
N	-1.794618	2.204801	-1.006864
C	-0.790051	-0.038126	-1.158746
N	-1.077418	-0.473626	1.724600
H	0.000227	1.066887	2.666920
N	1.077617	-0.473673	1.724426
C	0.790060	-0.038165	-1.158857
N	1.795682	2.204232	-1.006225
O	-2.375796	1.932335	-2.022816
O	-1.742217	3.265545	-0.447939
H	-1.210164	0.050123	-2.154689
N	-1.245877	-1.252772	-0.555178
C	-0.788706	-1.542819	0.772135
N	-2.372777	-0.039694	1.915985
N	2.373014	-0.040024	1.915855
C	0.788768	-1.542855	0.772064
N	1.245962	-1.252783	-0.555212
H	1.210076	0.050045	-2.154859
O	2.377247	1.931562	-2.021918
O	1.743246	3.265043	-0.447405
N	-2.299014	-1.980734	-1.121804
H	-1.210958	-2.488097	1.092083
O	-3.241920	-0.808148	1.589377
O	-2.497650	1.050259	2.418994
O	3.242018	-0.808813	1.589639
O	2.498100	1.049894	2.418920
H	1.211070	-2.488155	1.091900
N	2.297831	-1.981807	-1.122611
O	-2.613802	-2.989623	-0.550204
O	-2.753057	-1.542613	-2.145508
O	2.751013	-1.544570	-2.147086
O	2.612237	-2.990875	-0.551103

Table S9. Optimized Cartesian coordinates for ONC at the ωB97XD/def2-TZVP level of theory

ONC (charge=0, multiplicity=1)			
atom	*x*	*y*	*z*
C	0.768688	0.696398	0.858238
C	-0.768261	-0.683857	-0.868167
N	1.609800	1.413401	1.838595
N	-1.609835	-1.481770	-1.783445
O	1.248050	1.304802	2.980584
O	-1.248800	-2.619839	-1.929229
O	2.568892	1.992341	1.404267
O	-2.568654	-0.929934	-2.252268
C	0.777013	0.856414	-0.689324
C	-0.774523	0.861060	-0.685679
N	1.626937	1.834789	-1.398725
N	-1.622574	1.768778	-1.485488
O	2.590798	1.398269	-1.968014
O	-2.586229	2.229695	-0.935414
C	-0.782722	0.678595	0.859271
C	0.783158	-0.691147	-0.849337
N	-1.640372	1.470568	1.764736
N	1.640338	-1.402436	-1.819928
O	-1.289228	2.611196	1.914621
O	1.290382	-1.297211	-2.965902
O	-2.600618	0.911909	2.222405
O	2.598902	-1.973924	-1.374738
C	0.774821	-0.851155	0.698239
C	-0.776475	-0.866356	0.676774
N	1.623255	-1.823835	1.417231
N	-1.627596	-1.779547	1.467026
O	1.271803	-2.969012	1.308357
O	-1.277925	-1.925353	2.608638
O	2.577502	-1.380946	1.997649
O	-2.581847	-2.246946	0.906161
O	1.266426	2.977540	-1.294239
O	-1.260687	1.917495	-2.622891

