Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic supplementary information

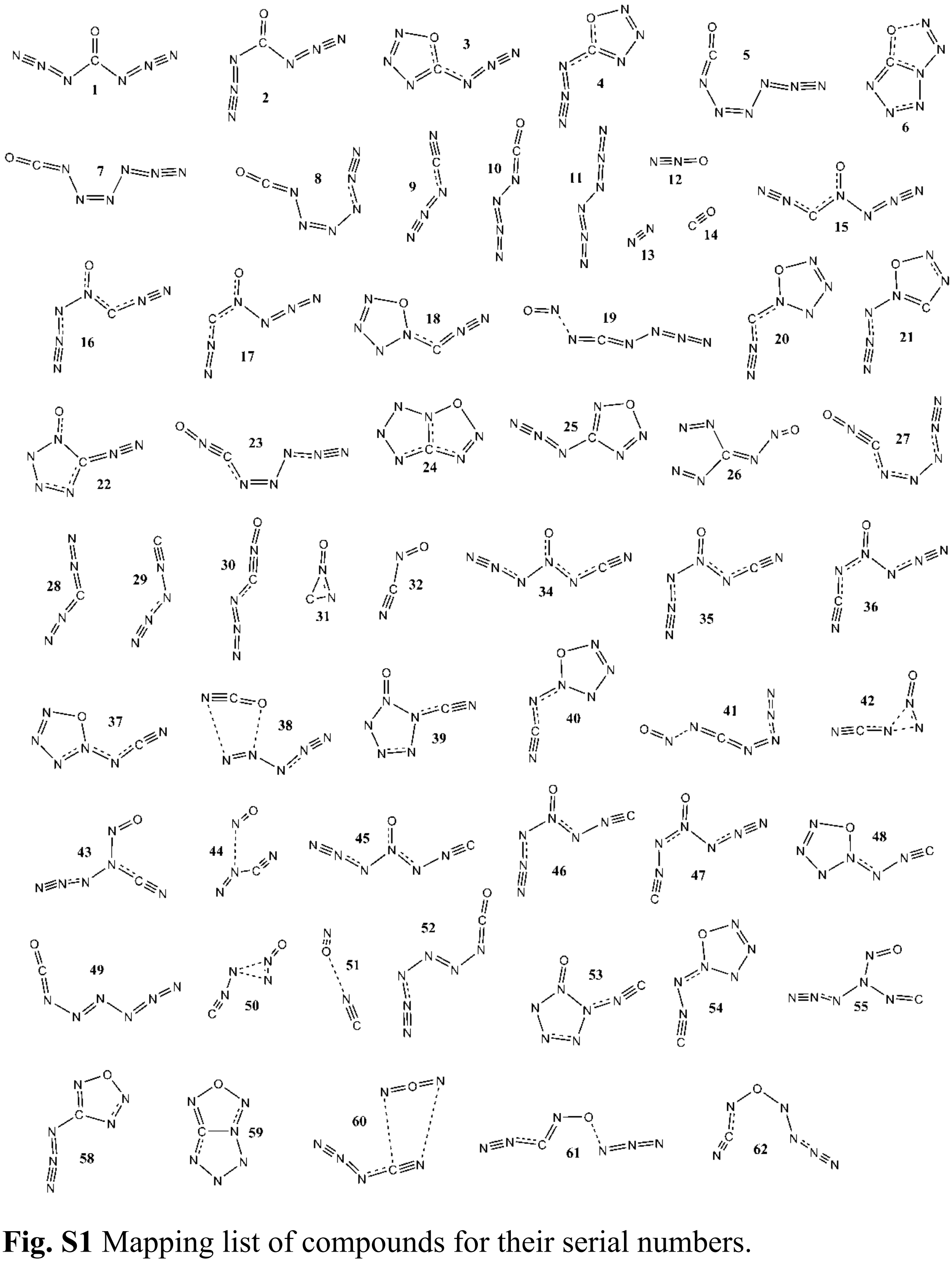

Fig. S1 Mapping list of compounds for their serial numbers.

