Electronic Supplementary Material (ESI) for RSC Advances.

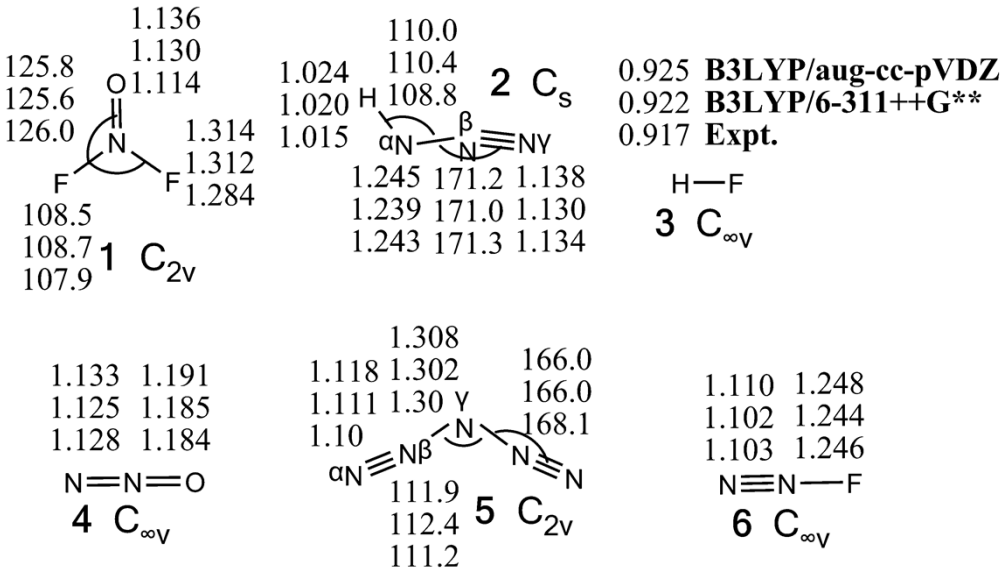

Fig. S1 Computed (B3LYP method with aug-cc-pVDZ and 6-311++G**[α] basis sets) and experimental geometries of F_2NO^+ (**1**), HN_3 (**2**), HF (**3**), N_2O (**4**), N_5^+ (**5**) and N_2F^+ (**6**). The bond lengths in angstroms and bond angles in degrees. [α]W. J. Hehre, L Rodom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986. 6-311++G** is equal to 6-311+G* for the systems without hydrogen atoms

Table S1 Computed (at B3LYP/aug-cc-pVDZ, B3LYP/6-311++G**, G3B3 and CBS-QB3[α] levels) and experimental enthalpies (in kcal/mol) of formation in the gas phase at 298.15 K for NF_2O^+, HN_3, HF, N_2O, N_5^+ and N_2F^+.

Species	B3LYP/aug-cc-pVDZ	B3LYP/6-311++G**	G3B3	CBS-QB3	Expt.
F_2NO^+ (**1**)	234.6	242.8	233.4	231.8	232.4
HN_3 (**2**)	68.0	67.5	70.0	69.7	70.3
HF (**3**)	-61.8	-61.7	-65.2	-66.0	-65.1
N_2O (**4**)	21.7	22.4	19.4	18.5	19.6
N_5^+ (**5**)	348.4	348.8	351.2	351.2	-
N_2F^+ (**6**)	293.5	296.1	290.6	290.3	283.4±4.6

[α]J. A. Montgomery Jr., M. J. Frisch, J. W. Ochterski, and G. A. Petersson, *J. Chem. Phys.*, 1999, **110**, 2822. J. A. Montgomery Jr., M. J. Frisch, J. W. Ochterski, and G. A. Petersson, *J. Chem. Phys.*, 2000, **112**, 6532.

