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Electronic Supplementary Information (ESI)

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S1. Crystallographic information of cubane and nitrocubanes.

Table s1. Crystallographic information of cubane and nitrocubanes.

Explosives	Cubane[1]	MNC[2]	BNC[3]	TrNC[4]	TeNC[4]	PNC[5]	HexNC[6]	HepNC[7]	ONC[7]
Refcode	CUBANE	TAHMEV	CEDZUG	HASHAK	HASHEO	NACXEU	UGUGUY	CUGCOW	CUGDIR
Formula	C_8H_8	$C_8H_7N_1O_2$	$C_8H_6N_2O_4$	$C_8H_5N_3O_6$	$C_8H_4N_4O_8$	$C_8H_3N_5O_{10}$	$C_8H_2N_6O_{12}$	$C_8H_1N_7O1_4$	$C_8N_8O_{16}$
Space group	R-3r	Pnma	P21/c	Pbca	P21/a	P21/c	Pnma	Pbcn	C2/c
a(Å)	5.340	17.507(5)	5.482(<1)	11.656(2)	12.255(2)	6.637(3)	13.936(2)	23.594(1)	12.785(<1)
b(Å)	5.340	6.584(2)	6.258(<1)	11.946(2)	7.007(1)	23.275(14)	10.887(1)	8.174(<1)	8.840(<1)
c(Å)	5.340	5.832(2)	11.581(<1)	13.130(2)	13.346(2)	7.860(5)	8.483(1)	14.264(<1)	13.924(<1)
α(°)	72.25	90	90	90	90	90	90	90	90
β(°)	72.25	90	102.38(1)	90	114.78(<1)	113.21(5)	90	90	98.03(<1)
γ(°)	72.25	90	90	90	90	90	90	90	90
V(Å^3)	134.298	672.232	388.004	1828.255	1040.569	1115.915	1287.097	2750.811	1558.173
Z	1	4	2	8	4	4	4	8	4
Density (g/cm^3)	1.288	1.474	1.662	1.738	1.814	1.959	1.931	2.024	1.978
decomposition temperature	>200℃		260℃	250℃	270℃	>250℃		>200℃	>200℃

Note, apart from MNC, other information is of common conditions.

S2. Comparison in crystal packing of HexNC with disordered nitro O atoms attached to N7.

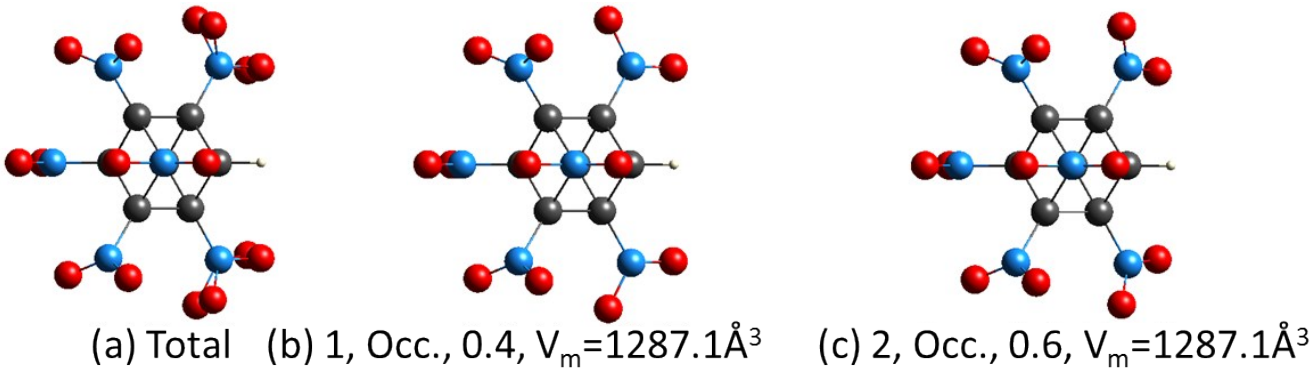

Fig. s1 Molecular structures and V_m of HexNC in crystal.

