Supporting information

Theoretical insight into density and stability differences on RDX, HMX and CL-20

Siwei Song [1], Xiaolan Tian [1,2], Yi Wang [1*], Xiujuan Qi [2], Qinghua Zhang [1*]

(1. Institute of Chemical Materials, China academy of engineering physics, Mianyang, China, 621000;
2. School of Material Science and Engineering, Southwest University of Science and Technology, Mianyang, China, 621010.)

Content

Supplementary note 1. Similarity calculation by SOAP descriptor

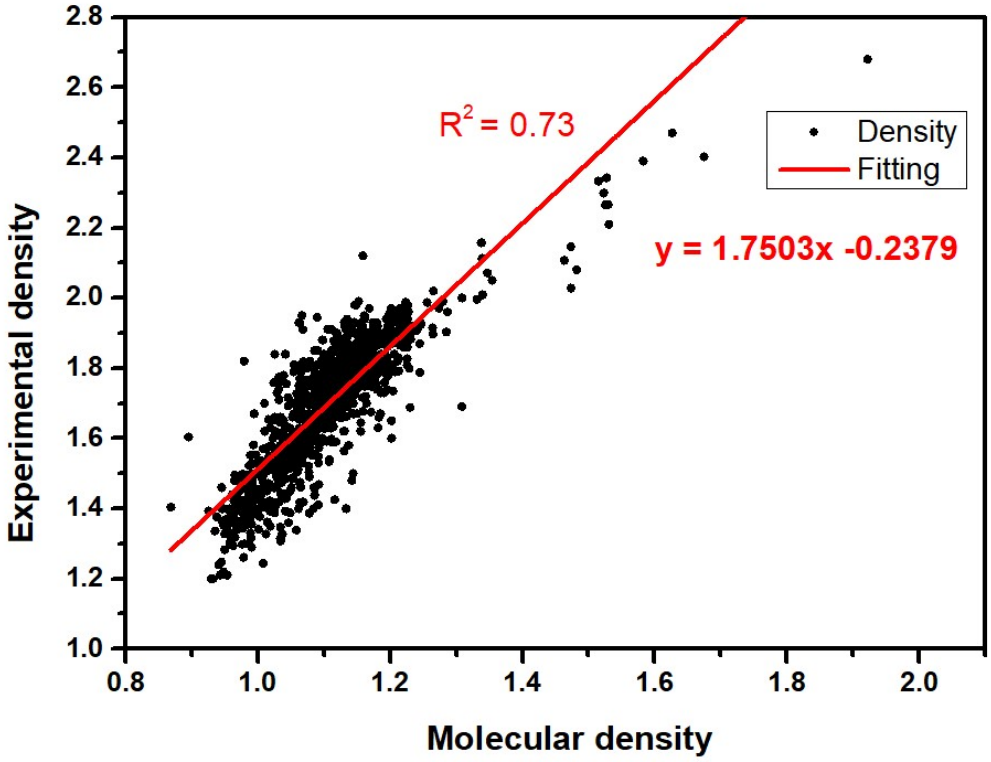
According to our experience, traditional similarity comparison based on RMSD of atomic coordinates may be invalid in cases such as symmetric structures with different coordinates though their energy is pretty close. Hence, here we applied a similarity comparison method based on Smooth Overlap of Atomic Positions (SOAP), which has been proved to be more effective in correlating structure differences with energy. SOAP is a descriptor that encodes regions of atomic geometries by using a local expansion of a gaussian smeared atomic density with orthonormal functions based on spherical harmonics and radial basis functions. Thus, SOAP can be used to compare individual local atomic environments, but additional tools are needed to make comparison of entire structures based on local environments. Here, we adopted REMatch kernel defined in Dscribe to calculate the similarity between SOAP of structure A and B as follows: [1,2]

$K(A,B) = T_r P^{\alpha} C(A,B)$

$$P^{\alpha} = \underset{P \in u(N,N)}{argmax} \sum_{ij} P_{ij}\left(1 - C_{ij} + \alpha In P_{ij}\right)$$

