Supplementary Material

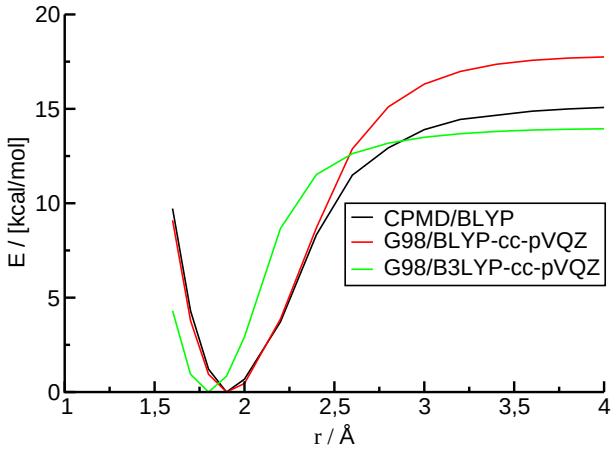

Figure SI: Potential energy curves of the dissociation of the N-N bond of NTO. Comparison of the plane wave approach used within the CPMD code and the local basis sets employed by the Gaussian code. Black: CPMD code, BLYP functional, Troullier-Martins pseudopotentials with a cutoff of 70 Ry. Red: Gaussian code, BLYP functional, cc-pVQZ basis set. Green: Gaussian code, B3LYP functional, cc-pVQZ basis set. Comparing the two BLYP calculations performed with CPMD and Gaussian, the basis set superposition error caused by the rather limited Gaussian basis set is apparent, leading to an overestimation of the depth of the potential well. Comparison with the B3LYP calculation illustrates the loss of accuracy in the simulations by the restriction to the less expensive GGA type functionals like BLYP: with the hybrid functional B3LYP the dissociation energy is smaller and the N-N bond is shorter. D_e: BLYP, plane wave basis set: 14.6 kcal/mol; BLYP, cc-pVQZ: 17.8 kcal/mol; B3LYP, cc-pVQZ: 13.9 kcal/mol, Exp.: 16.3 kcal/mol (M. L. McKee, J. Am. Chem. Soc. **1995**, *117, 1629. J. Koput, Chem. Phys. Lett.* **1995**, *240, 553. I. C. Hisatsune, J. Phys. Chem.* **1961**, *65, 2249.). D_0: BLYP, cc-pVQZ: 14.6 kcal/mol; B3LYP, cc-pVQZ: 10.3 kcal/mol, Exp.: 12.7 kcal/mol (I. C. Hisatsune, J. Phys. Chem.* **1961**, *65, 2249.).*

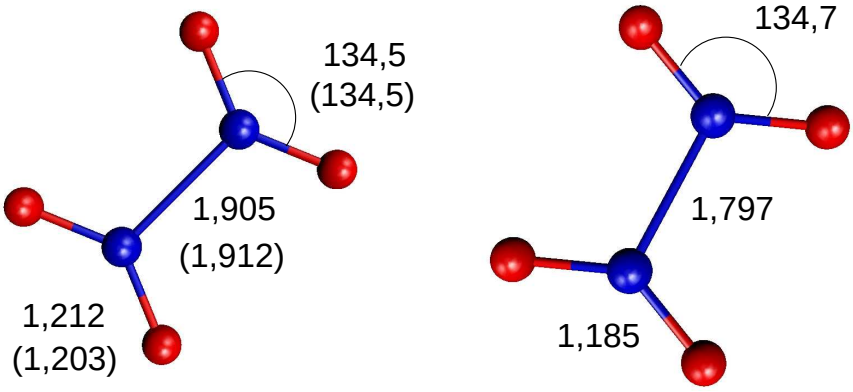

Figure SII: Optimized structure of NTO. Left side: BLYP, plane wave basis set, in brackets: BLYP, cc-pVQZ, right side: B3LYP, cc-pVQZ. Distances are given in Angstrom, angles in degrees.