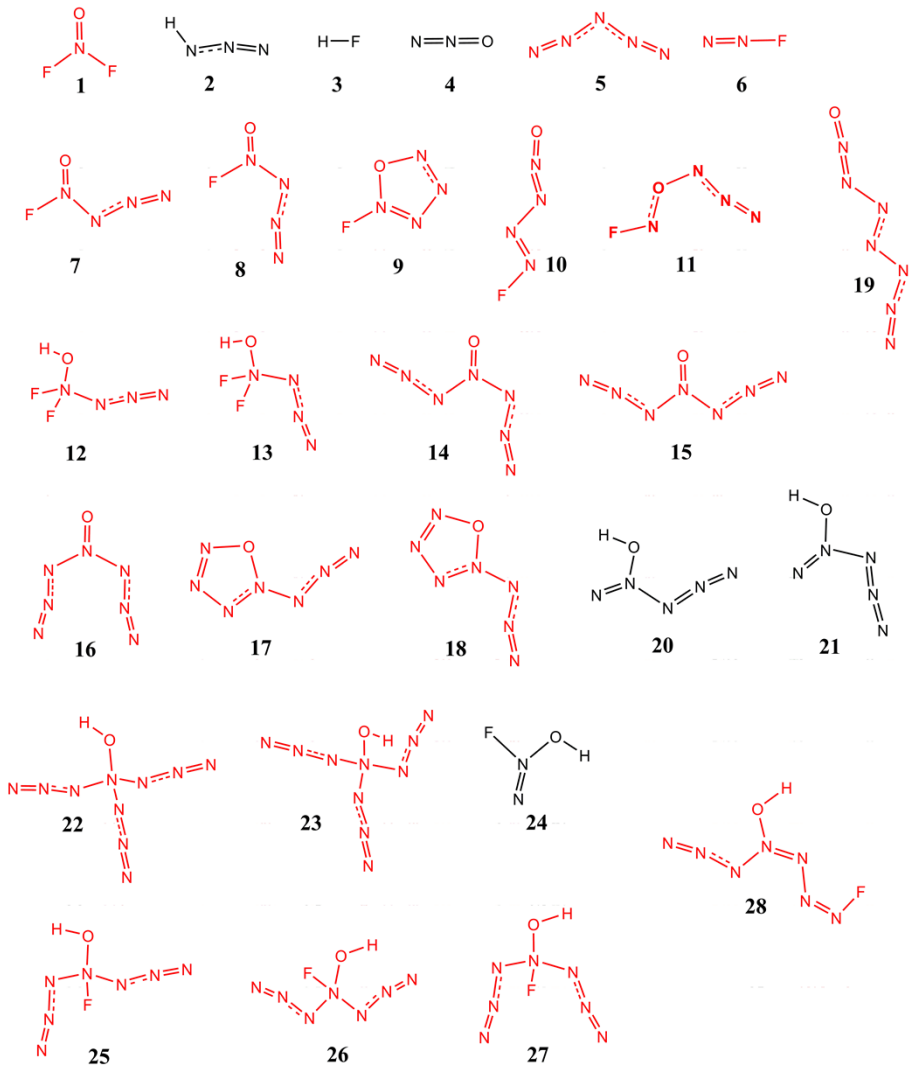

Fig. S2 Numbering scheme for compounds and cations. All cations with one positive charge are shown in red.

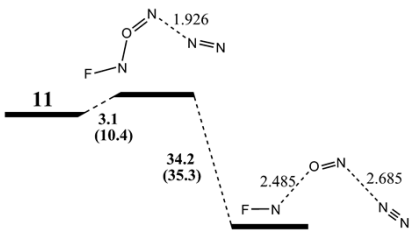

Fig. S3 Schematic potential energy surface of the decomposition of **11** at the G3B3 level. The activation free energy barriers at 240 K in kcal/mol, (B3LYP/aug-cc-pVDZ values in parentheses), bond lengths in angstroms, and all the systems possess one positive charge.

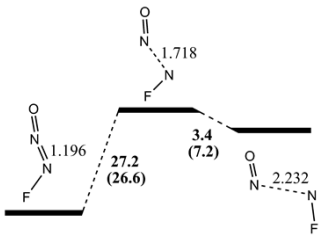

Fig. S4 Schematic potential energy surface of the decomposition of $ONNF^+$ at the G3B3 level. The activation free energy barriers at 240 K in kcal/mol, (B3LYP/aug-cc-pVDZ values in parentheses), bond lengths in angstroms, and all the systems possess one positive charge.