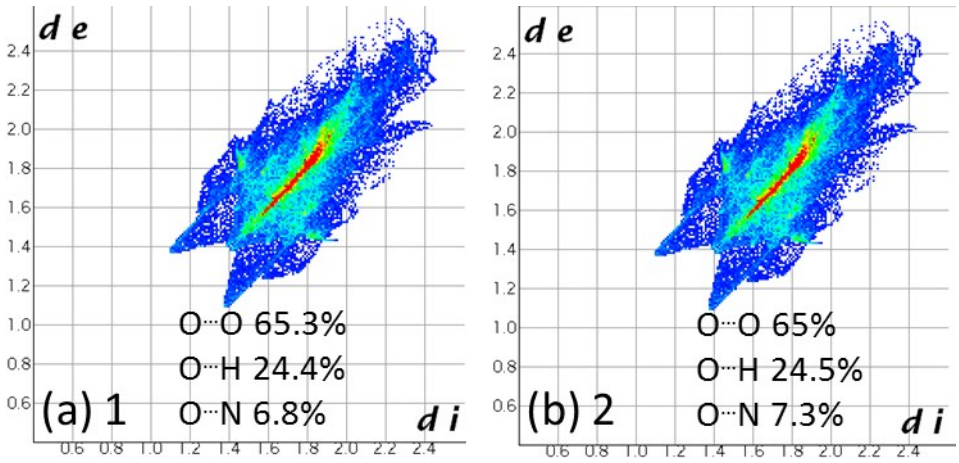

Fig. s2 Two-dimensional fingerprint plots of interatomic contacts in HexNC with differently sited nitro O atoms.

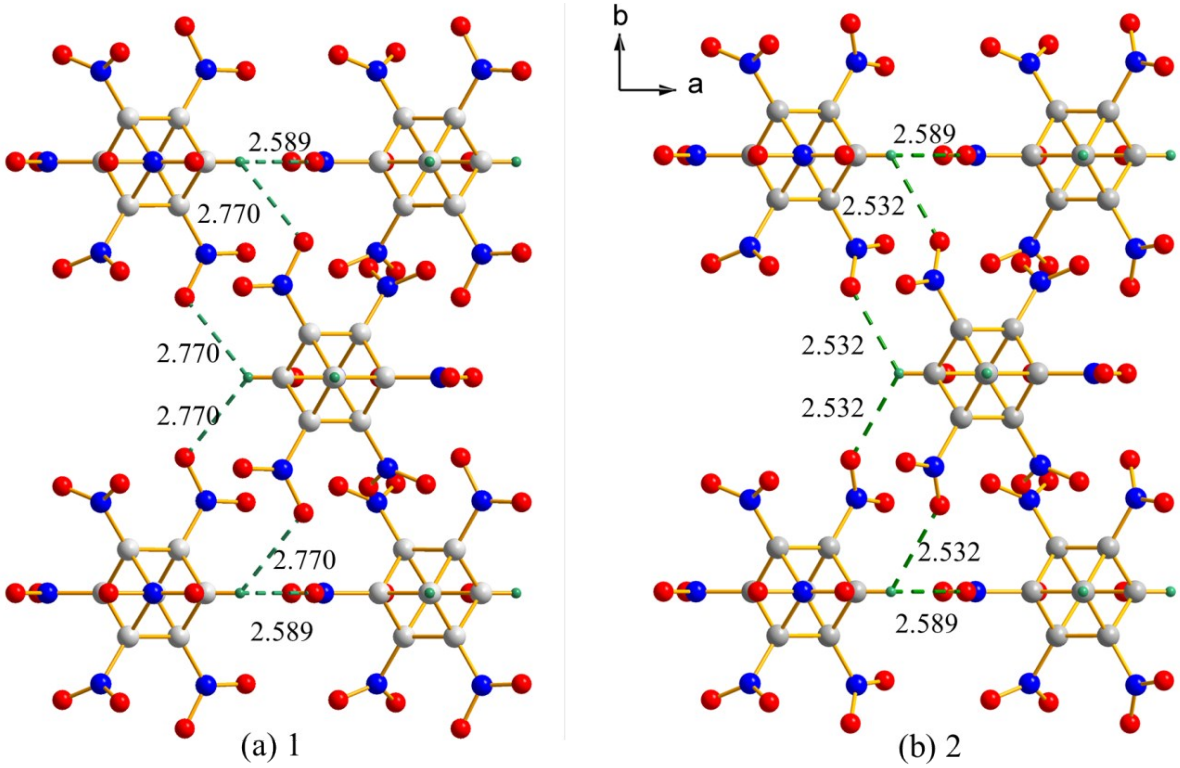

Fig. s3 Comparison in intermolecular hydrogen bonds of HexNC with differently sited nitro O atoms.

The nitro O atoms on N7 atom of HexNC are disordered in an occupancy ratio of 0.6:0.4. To clarify the influence of this disorder on the PC and the intermolecular interactions in text, we first pay attention to both cases of the disorder separately. From above Fig. s1, we can find that this disorder does not cause a difference in V_m, i.e., V_m of both cases are same, 1287 $Å^3$, calculated by a van de Waal radius method. Because of a same V_m and a same chemical molecule, PCs of the two cases are same as each other.