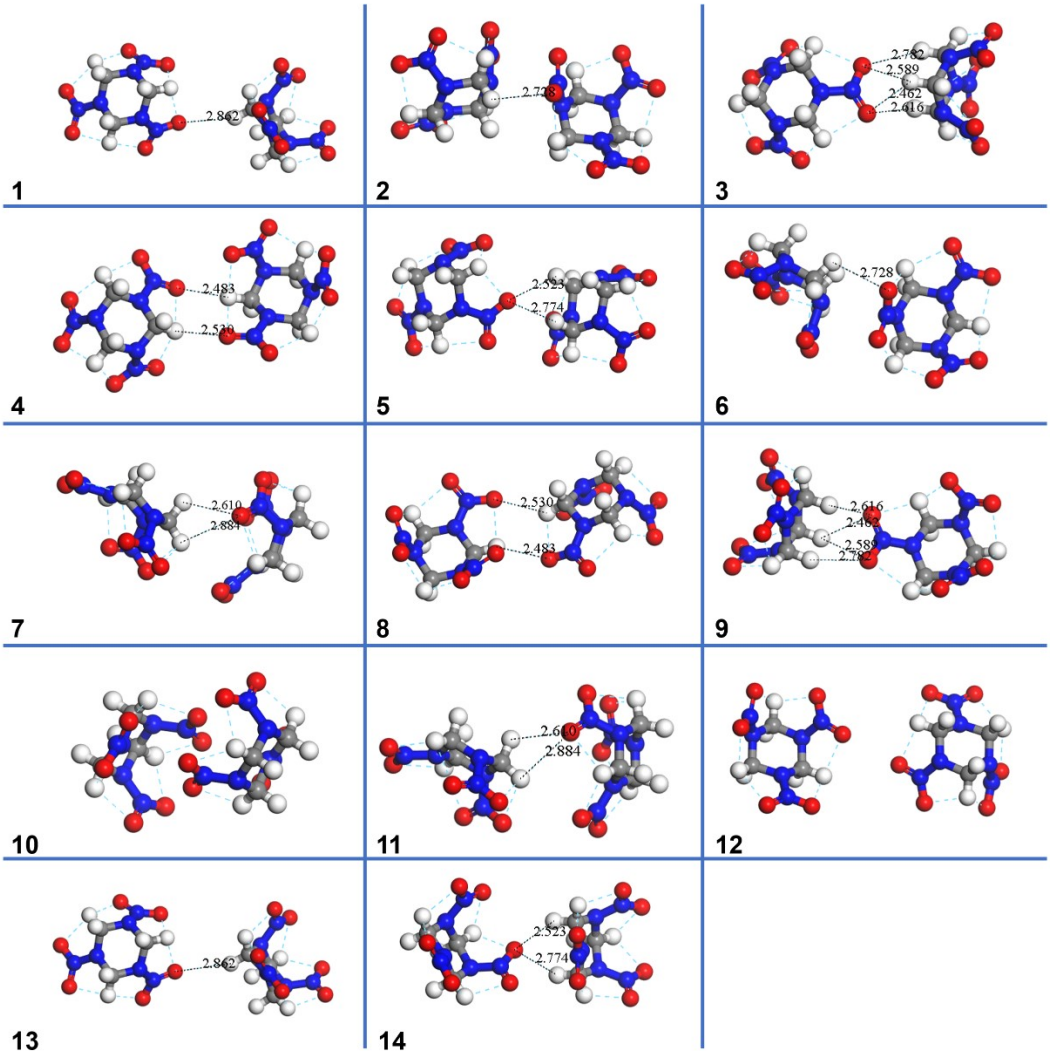
where the similarity between local atomic environments Cij can once again be calculated with any pairwise metric (e.g.linear, gaussian) and parameter α determines the contribution of the two: $\alpha = 0$ means only the similarity of the best matching local environments is taken into account and $\alpha \to \infty$ channels in the average solution. In our cases, the pairwise metric was chosen as linear kernel and α was set to 0.00001.

Figure S1. Scatter plot for experimental density and molecular density.



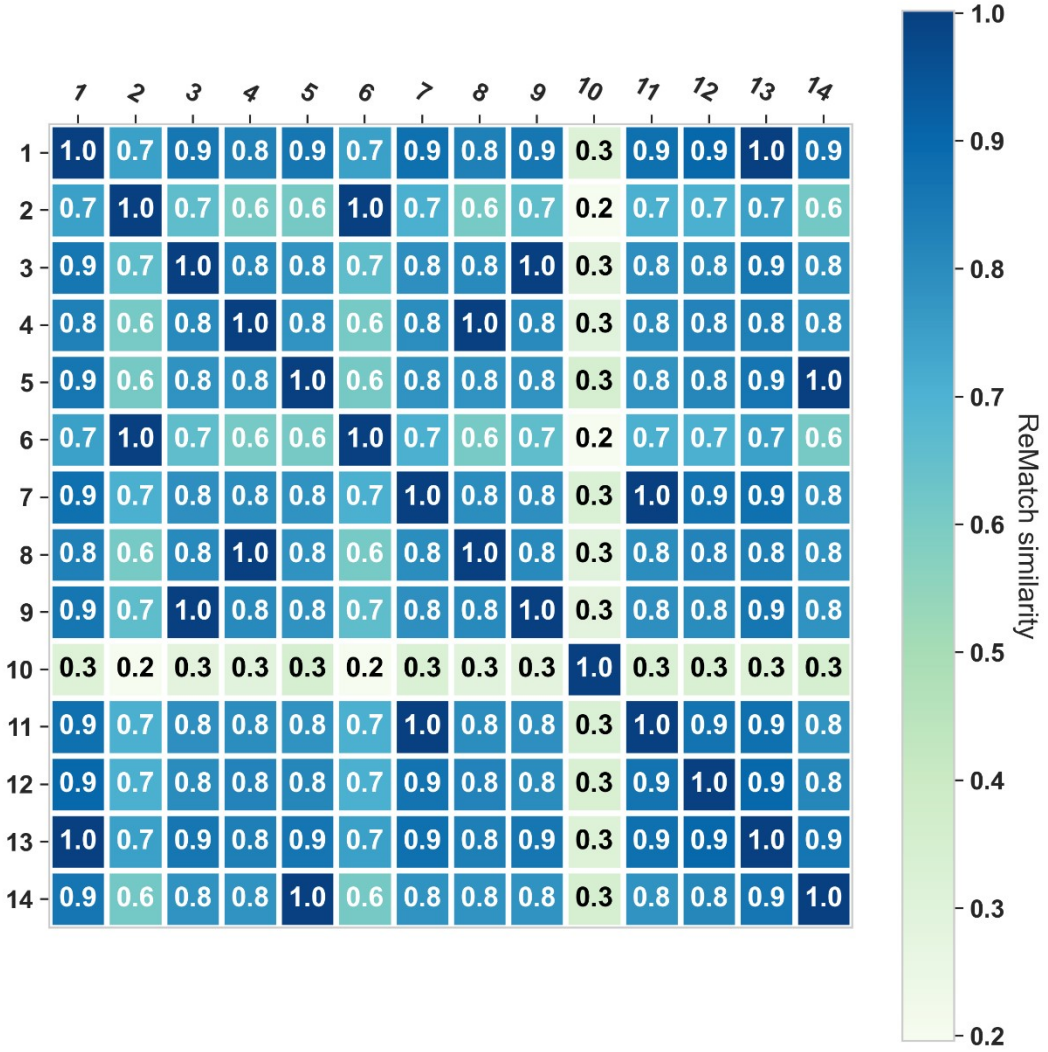
As we can see from Figure S1, an obvious correlation (R2=0.73) was observed between experimental density and molecular density on a dataset containing more than one thousand energetic compounds.