Kamlet-Jacobs equation:

$$D_v = 1.01\left(NM^{\frac{1}{2}}Q^{\frac{1}{2}}\right)^{\frac{1}{2}}(1 + 1.3\rho)$$

$$D_p = 1.558\rho^2 NM^{\frac{1}{2}}Q^{\frac{1}{2}}$$

where D_v represents detonation velocity in km s^{-1}, D_p represents detonation pressure in GPa, ρ represents charge density in g cm^{-3}, N represents quantity of gaseous products in mol g^{-1}, N represents mass of gaseous products in g mol^{-1} and Q represents detonation heat in J g^{-1}.

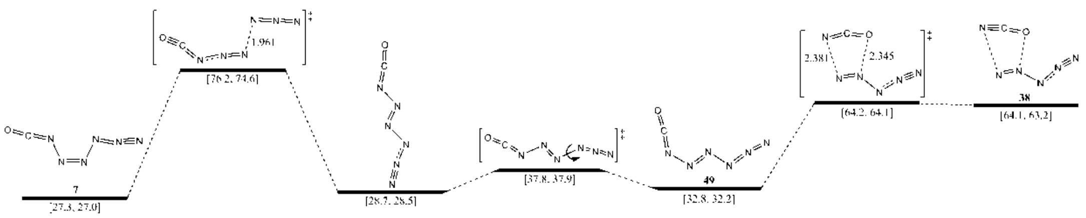

Fig. S2 Schematic potential energy surface of isomerization of 1-azido-2-isocyanatodiazene at the B3LYP/aug-cc-pVDZ level. Gibbs free energies at 0 K (former) and 298 K (latter) are in brackets. The energy scales are offset to 0 kcal mol^{-1} for *syn*-*syn* carbonyl diazide as the reference. The crucial bond lengths are labeled in angstroms.

Table S1 The limiting pathways of conversion and their activation free energy barriers in kcal mol^{-1} at B3LYP/aug-cc-pVDZ and G3B3 level for different isomers of CN_6O.

Compound	Pathway	Barrier			
		B3LYP		G3B3	
		0 K	298.15 K	0 K	298.15 K
1	**2→TS8**	31.6	30.7	31.3	30.4
3	**3→TS1**	0.9	0.9	1.2	1.3
6	**6→TS13**	6.2	5.9	8.7	8.3
7	**7→TS17**	9.7	10.3	7.9	8.6
15	**15→TS19**	13.2	14.0	14.5	15.3
23	**23→TS48**	12.2	12.8	10.3	10.7
24	**24→TS45**	11.8	10.3	10.1	10.2
25	**58→TS102**	13.3	12.5	13.5	12.6
34	**34→TS50**	17.0	17.8	19.1	19.9
39	**39→TS64**	13.4	12.5	16.6	15.7
45	**45→TS71**	14.1	14.8	13.8	14.5
53	**53→TS88**	14.1	13.7	16.4	16.0
59	**59→TS97**	5.7	5.6	6.4	6.3

Table S2 The gas phase enthalpies of formation in kcal mol^{-1} at B3LYP/aug-cc-pVDZ and G3B3 level at 298.15 K for different isomers of CN_6O.

Compound	Enthalpy of formation	
	B3LYP	G3B3
1	115.7	111.0
3	139.3	135.3
6	160.5	156.1
7	143.1	144.1
15	202.7	203.6
23	193.8	196.0
24	177.5	174.9
25	145.0	146.6
34	179.0	176.1
39	179.4	176.7
45	215.7	214.5
53	219.0	219.2
59	185.3	182.7

Table S3 The frontier orbital energies in hartree for different isomers of CN_6O.