Next, we pay attention to the difference in close interatomic contacts between the two cases. As illustrated in Fig. s2, the shapes and color distributions of the two-dimensional plots of the two cases are almost same too. And the largest difference in close contact distribution is only 0.5 %, suggesting a slight difference in intermolecular interactions.

Besides, we examine the distances of intermolecular hydrogen bonding between the two cases caused by the disorder. As demonstrated in Fig. s3, 0.238 Å, showing a rather large difference in the distance. However, because both 2.532 and 2.770 Å show the weak hydrogen bonding, this rather large distance difference could not represent too much difference in interaction strength.

Overall, comparing the analyzing results of the two cases caused by the disorder of the nitro O atoms on N7 atom, we confirm there no difference in PC and a slight difference in intermolecular interactions. In text, only the case of the occupancy of 0.6 is described.

S3. Details of H···H, H···O and O···O interactions in crystals.

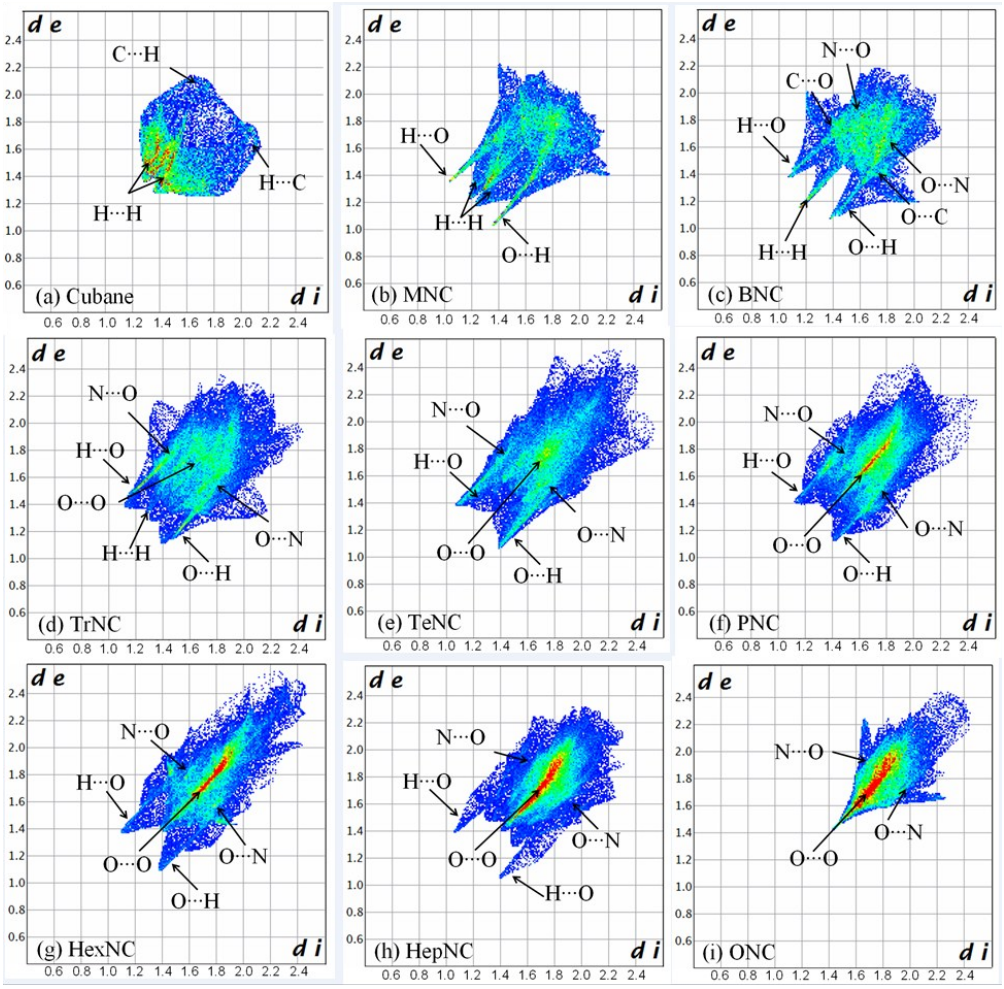

Fig. s4 Two-dimensional fingerprint plots of interatomic contacts in cubane and its nitro-derivatives.

Table s2. Geometric analyses of the intermolecular H···H interactions in crystals.