2. The HOMO and LUMO of the designed compounds.

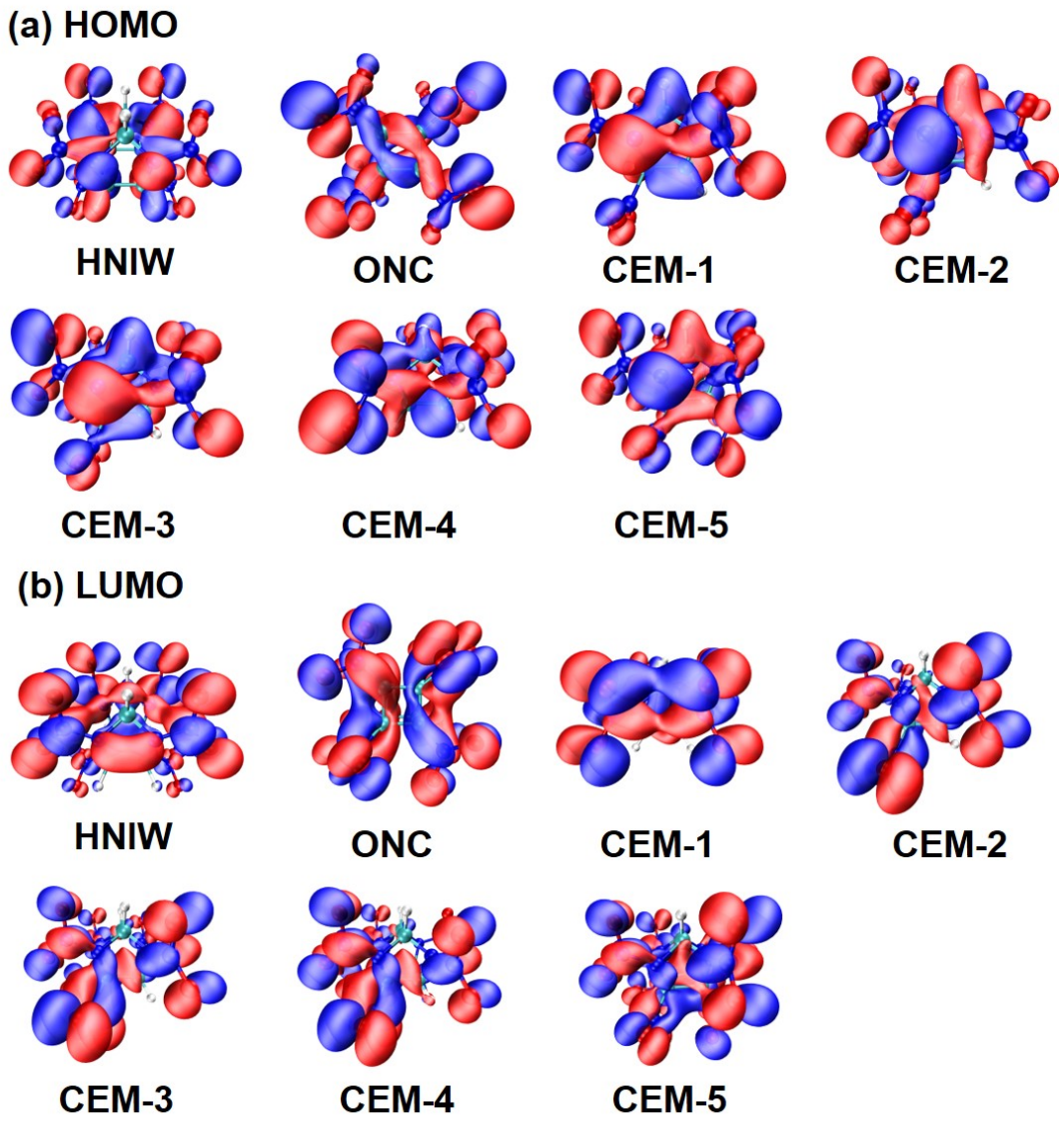
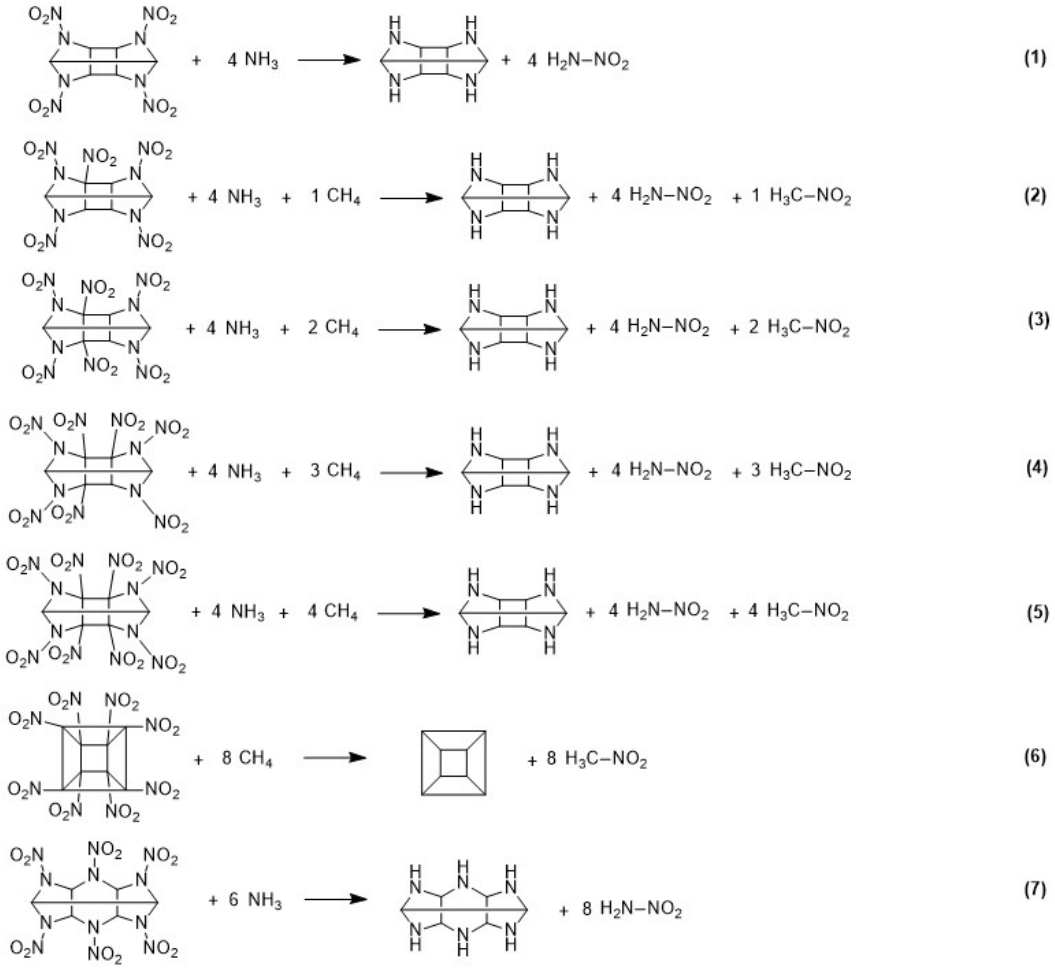