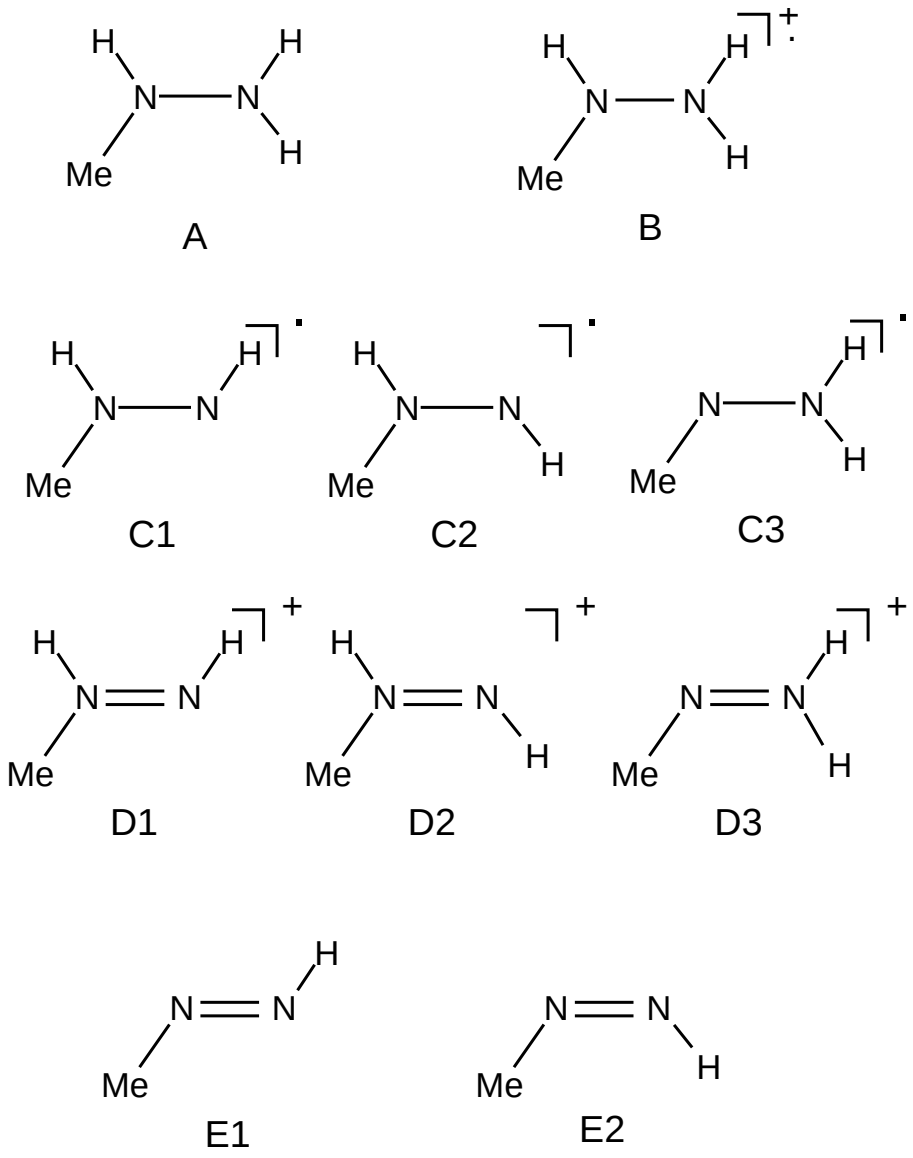

Figure SIII: MMH and consecutive products (cf. Table I).

	r(N-N)		r(N-C)		a(N-N-C)	
	BLYP	B3LYP	BLYP	B3LYP	BLYP	B3LYP
A	1,454	1,424	1,475	1,454	114,8	114,5
B	1,333	1,317	1,471	1,455	122,1	121,6
C1	1,359	1,341	1,465	1,446	117,1	116,8
C2	1,359	1,340	1,471	1,450	123,2	123,1
C3	1,366	1,347	1,460	1,441	110,4	110,5
D1	1,240	1,221	1,491	1,474	121,4	121,8
D2	1,240	1,221	1,487	1,479	129,7	128,3
D3	1,245	1,225	1,441	1,449	118,3	118,0
E1	1,252	1,233	1,479	1,472	112,9	112,6
E2	1,244	1,228	1,481	1,461	119,3	119,1

Table SI: Structural parameters of MMH and consecutive products (cf. Fig. III). Distances are given in Angstrom, angles in degrees. The BLYP results were obtained using CPMD (plane wave basis set), the B3LYP results using Gaussian (cc-pVQZ basis set).