Molecule	atom1	atom2	Length, Å	Symmetry Operations
Cubane	H1	H1A	2.73	-1+y,z,1+x;-1-x,-y,1-z;-1+z,1+x,y;-1-x,1-y,-z;-z,-1-x,1-y;y,-1+z,1+x; -y,1-z,-1-x;z,1+x,-1+y;1+x,-1+y,z;1-z,-1-x,-y;1+x,y,-1+z;1-y,-z,-1-x;
	H1	H1C	2.92	-1+y,z,1+x;-1-x,1-y,-z;-z,-1-x,1-y; z,1+x,-1+y;1+x,-1+y,z;1-y,-z,-1-x;
MNC	H1	H1B	2.91	x,-1+y,z;x,1.5-y,z;
	H1	H3	2.71	1-x,-1/2+y,-z;1-x,-y,-z;1-x,1-y,-z(2);
	H3	H4	2.61	1-x,-1/2+y,1-z;1-x,-y,1-z;1-x,1-y,1-z(2);
	H4	H4B	2.90	x,-1+y,z;x,1.5-y,z;
BNC	H2	H3	2.48	x,-1+y,z;-x,-1-y,1-z;x,1+y,z; -x,1-y,1-z;
TrNC	H1	H4	2.78	x,1/2-y,1/2+z; x,1/2-y,-1/2+z;

Table s3. Geometric analyses of the intermolecular HBs in crystals.

Molecule	D	H	A	D-H, Å	H···A, Å	A···D, Å	A-H···D,°	Symmetry Operation
MNC	C2	H1	O1	0.93	2.52	3.41	161.3	1/2-x,-1/2+y,1/2-z; 1/2-x,-1-y,1/2+z; 1/2-x,1/2+y,-1/2-z; 1/2-x,-1/2+y,-1/2+z;
	C6	H5	O2	0.87	2.58	3.54	177.3	x,y,-1+z; x,y,1+z;
BNC	C3	H2	O1	0.96	2.53	3.32	139.6	-1+x,-1/2-y,-1/2+z; -1+x,1/2-y,-1/2+z; 1-x,-1/2+y,1.5-z; 1-x,1/2+y,1.5-z;
TrNC	C1	H1	O1	0.92	2.56	3.01	110.4	-x,1/2+y,1/2-z; -x,-1/2+y,1/2-z;
	C8	H5	O6	0.94	2.55	3.11	118.3	-1/2+x,1/2-y,-z; 1/2+x,1/2-y,-z;
TeNC	C4	H2	O4	0.92	2.55	3.22	129.6	-1/2+x,-1/2-y,z; 1/2+x,-1/2-y,z;
	C8	H4	O8	0.94	2.54	3.16	123.7	-1/2+x,-1/2-y,z; 1/2+x,-1/2-y,z;
PNC	C4	H2	O5	0.92	2.55	3.29	137.7	1/2-x,-1/2+y,-z; 1/2-x,1/2+y,-z;
	C8	H3	O1	0.95	2.59	3.12	115.3	1-x,1-y,1-z,(2);
	C8	H3	O10	0.95	2.59	3.25	126.6	-x,1-y,-z,(2);
HexNC	C6	H2	O5	0.92	2.59	3.15	119.5	-1/2+x,y,1.5-z; 1/2+x,y,1.5-z;
	C6	H2	O8	0.92	2.53	3.11	121.4	1-x,-y,2-z,(2); 1-x,1/2+y,2-z; 1-x,1-y,2-z;
HepNC	C8	H1	O9	0.98	2.53	3.49	116.5	x,-1+y,z; x,1+y,z;