Figure S2. Dimer configurations extracted from RDX cluster.



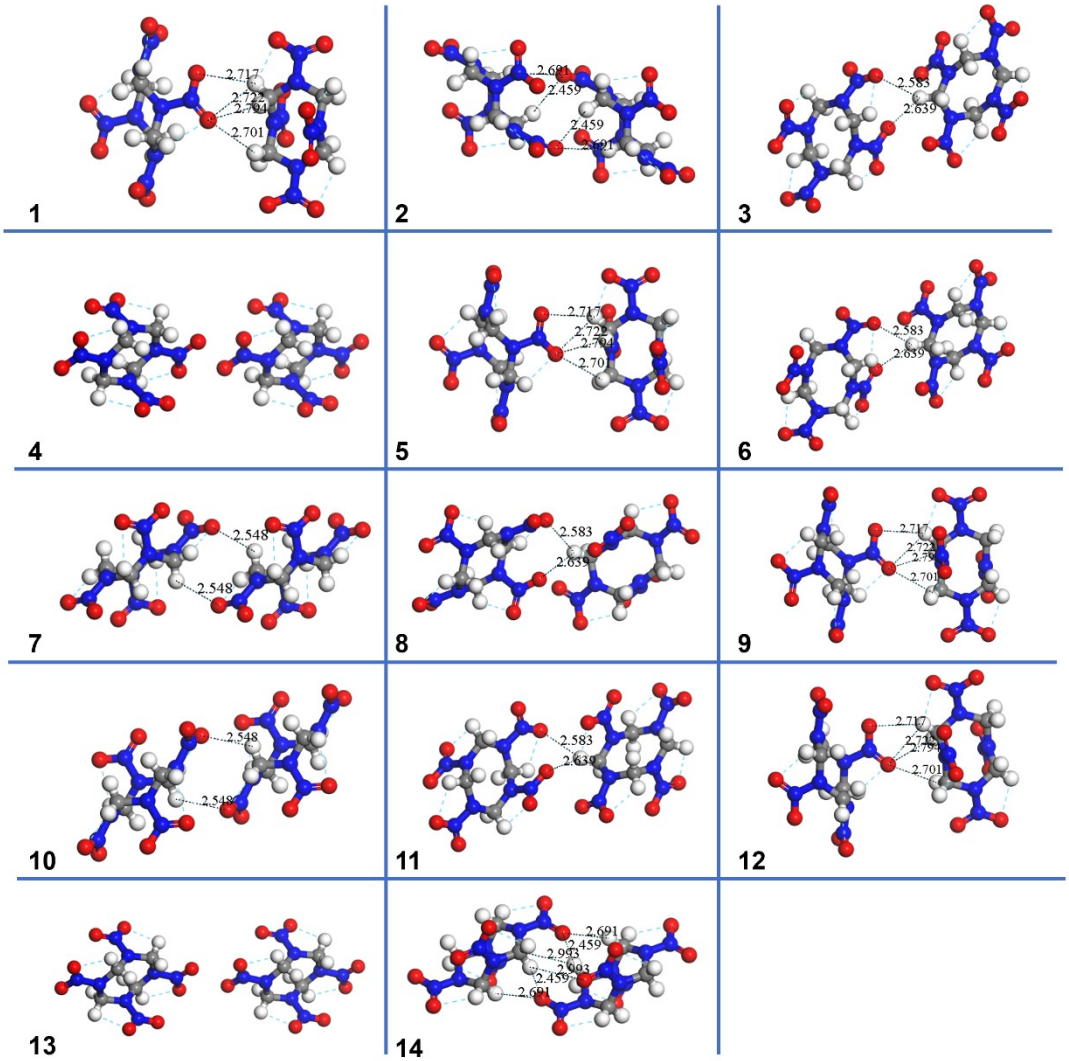
There are 14 dimer configurations in total extracted from RDX crystal as shown in Figure S2. Some of them are equivalent, such as 1 and 13 or 3 and 9. Equivalent configuration has same interaction energy. Thus, for consuming time only one among the equivalent configurations are calculated.

Figure S3. Similarity comparison for RDX dimers.