Figure S1. The HOMO (a) and LUMO (b) of HNIW, ONC, and the designed compounds.

3. Isodesmic reactions for the designed compounds.



Scheme S1. The isodesmic reactions for HNIW, ONC, and the designed compounds.

4. ESP analysis supplementary details.

Table S10. ESP analysis supplementary details.

Compd.	σ_{tot}^{2}[a]	σ^{+2}[b]	υ[c]	$\upsilon\sigma_{tot}^{2}$
	$(kcal/mol)^2$	$(kcal/mol)^2$		$(kcal/mol)^2$
CEM-1	219.09	189.68	0.12	25.46
CEM-2	200.91	183.69	0.08	15.75
CEM-3	239.57	222.61	0.07	15.76
CEM-4	201.14	187.50	0.06	12.71
CEM-5	211.49	199.14	0.05	11.62
HNIW	255.06	239.03	0.06	15.02
ONC	136.24	131.53	0.03	4.55

[a] Overall variance, [b] Positive variance, [c] Balance of charges.

5. Density calculation comparison.

Table S11. Density calculation comparison. Optimized Cartesian coordinates for those compounds at the ωB97XD/def2-TZVP level of theory in our calculation.

	Compound Name	Density Exp [4]	Politer's results [4]	Our results
1	3,5-Diamino-2,4,6-trinitrophenol	1.89	1.853	1.849
2	3,5-Diamino-2,4,6-trinitrobenzoic acid	1.863	1.912	1.846
3	1,1,3,3-Tetranitrocyclobutane	1.831	0.805	1.83
4	1,3,5,7-Tetranitrocubane	1.814	1.809	1.838
5	1,3,5-Trinitro-1,3,5-triazacyclohexane	1.806	1.796	1.796
6	1,4-Dinitroimidazole	1.8	1.818	1.768
7	1,2,4-Trinitrobenzene	1.794	1.74	1.735
8	2,4,6-Trinitroaniline	1.773	1.768	1.779
9	4-Nitro-1H-1,2,3-triazole	1.689	1.773	1.673
10	2,4-Dinitrophenol	1.668	1.69	1.696
11	N-Nitropyrazole	1.585	1.596	1.576
12	1,3-Dinitro-1,3-diazacyclohexane	1.572	1.615	1.599
13	NC-N(NO2)-(CH2)4-N(NO2)-CN	1.527	1.557	1.524
14	H3C-N(NO2)-CH(OCH3)-N(NO2)-CH3	1.518	1.561	1.546
15	6-Methyl-2-nitrobenzonitrile	1.441	1.456	1.413
16	H3C-C(CH3)NO2-C(CH3)NO2-CH3	1.43	1.392	1.414
17	Nitromethane	1.422	1.438	1.418
18	Dimethylnitramine	1.363	1.385	1.364
19	Octanitrocubane	1.978	1.982	2.06
20	[(O2N)3C-CH2]2N-NO2	1.953	1.932	1.797
21	5-Nitro-2,4-dihydro-3H-1,2,4-triazole-3-one	1.927	1.81	1.762
22	Benzotrifuroxan	1.901	1.894	1.966
23	1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane	1.894	1.821	1.9
24	1,3,5-Trinitro-2,4,6-trihydroxybenzene	1.887	1.922	1.954
25	1,1-Diamino-2,2-dinitroethene	1.883	1.868	1.734
26	1,3,3-Trinitroazetidine	1.961	1.772	1.787
27	2,4,6-Trinitrobenzoic acid	1.786	1.862	1.82
28	Nitromalonamide	1.78	1.775	1.676
29	2,4,6-Trinitro-N-methyl-N-nitroaniline	1.731	1.775	1.784
30	2,2,3,3-Tetranitrobutane	1.716	1.752	1.796
31	3-Methoxy-2,4,6-trinitroaniline	1.71	1.737	1.74
32	O2N-NH-(CH2)2-NH-NO2	1.709	1.653	1.598
33	HO-CH2-C(NO2)2-CH2-OH	1.652	1.697	1.678
34	3,4-Diaminofurazan	1.609	1.594	1.495
35	Trans-1,2-dinitrocyclopropane	1.603	1.631	1.633
36	H2N-(CH2)2-NH-NO2	1.563	1.478	1.371

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