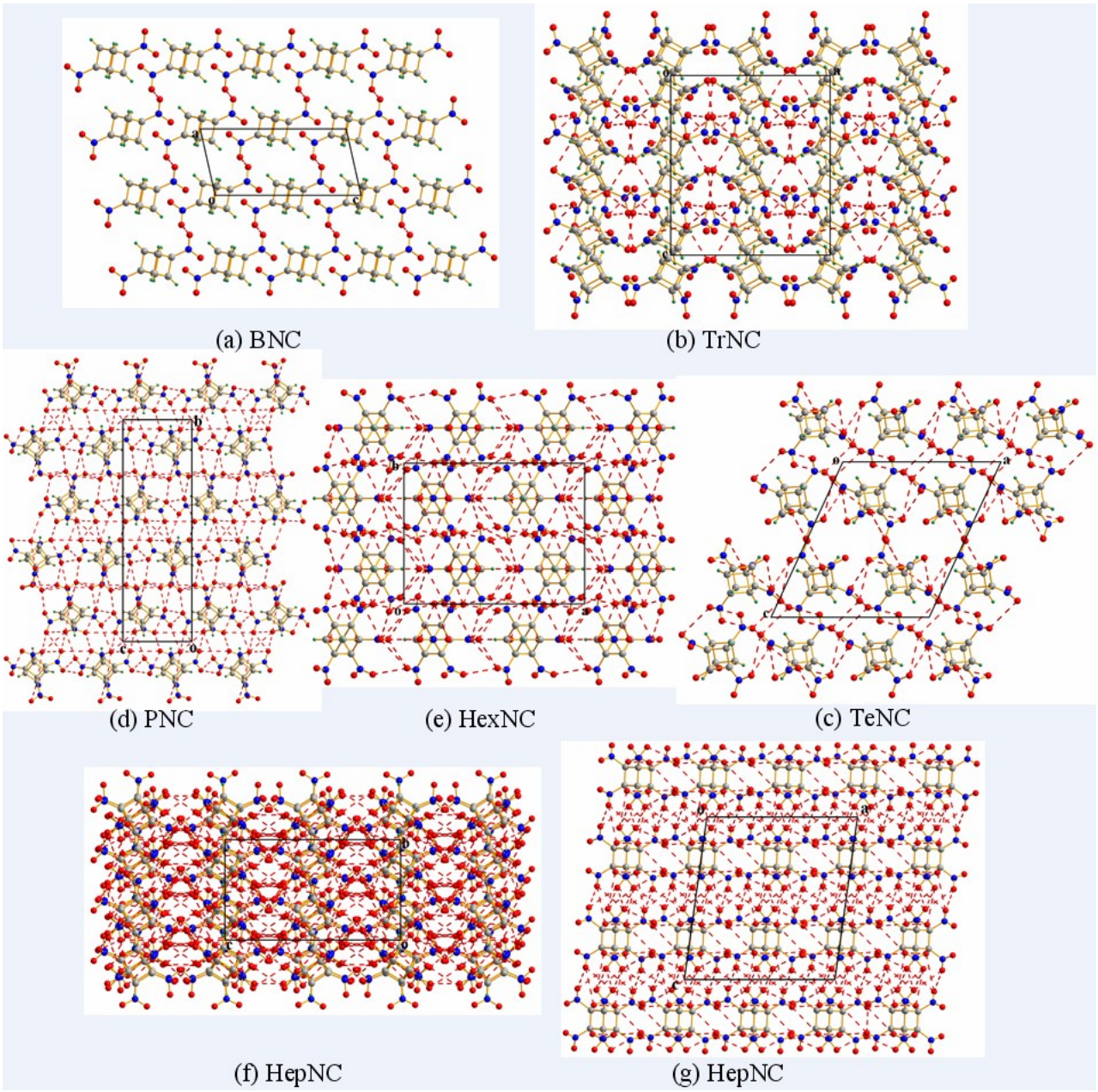

Fig. s5 O···O contacts in nitrocubanes represented by red dashes.

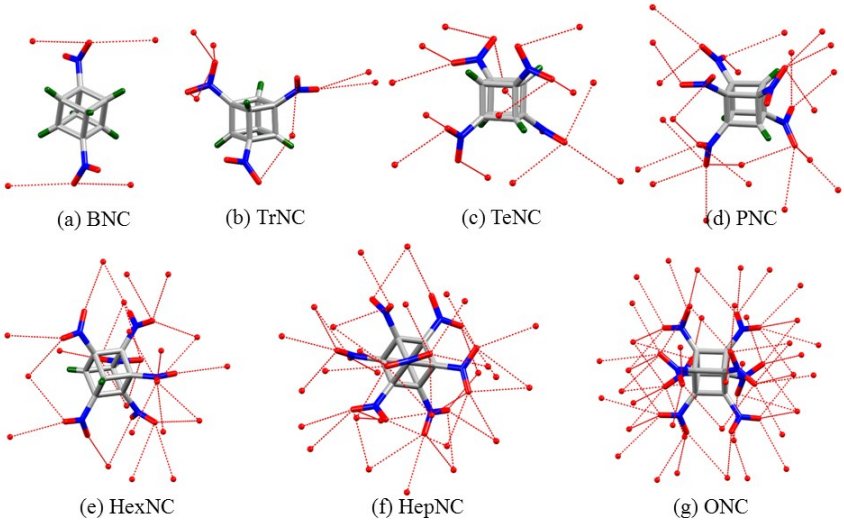

Fig. s6 O···O contacts around one molecule in nitrocubanes represented by red lines.