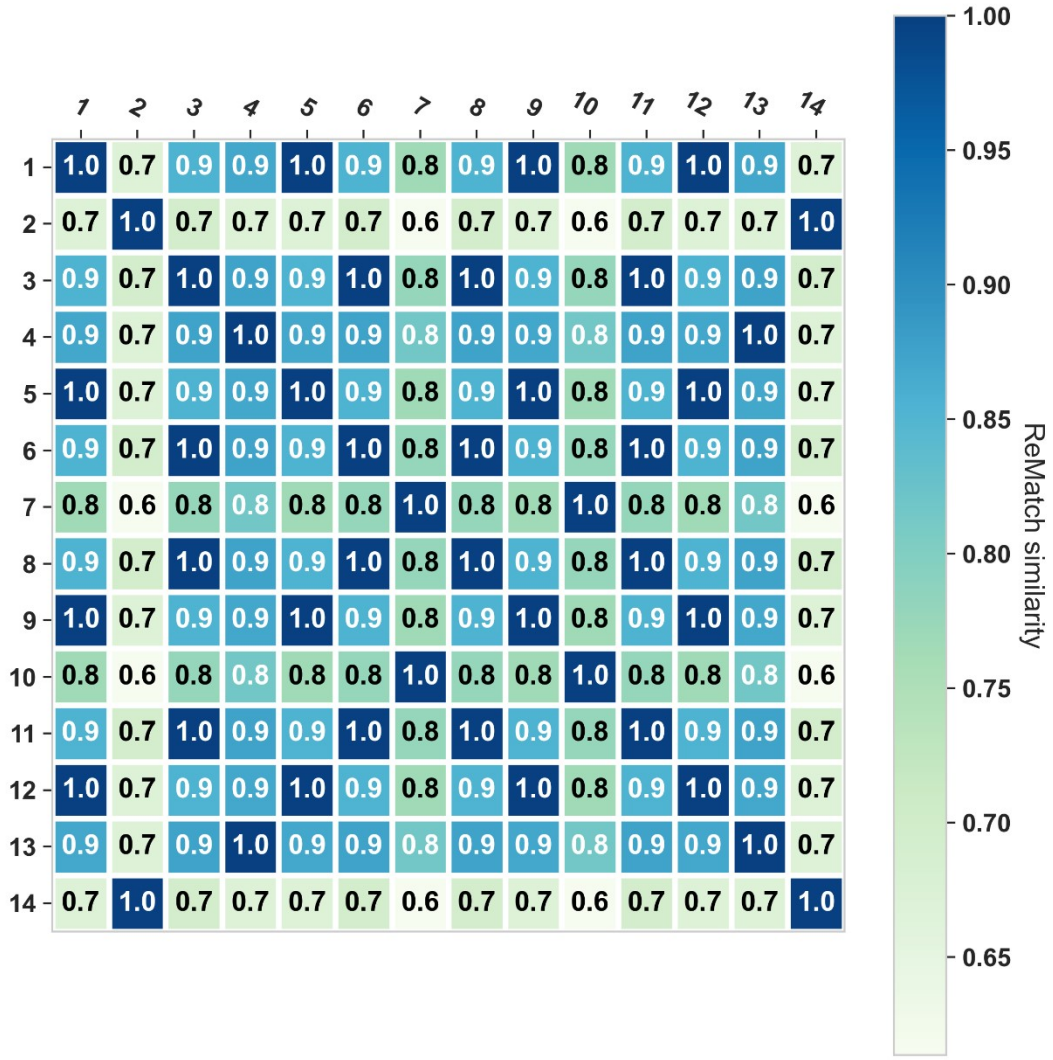
Traditional RMSD value is ineffective for measuring the similarity between dimer configurations. In this case similarity are calculated by SOAP descriptor in Dscribe library. The similarity approaching to 1.0 indicates equivalent configuration. Hence, from Figure S3 we can see that (1, 13) or (2, 6) or (3, 9) or (4, 8) or (5, 14) or (7, 11) are equivalent. However, configuration 10 or 12 has no equivalent one.

Figure S4. Dimer configurations extracted from HMX cluster.



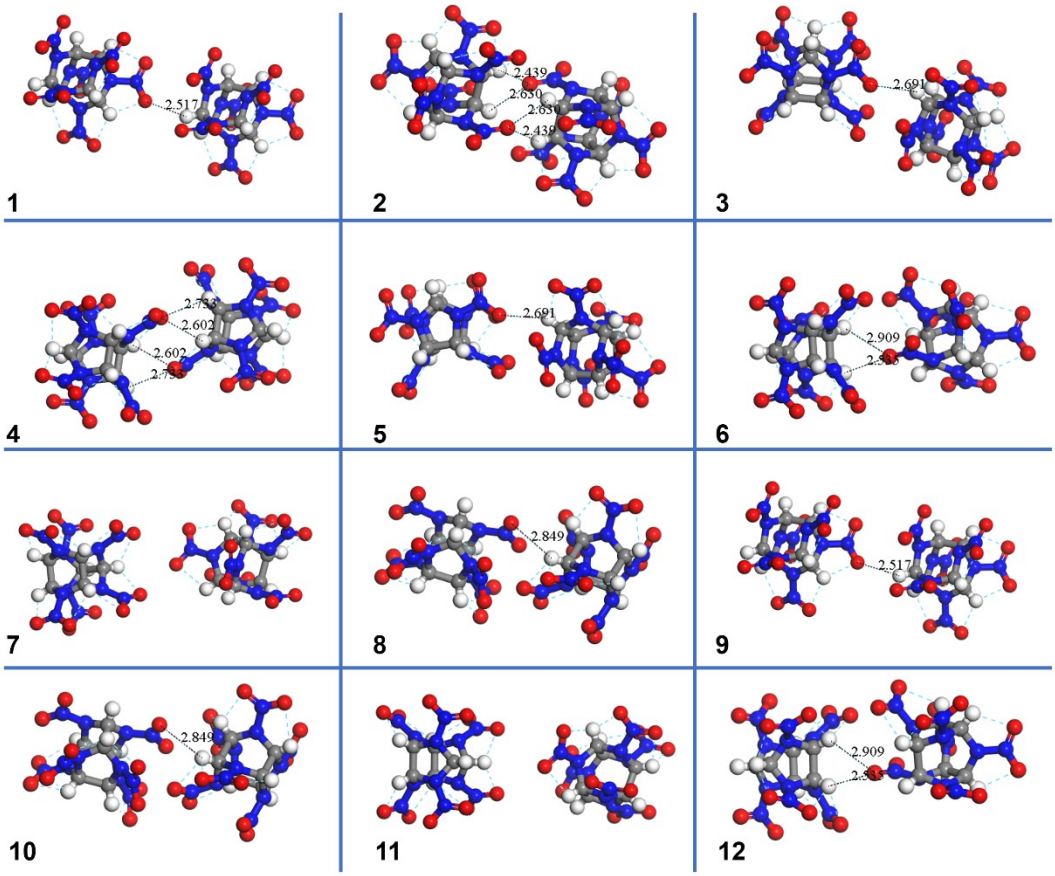
There are 14 dimer configurations in total extracted from HMX crystal.