Compound	Frontier orbital energy		
	LUMO	HOMO	Gap
1	-0.09400	-0.31243	0.21843
3	-0.10077	-0.31065	0.20988
6	-0.12864	-0.33835	0.20971
7	-0.09639	-0.29176	0.19537
15	-0.13510	-0.27630	0.14120
23	-0.12682	-0.27881	0.15199
24	-0.14033	-0.33469	0.19436
25	-0.10618	-0.30173	0.19555
34	-0.14143	-0.31274	0.17131
39	-0.13874	-0.32745	0.18871
45	-0.12992	-0.30619	0.17627
53	-0.12853	-0.31997	0.19144
59	-0.15987	-0.31727	0.1574

Table S4 The enthalpy of formation (EOF in kcal mol^{-1}) effect on specific impulse (I_{sp} in s) and chamber combustion temperature (T_c in K) for CN_6O.

EOF	I_{sp}	T_c
90	252.3	3771
100	261.7	4045
110	270.7	4315
120	279.4	4576
130	287.8	4826
140	295.8	5062
150	303.7	5280
160	311.2	5481
170	318.5	5664
180	325.5	5830
190	332.2	5981
200	338.7	6119
210	345.0	6245
220	351.0	6361

Table S5 Calculated rocket performances of some classical compounds as a comparative set. The enthalpy of formation (EOF) in kcal mol^{-1}, specific impulse (I_{sp}) in s and chamber combustion temperature (T_c) in K.

Species[a]	EOF	I_{sp}	T_c
TNT	-19.25[b]	208.6	2975
RDX	18.9[c]	267.7	3305
HMX	24.5[c]	267.5	3302
CL-20	98.7[d]	272.6	3589
FTDO	160.9[e]	297.0	4515

[a] TNT, trinitrotoluene; RDX, cyclotrimethylene trinitramine; HMX, cycloteramethylene tetranitramine; CL-20, hexanitrohexaazaisowuritane, FTDO, [1,2,5]oxadizolo[3,4-4][1,2,3,4]tetrazine-4,6-di-N-dioxide.

[b] C. Lenchitz, R. W. Velicky, G. Silvestro, L. P. Schlosberg, *J. Chem. Thermodyn.*, 1971, **3**, 689.

[c] G. Krien, H. H. Licht, J. Zierath, *Thermochim. Acta*, 1973, **6**, 465.

[d] Yu. A. Bogdanova, S. A. Gubin, B. L. Korsunskii, V. I. Pepekin, *Combust., Expl., Shock Waves*, 2009, 45, 728.

[e] V. I. Pepekin, Yu. N. Matyushin, T. V. Gubina, Russ. J. Phys. Chem. B, 2011, 5, 97.

Table S6 Molecular volumes (V_m) in cm^3 mol^{-1} inside a contour of 0.003 electrons Bohr^{-3} density and calculated densities (ρ) in g cm^{-3} with a 73.6% space occupancy for different isomers of CN_6O.

Compound	V_m	ρ
1	48.143	1.712
3	46.603	1.769
6	46.038	1.790
7	48.660	1.694
15	49.142	1.677
23	48.993	1.682
24	46.317	1.779
25	48.134	1.712
34	48.587	1.696
39	46.790	1.762
45	50.145	1.644
53	49.405	1.668
59	45.359	1.817

Table S7 Calculated detonation performances of some classical compounds as a comparative set. The density (ρ) in g cm^{-3}, detonation velocity (D_v) in m s^{-1} and detonation pressure (D_p) in GPa.

Species[a]	ρ	D_v	D_p
TNT	1.654[b]	6997.1	20.61
RDX	1.816[b]	8872.0	35.10
HMX	1.910[b]	9191.0	38.80
CL-20	1.970[b]	9414.3	41.43
FTDO	1.850[c]	9309.2	39.07

[a] TNT, trinitrotoluene; RDX, cyclotrimethylene trinitramine; HMX, cycloteramethylene tetranitramine; CL-20, hexanitrohexaazaisowuritane, FTDO, [1,2,5]oxadizolo[3,4-4][1,2,3,4]tetrazine-4,6-di-N-dioxide.

[b] H. Shekhar, *Cent. Eur. J. Energ. Mat.*, 2012, **9**, 39.

[c] D. B. Lempert, G. N. Nechiporenko and S. I. Soglasnova, *Khim. Fiz.* 2004, **23**, 75.