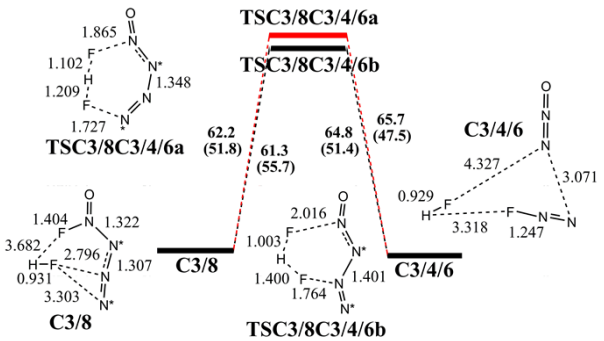

Fig. S5 Schematic potential energy surface of the decomposition of **8** with **3** at the G3B3 level. The activation free energy barriers at 240 K in kcal/mol, (B3LYP/aug-cc-pVDZ values in parentheses), and bond lengths in angstroms. The possible nitrogen atoms labeled by 15N are marked with asterisks, the pathway in conformity with the 15N labels is shown in red, and all the systems are with one positive charge.

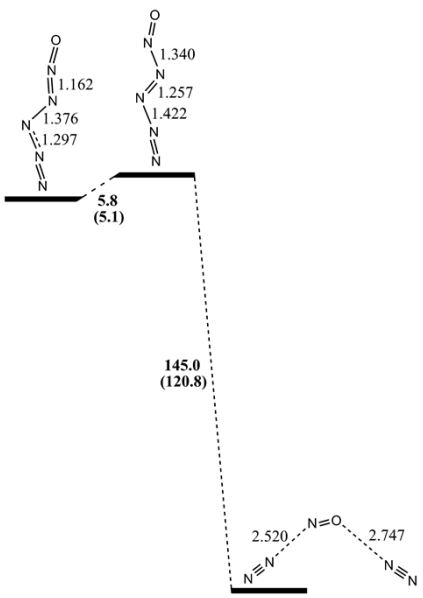

Fig. S6 Schematic potential energy surface of decomposition of N_5O^+ at the G3B3 level. The activation free energy barriers at 240 K in kcal/mol, (B3LYP/aug-cc-pVDZ values in parentheses), bond lengths in angstroms, and all the systems possess one positive charge.

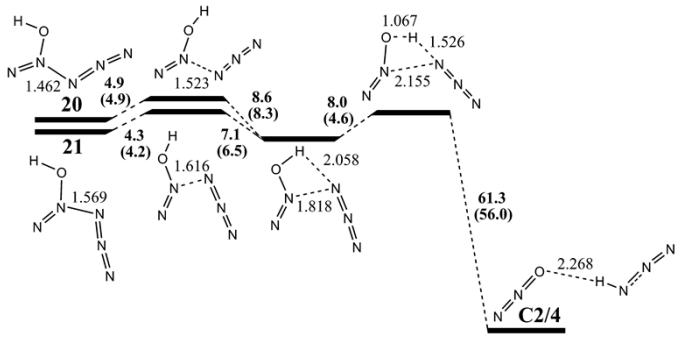

Fig. S7 Schematic potential energy surface of decomposition of **20** and **21** at the G3B3 level. The activation free energy barriers at 240 K in kcal/mol, (B3LYP/aug-cc-pVDZ values in parentheses), and bond lengths in angstroms.

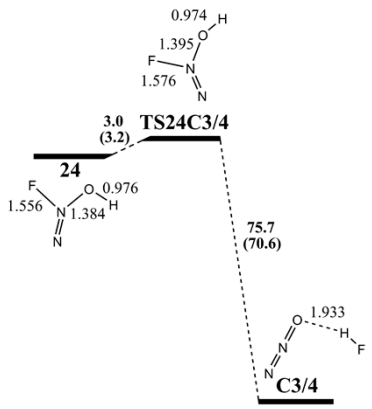

Fig. S8 Schematic potential energy surface of decomposition of **24** at the G3B3 level. The activation free energy barriers at 240 K in kcal/mol, (B3LYP/aug-cc-pVDZ values in parentheses), and bond lengths in angstroms.