Figure S5. Similarity comparison for HMX dimers.



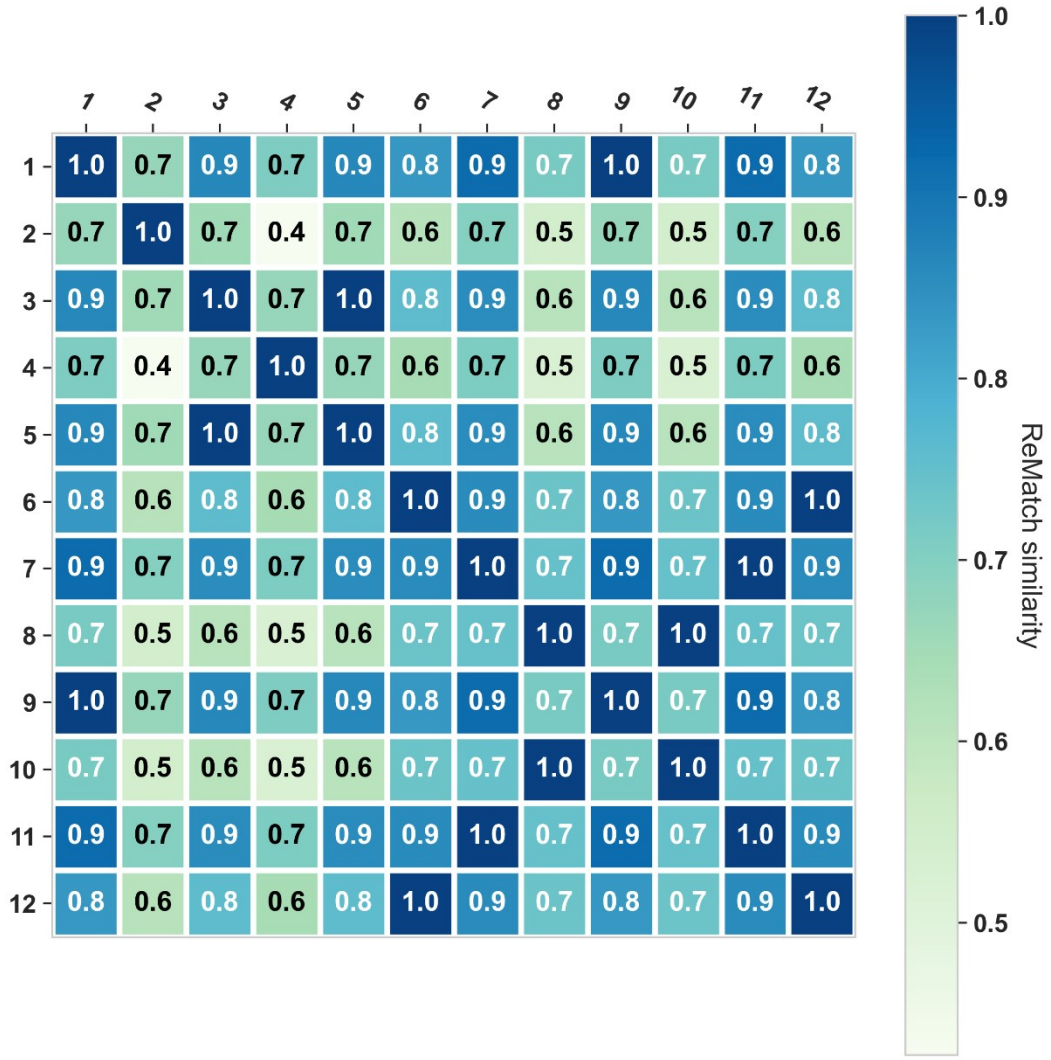
Configuration (1, 5, 9, 12) or (2, 14) or (3, 6, 8, 11) or (4, 13) or (7, 10) are equivalent.

Figure S6. Dimer configurations extracted from CL-20 cluster.



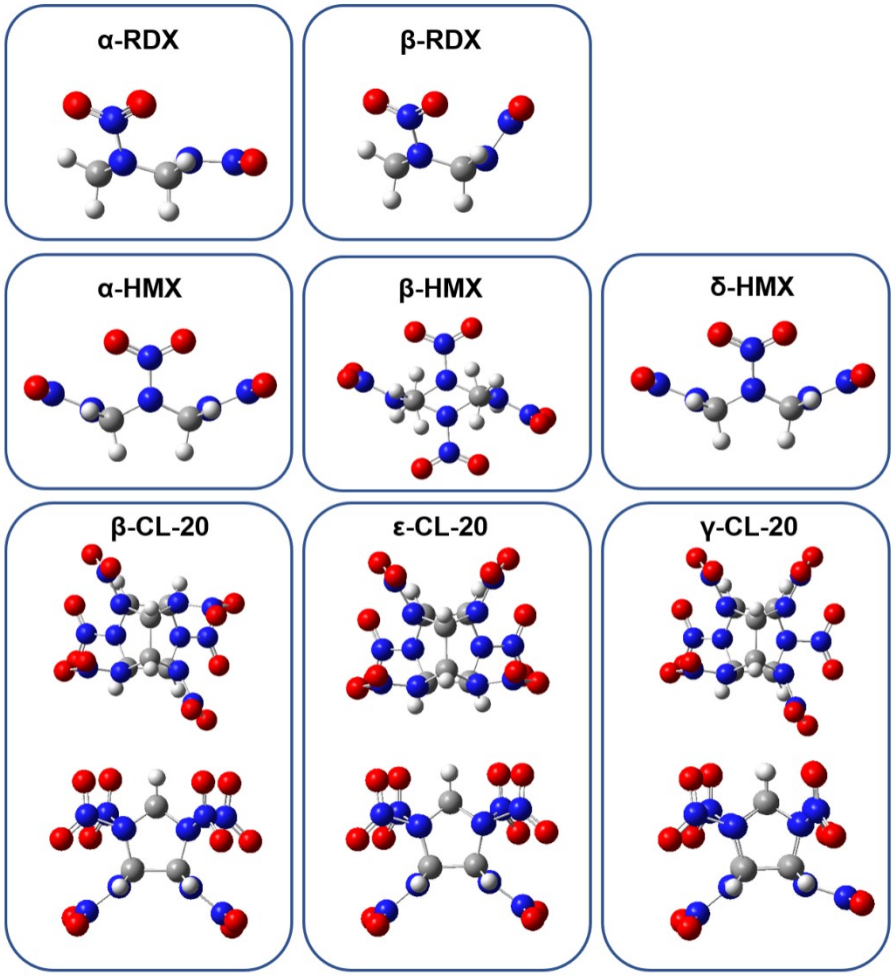
There are 12 dimer configurations in total extracted from CL-20 crystal.