Table s4. Geometric analyses of the intermolecular O···O interactions in crystals.

Molecule	atom1	atom2	Length, Å	Symmetry Operations
BNC	O1B	O1B	3.292	-1+x,-1/2-y,-1/2+z,(2);
	O1	O1	3.292	1-x,-1/2+y,1.5-z,(2);
TrNC	O2	O3	2.993	-x,1/2+y,1/2-z; -x,-1/2+y,1/2-z;
	O2	O4	2.941	x,1/2-y,1/2+z;x,1/2-y,-1/2+z;
	O2	O5	3.201	1/2+x,y,1/2-z;-1/2+x,y,1/2-z;
TeNC	O1	O3	2.957	x,1+y,z; x,-1+y,z;
	O3	O8	2.946	-1/2+x,-1/2-y,z; 1/2+x,-1/2-y,z;
	O4	O6	2.998	-1/2+x,-1/2-y,z; 1/2+x,1/2-y,z;
	O5	O6	3.066	1/2-x,-1/2+y,-z; 1/2-x,1/2+y,-z;
	O7	O7	2.939	1-x,-y,1-z;
PNC	O1	O1	3.225	1-x,1-y,1-z;
	O1	O9	3.052	1-x,1-y,1-z,(2);
	O1	O10	3.149	1+x,y,1+z; -1+x,y,-1+z;
	O2	O5	3.244	x,y,1+z; x, y,-1+z;
	O2	O6	3.257	1+x,y,1+z; -1+x,y,-1+z;
	O2	O7	3.036	1+x,1/2-y,1/2+z; -1+x,1/2-y,-1/2+z;
	O4	O5	2.920	x,1/2-y,1/2+z; x,1/2-y,-1/2+z;
	O4	O7	3.127	1+x,1/2-y,1/2+z; -1+x,1/2-y,-1/2+z;
	O4	O8	2.850	x,1/2-y,1/2+z; x,1/2-y,-1/2+z;
	O5	O8	2.884	x,1/2-y,-1/2+z; x,1/2-y,1/2+z;
	O5	O10	3.024	1+x,y,z; -1+x,y,z;
	O6	O9	3.245	-x,1-y,-z,(2);
	O7	O8	2.749	x,1/2-y,-1/2+z; x,1/2-y,1/2+z;
	O9	O9	3.245	-x,1-y,1-z;
	O10	O10	2.982	-x,1-y,-z;
HexNC	O1	O4	3.215	1/2-x,1/2+y,1/2+z; 1/2-x,-y,1/2+z; 1/2-x,-1/2+y,-1/2+z; 1/2-x,1/2+y,-1/2+z;
	O1	O6	3.094	1/2+x,y,2.5-z; -1/2+x,y,2.5-z;
	O2	O4	3.242	1/2-x,1/2+y,1/2+z; 1/2-x,-y,1/2+z; 1/2-x,-1/2+y,-1/2+z; 1/2-x,1/2+y,-1/2+z;
	O3	O4B	2.766	1/2-x,-y,1/2+z; 1/2-x,1/2+y,1/2+z; 1/2-x,-y,-1/2+z; 1/2-x,1/2+y,-1/2+z;
	O3	O5	3.014	1/2-x,-1/2+y,1/2+z; 1/2-x,-y,-1/2+z; 1/2-x,1/2+y,-1/2+z; 1/2-x,1/2+y,1/2+z;
	O4	O7	3.185	-1/2+x,y,1.5-z; -1/2+x,1/2-y,1.5-z; 1/2+x,1/2-y,1.5-z;1/2+x,y,1.5-z;
	O4	O7B	2.915	1/2-x,-y,1/2+z; 1/2-x,1/2+y,1/2+z; 1/2-x,-y,-1/2+z; 1/2-x,1/2+y,-1/2+z;
	O5	O7	3.119	-1/2+x,y,1.5-z; -1/2+x,1/2-y,1.5-z; 1/2+x,y,1.5-z,(2);
	O5	O8	3.236	1/2-x,1/2+y,-1/2+z; 1/2-x,-1/2+y,1/2+z; 1/2-x,-y,-1/2+z; 1/2-x,1/2+y,1/2+z;
	O6	O7	2.958	-1/2+x,y,1.5-z; -1/2+x,1/2-y,1.5-z; 1/2+x,y,1.5-z; 1/2+x,y,1.5-z;
	O8	O8	2.876	1-x,-y,2-z; 1-x,1/2+-y,2-z;
HepNC	O1	O2	2.967	1/2-x,-1/2+y,z,(2);
	O1	O3	3.236	1/2-x,1/2-y,-1/2+z; 1/2-x,1/2-y,1/2+z;
	O1	O6	2.873	x,1-y,1/2+z,;x,1-y,-1/2+z;
	O1	O12	3.044	1/2-x,-1/2+y,z,(2);

	O2	O9	3.005	1/2-x,-1/2+y,z,(2);
	O2	O12	3.252	1/2-x,-1/2+y,z,(2);
	O3	O4	3.048	1/2-x,-1/2+y,z,(2);
	O3	O10	3.173	1/2-x,-1/2+y,z,(2);
	O3	O12	3.121	1/2-x,1/2-y,-1/2+z; 1/2-x,1/2-y,1/2+z;
	O5	O9	3.055	x,-y,1/2+z,(2);
	O6	O10	3.040	x,1+y, z; x,-1+y, z;
	O6	O13	3.037	x,1-y,-1/2+z;x,1-y,1/2+z;
	O7	O7	2.887	1-x,y,1.5-z;
	O7	O9	3.124	1-x,-y,1-z,(2);
	O7	O13	2.846	1-x,1-y,1-z,(2);
	O8	O8	2.790	1-x,-y,1-z;
	O8	O11	3.146	x,-y,1/2+z; x,-y,-1/2+z;
	O8	O14	2.946	1-x,-y,1-z,(2);
	O9	O14	3.104	1-x,-y,1-z,(2);
	O10	O11	3.247	x,-y,1/2+z; x,-y,-1/2+z;
	O10	O12	3.030	x,-y,1/2+z; x,-y,-1/2+z;
	O11	O8	3.102	1-x,-y,1-z,(2);
	O13	O13	2.878	1-x, y,1/2-z;
	O14	O14	2.977	1-x,1-y,1-z;
ONC	O1	O3F	3.251	1/2-x,1/2+y,1/2-z,(2); 1/2+x,-1/2+y,z; 1/2+x,1/2+y, z;
	O1	O4	3.178	-1/2+x,1/2+y,z; 1/2-x,-1/2+y,1/2-z; 1/2+x,-1/2+y,z; 1.5-x,1/2+y, z;
	O1	O5F	2.832	1/2-x,1/2+y,1/2-z; 1/2-x,-1/2+y,1/2-z; 1/2+x,-1/2+y,z;1/2+x,1/2+y, z;
	O1	O7	3.161	-1/2+x,-1/2+y,z; 1/2-x,1/2+y,1/2-z; 1.5-x,-1/2+y,1/2-z; 1/2+x,1/2+y, z;
	O2	O2F	3.154	1/2-x,1/2-y,1-z; 1/2+x,1/2-y, -1/2+z
	O2	O6	3.261	x,1-y,1/2+z; 1-x,1-y,1-z; x,1-y,-1/2+z; 1-x,1-y,-z;
	O2	O8F	3.170	x,1-y,-1/2+z,(2); 1-x,1-y,1-z,(2);
	O3	O4F	3.274	1-x,-y,1-z,(2); x,-y,-1/2+z,(2);
	O3	O5F	3.132	1/2-x,-1/2+y,1/2-z; 1/2+x,1/2+y, z; 1/2-x,1/2+y,1/2-z; 1/2+x,-1/2+y,z
	O3	O7	3.140	x,-1+y,z,(2); -x,-1+y,1/2-z;1-x,1-y, 1/2-z;
	O4	O4F	3.167	1-x,-y,1-z; x,-y,-1/2+z;
	O4	O6	3.082	-1/2+x,1/2-y,-1/2+z; 1/2-x,1/2-y,-z; 1/2+x,1/2-y,1/2+z; 1.5-x,1/2-y,1-z
	O4	O8F	3.297	1-x,1-y,1-z,(2); x,1-y,-1/2+z,(2);
	O5	O8F	3.014	1/2-x,-1/2+y,1/2-z; 1/2-x,1/2+y,1/2-z; 1/2+x,-1/2+y,z; 1/2+x,1/2+y, z;
	O6	O8	3.002	x,1-y,-1/2+z; 1-x,1-y,-z; x,1-y,1/2+z; 1-x,1-y,1-z;
	O8	O8F	2.916	1-x,1-y,1-z; x,1-y,-1/2+z;

S4. Details of C-C and C-N bond length in crystallized and isolated cubane and nitrocubanes.