Figure S7. Similarity comparison for CL-20 dimers.



Configuration (1, 9) or (3, 5) or (6, 12) or (7, 11) or (8, 10) are equivalent. Configuration 2 or 4 has no equivalent one.

Figure S8. Optimized conformations of polymorphs for each compound.



All the conformations were optimized at the level of UB3LYP/6-311++G**, the geometries are shown in Figure S8. Nitro groups in α-RDX and β-RDX have pseudoaxial and pseudoequatorial orientations pertaining to cyclic framework, respectively. α-HMX and δ-HMX both demonstrate same boat-like conformations, thus their molecular densities are identical, whereas β-HMX possesses chair-like conformation. The conformations for CL-20 are featured by C1(β-CL-20ε-CL-20) and C2(γ-CL-20) point groups, respectively, which is in line with previous report. [3]

Table S1. Bond dissociation enthalpy, Laplacian bond order and bond length of trigger bonds.

Label	BDE (kJ mol^{-1})	LBO	Bond length (Å)
RDX_1	163.839	0.609	1.403
RDX_2	162.920	0.507	1.433
HMX_1	178.996	0.638	1.393
HMX_2	162.689	0.652	1.391
CL-20_1	160.586	0.636	1.395
CL-20_2	175.887	0.525	1.419
CL-20_3	157.832	0.463	1.441

Table S2. Molecular density, crystal density and BEC for polymorphs.

Polymorphs	Molecular density	Crystal density	Δ_{OED}	Binding energy in cluster	Number of dimer configurations	Mean binding energy
α-RDX	1.735	1.806	0.071	-309.738	14	-22.124
β-RDX	1.742	1.795	0.053	-218.665	14	-15.619
α-HMX	1.772	1.840	0.068	-255.643	14	-18.262
β-HMX	1.774	1.904	0.130	-391.074	14	-27.934
δ-HMX	1.772	1.760	-0.011	-293.338	12	-24.445
β-CL-20	1.974	1.985	0.011	-366.426	14	-26.173
ε-CL-20	1.975	2.044	0.069	-398.445	12	-33.204
γ-CL-20	1.969	1.916	-0.053	-378.224	12	-31.519

Cartesian coordinates for optimized α-RDX

C	-0.76539300	-1.23641800	0.76362800
C	1.27171500	0.00051100	1.35740400
C	-0.76651900	1.23578600	0.76425800
H	-1.11639800	-1.29869500	1.80090300
H	-1.11642900	-2.09361200	0.20447000
H	2.34244500	0.00093200	1.19326300
H	1.05831600	0.00029500	2.42716300
H	-1.11742700	1.29699000	1.80161400
H	-1.11839000	2.09282100	0.20542900
N	-1.24739400	-0.00043400	0.12607300
N	0.68142000	-1.21437100	0.79850000
N	0.68035500	1.21500000	0.79890100
N	-2.60059200	-0.00096000	-0.24443400
N	1.34296900	-1.77602100	-0.34233300
N	1.34105900	1.77705400	-0.34238500
O	-3.12338900	1.08874000	-0.40545000
O	-3.12278600	-1.09097500	-0.40469800
O	2.53189800	-1.55257400	-0.43241100
O	0.67121000	-2.48028400	-1.06888000
O	2.52983000	1.55336900	-0.43367900
O	0.66878100	2.48174000	-1.06798700

Cartesian coordinates for optimized β-RDX

C	-0.76539300	-1.23641800	0.76362800
C	1.27171500	0.00051100	1.35740400
C	-0.76651900	1.23578600	0.76425800
H	-1.11639800	-1.29869500	1.80090300
H	-1.11642900	-2.09361200	0.20447000
H	2.34244500	0.00093200	1.19326300
H	1.05831600	0.00029500	2.42716300
H	-1.11742700	1.29699000	1.80161400
H	-1.11839000	2.09282100	0.20542900
N	-1.24739400	-0.00043400	0.12607300
N	0.68142000	-1.21437100	0.79850000
N	0.68035500	1.21500000	0.79890100
N	-2.60059200	-0.00096000	-0.24443400
N	1.34296900	-1.77602100	-0.34233300
N	1.34105900	1.77705400	-0.34238500
O	-3.12338900	1.08874000	-0.40545000
O	-3.12278600	-1.09097500	-0.40469800
O	2.53189800	-1.55257400	-0.43241100
O	0.67121000	-2.48028400	-1.06888000
O	2.52983000	1.55336900	-0.43367900
O	0.66878100	2.48174000	-1.06798700