Each of the discussed molecules can structurally be partitioned into cage and substituted nitro groups (hydrogen atoms saturate the cages, and a small length difference is found in all C-H bonds because no strong hydrogen bonding, HB, exists in these crystals). Therefore, the C-C bonds of the cages and the C-N bonds related with nitro groups should be focused on. Moreover, these molecular structures in the crystallized state should be compared with those relaxed in gaseous state to investigate the crystal effect. Given the large amount of these bonds, we will discuss these bonds by averaging or abstracting the maximal difference between the longest and shortest bonds of the same kind. We first focused on the average C-C bond length and the average C-N bond length in both crystallized and isolated states. With respect to the C-C bonds of crystallized cubane and nitrocubane molecules, they show a fluctuation in a range of 0.023 Å when the nitryl amount was increased. The shortest and longest average C-C bond lengths, 1.542 and 1.565 Å, appears in MNC and HexNC, respectively. In contrast to that of cubane, these average length of C-C bonds varies from -0.5 to 1.0 %. Considering the esds in Table s1, these variations can be overlooked. Meanwhile, for molecules that are relaxed as isolated ones, the C-C bond length changes smoothly from an initial decrease and a subsequent increase when nitro groups are increased. These changes are slight and are within 0.009 Å only, which is less than that of crystallized state (0.023 Å). Moreover, as expected, the average C-C bond length of the crystallized state increases for each molecule after relaxation. In contrast to crystallized C-C bonds, crystallized C-N bonds vary smoothly in terms of their average length (i.e., increase first and decrease later), to an extent of 0.023 Å, as well. In the isolated molecules, the C-N bonds increase successively with increasing nitro groups from 1.458 Å to 1.478 Å. Surprisingly, these bonds shrunk after molecular relaxation, which may be attributed to the enlargement of cages by C-C bond relaxation. As a whole, for the C-C and C-N bonds in both crystallized

and isolated states, the average length varies in a small range with increasing nitro groups.

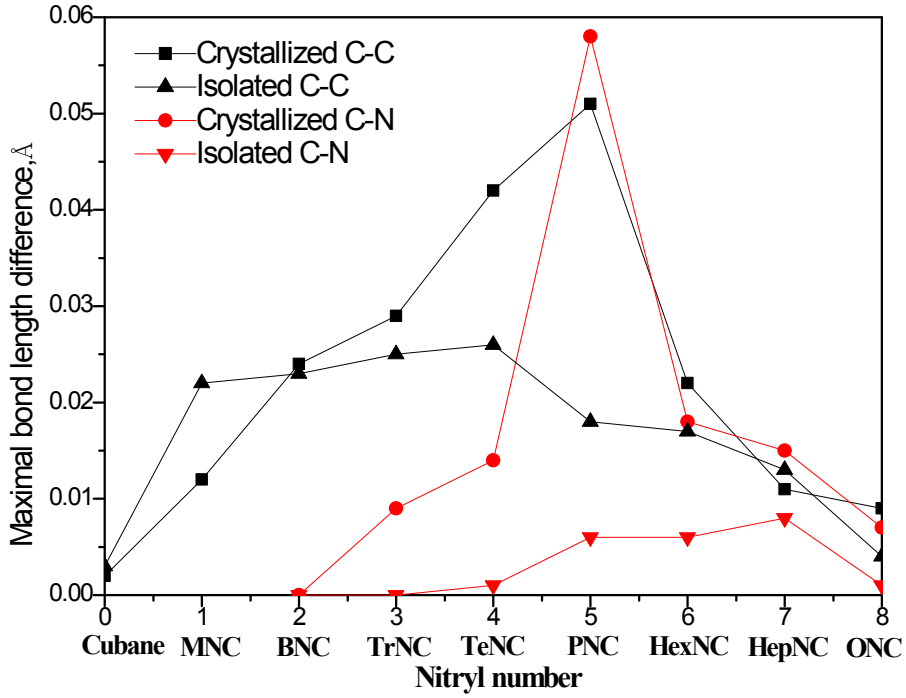

Figure s7. Maximal bond length differences of C-C and C-N of crystallized and isolated cubane and nitrocubanes.

However, after a careful examination of individual bonds, we find that much larger differences exist between the shortest and the longest bonds of both C-C and C-N in crystallized state relative to the isolated state, suggesting that crystal packing leads to multiple changes in molecular structures. Figure s6 exhibits the largest length differences of C-C and C-N bonds in PNC, namely, 0.051 and 0.058 Å, respectively, which indicate the largest molecular distortion.

S5. References.

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