Cartesian coordinates for optimized α-HMX

C	1.26778500	1.28368400	-1.09147000
C	1.26845000	-1.28351700	-1.09102200
H	1.31705500	1.09457100	-2.16724100
H	2.04994200	1.98212000	-0.81044700
H	1.31834100	-1.09492300	-2.16677200
H	2.05060000	-1.98157500	-0.80917100
N	1.49131200	0.00025700	-0.45086000
N	-0.00029900	1.90409300	-0.76034200
N	1.78818600	0.00054700	0.91601700
N	-0.00029900	3.20606800	-0.22041600
O	1.90110100	-1.09192700	1.44221500
O	1.90132600	1.09329600	1.44163200
O	1.08613500	3.71741300	-0.02608500
O	-1.08676200	3.71718100	-0.02553900
C	-1.26778500	-1.28368400	-1.09147000
C	-1.26845000	1.28351700	-1.09102200
H	-1.31705500	-1.09457100	-2.16724100
H	-2.04994200	-1.98212000	-0.81044700
H	-1.31834100	1.09492300	-2.16677200
H	-2.05060000	1.98157500	-0.80917100
N	-1.49131200	-0.00025700	-0.45086000
N	0.00029900	-1.90409300	-0.76034200
N	-1.78818600	-0.00054700	0.91601700
N	0.00029900	-3.20606800	-0.22041600
O	-1.90110100	1.09192700	1.44221500
O	-1.90132600	-1.09329600	1.44163200
O	-1.08613500	-3.71741300	-0.02608500
O	1.08676200	-3.71718100	-0.02553900

Cartesian coordinates for optimized β-HMX

N	0.14102700	1.37709400	0.26470000
O	-1.77400600	2.36285000	0.79306000
N	-0.90535300	2.23951200	-0.05488300
N	0.90208100	0.27111400	-1.72717900
O	1.73688000	-0.79285700	-3.50845200
N	1.92970300	0.03051500	-2.63342000
O	-0.87059700	2.76222500	-1.15646400
C	1.22891800	1.24631000	-0.66946400
H	2.11194000	0.92216200	-0.11702100
H	1.43985500	2.20470000	-1.13632500
O	2.92975000	0.72100200	-2.48487600
C	0.12850400	0.73534500	1.57584700
H	1.11160000	0.28096600	1.69428700
H	-0.03019600	1.46198300	2.36920400
N	-0.14102700	-1.37709400	-0.26470000
O	1.77400600	-2.36285000	-0.79306000
N	0.90535300	-2.23951200	0.05488300
N	-0.90208100	-0.27111400	1.72717900
O	-1.73688000	0.79285700	3.50845200
N	-1.92970300	-0.03051500	2.63342000
O	0.87059700	-2.76222500	1.15646400
C	-1.22891800	-1.24631000	0.66946400
H	-2.11194000	-0.92216200	0.11702100
H	-1.43985500	-2.20470000	1.13632500
O	-2.92975000	-0.72100200	2.48487600
C	-0.12850400	-0.73534500	-1.57584700
H	-1.11160000	-0.28096600	-1.69428700
H	0.03019600	-1.46198300	-2.36920400

Cartesian coordinates for optimized δ-HMX

C	-1.28357100	1.26769600	-1.09159000
C	-1.28366200	-1.26852200	-1.09109400
C	1.28356200	1.26744900	-1.09190000
C	1.28358600	-1.26867400	-1.09111900
H	-1.98174200	2.05001500	-0.81036200
H	-1.09490600	1.31676300	-2.16744900
H	-1.98192500	-2.05065100	-0.80968900
H	-1.09485000	-1.31793700	-2.16693800
H	1.09447600	1.31628600	-2.16770000
H	1.98187100	2.04981800	-0.81111100
H	1.09476400	-1.31835800	-2.16693300
H	1.98177000	-2.05081400	-0.80962000
N	-3.20586100	-0.00018900	-0.22032400
N	0.00006300	1.49092800	-0.45144700
N	1.90416300	-0.00048400	-0.76050100
N	0.00019900	1.78846100	0.91552700
N	-0.00005800	-1.49169600	-0.45082100
N	-0.00009000	-1.78730400	0.91662800
N	3.20581100	-0.00032100	-0.22028800
N	-1.90413600	-0.00031100	-0.76013100
O	-3.71722900	-1.08661600	-0.02548600
O	1.09281100	1.90173900	1.44121000
O	3.71702400	1.08617300	-0.02578700
O	-1.09266100	-1.89999400	1.44252700
O	3.71708900	-1.08675300	-0.02532600
O	1.09248700	-1.89965700	1.44263000
O	-3.71713000	1.08632600	-0.02574100
O	-1.09233800	1.90173100	1.44141400

Cartesian coordinates for optimized β-CL-20

C	0.21963600	-1.44565300	-0.76333900
H	0.33127900	-2.45760800	-1.13127200
N	1.44991100	-0.68640500	-0.91248600
N	2.34084800	-1.15314300	-1.95133500
O	3.07021400	-0.31692500	-2.43512900
O	2.30743700	-2.33962300	-2.18338100
C	1.09232200	0.74795900	-0.96814800
H	1.74467800	1.26289500	-1.66516400
N	1.20477500	1.35024100	0.32949100
N	2.27722900	2.23373300	0.61629500
O	3.02616500	2.47564600	-0.30663500
O	2.30247400	2.69115300	1.73691600
C	0.42809700	0.77888800	1.40052600
H	0.60231800	1.35266700	2.30371000
N	0.67641900	-0.65563700	1.61531500
N	1.98311000	-1.10829200	1.81377900
O	2.78074100	-0.28384800	2.21559400
O	2.17424100	-2.29013700	1.59288500
C	-0.21989500	-1.44532500	0.76386900
H	-0.33147200	-2.45712100	1.13219100
N	-1.45006600	-0.68597400	0.91288800
N	-2.34077300	-1.15226800	1.95218900
O	-2.30769300	-2.33876000	2.18421100
O	-3.06964500	-0.31577900	2.43621600
C	-1.09239200	0.74840000	0.96787600
H	-1.74470100	1.26368400	1.66468100
N	-1.20497400	1.34997400	-0.33010900
O	-3.02615700	2.47587300	0.30559700
O	-2.17437800	-2.29073200	-1.59230900
N	-2.27705100	2.23359800	-0.61717300
N	-0.67645900	-0.65628200	-1.61523300
O	-2.78077900	-0.28474300	-2.21599400
O	-2.30204800	2.69093100	-1.73785200
C	-0.42819000	0.77830800	-1.40090100
H	-0.60230200	1.35181000	-2.30423300
N	-1.98323500	-1.10900700	-1.81364800

Cartesian coordinates for optimized γ-CL-20

C	0.21583700	0.89998200	-1.20443700
H	0.41344600	1.46213600	-2.10929600
N	1.41905800	0.77603300	-0.37840400
N	2.44473700	1.76228700	-0.59658600
O	3.15199700	2.01186700	0.35489500
O	2.52787900	2.19354800	-1.72424100
C	0.98005000	0.56406600	1.01163700
H	1.63416300	1.09451500	1.69580200
N	0.96751200	-0.83319000	1.33982600
N	1.96823600	-1.38056200	2.18138600
O	1.89423800	-2.57143700	2.38900200
O	2.76014500	-0.58860400	2.64733900
C	0.16166200	-1.69318300	0.51521700
H	0.24217500	-2.70973800	0.88309800
N	0.48431300	-1.61355100	-0.92162000
N	1.79878800	-1.81008500	-1.34946700
O	2.52052200	-2.43297000	-0.59555400
O	2.07071300	-1.36437000	-2.44910100
C	-0.31503400	-0.55505400	-1.54828600
H	-0.37765800	-0.69022700	-2.62059900
N	-1.59745900	-0.79863300	-0.90831000
N	-2.45779700	-1.71032100	-1.62552000
O	-2.38104500	-1.66737800	-2.83367700
O	-3.21215700	-2.37592800	-0.95193100
C	-1.32078000	-1.15605200	0.50087000
H	-2.03902100	-1.89579100	0.83364300
N	-1.39285000	0.00842100	1.35416100
N	-2.69863400	0.36797900	1.81786800
O	-2.81890100	1.49647100	2.24182300
O	-3.53461300	-0.50864100	1.78602200
C	-0.50617400	1.10617500	1.02869300
H	-0.65018200	1.91305500	1.73784200
N	-0.73849800	1.59229200	-0.33882200
N	-0.81693500	3.01733500	-0.52009200
O	-1.06575500	3.67416100	0.46759200
O	-0.68547200	3.40633200	-1.66011600

Cartesian coordinates for optimized ε-CL-20

C	-0.00012500	1.42016100	0.54145400
H	-0.00038700	2.45388700	0.86515600
N	1.15479600	1.11716600	-0.30583500
N	1.77818300	2.24283200	-0.95545300
O	2.33145000	2.00961200	-2.00789900
O	1.73261100	3.28932200	-0.35017200
C	0.79302500	-0.02613000	-1.15814300
H	1.21865000	0.09662100	-2.14867300
N	1.24725500	-1.26602700	-0.59025600
N	2.36182800	-1.94372300	-1.14824500
O	2.68748400	-2.97241700	-0.59834800
O	2.83742500	-1.44721600	-2.14703300
C	0.79183500	-1.59436800	0.73560900
H	1.21708100	-2.54741400	1.02866300
N	1.08573200	-0.54643700	1.72965900
N	2.39328300	-0.08600300	1.88656500
O	3.27018500	-0.83277200	1.49850500
O	2.51527300	0.99819500	2.42566000
C	0.00005900	0.42193500	1.78331100
H	-0.00001000	0.97102300	2.71722200
N	-1.08531300	-0.54679600	1.72972800
N	-2.39298300	-0.08678300	1.88641900
O	-3.26962400	-0.83396500	1.49851200
O	-2.51541700	0.99754000	2.42520100
C	-0.79106300	-1.59465000	0.73563700
H	-1.21595000	-2.54785700	1.02867700
N	-1.24680500	-1.26638000	-0.59008300
N	-2.36056400	-1.94501200	-1.14835500
O	-2.83632400	-1.44904800	-2.14738900
O	-2.68577100	-2.97373400	-0.59823700
C	-0.79292400	-0.02630400	-1.15815600
H	-1.21855800	0.09610600	-2.14871300
N	-1.15482200	1.11674900	-0.30597800
N	-1.77986500	2.24174200	-0.95457400
O	-2.33362400	2.00819300	-2.00674000
O	-1.73501000	3.28810200	-0.34902800

References

1. S. De, A. P. Bartók, G. Csányi and M. Ceriotti, Phys. Chem. Chem. Phys., 2016, 18, 13754–13769.
2. L. Himanen, M. O. J. Jäger, E. V. Morooka, F. Federici Canova, Y. S. Ranawat, D. Z. Gao, P. Rinke and A. S. Foster, Comput. Phys. Commun., 2020, 247, 106949.
3. Y. Kholod, S. Okovytyy, G. Kuramshina, M. Qasim, L. Gorb and J. Leszczynski, J. Mol. Struct., 2007, 843, 14-25.