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Decomposition mechanisms of trinitroalkyl compounds: a theoretical study from aliphatic to aromatic nitro compounds

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SUPPORTING INFORMATION

Table S1 – Geometric parameters of trinitromethane

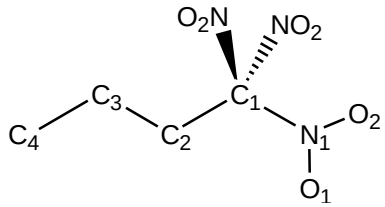
	Gas Electron Diffraction [1]	X-ray [2]	B3LYP 6-311G(d,p) [3]	B3LYP 6-311++G(d,p) [3]	PBE0 6-31+G(d,p)
bond lengths (in Å)					
C–N	1.505	1.505	1.523	1.526	1.508
N–O1	1.219	1.205	1.213	1.214	1.212
N–O2	1.219	1.207	1.209	1.209	1.208
C–H	1.13	0.90	1.084	1.085	1.088
angles (in degrees)					
N-C-N	110.7	108.6	109.6	109.8	109.6
N-C-H	108.2	110.4	109.3	109.2	109.3
C-N-O1	115.7	115.3	113.4	113.4	113.4
C-N-O2	115.7	117.5	117.8	118.0	117.9
O1-N-O2	128.6	127.2	128.8	128.6	128.8
dihedral angles (in degrees)					
H-C-N-O	26.3	44	43	42	43.0

1 N. I. Sadova, N. I. Popik and L. V. Vilkov, *J. Struct. Chem.*, 1976, **17**, 257-262.

2 H. Schodel, R. Dienelt and H. Bock, *Acta Cryst. C*, 1994, **50**, 1790-1792.

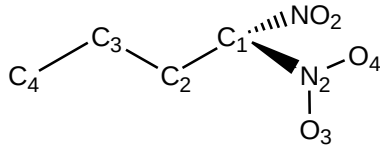
3 M. A. Tafipolsky, I. V. Tokmakov and V. A. Shlyapochnikov, *J. Mol. Struct.*, 1999, **510**, 149-156.

Table S2 – Main structural parameters of 1,1,1-trinitrobutane (n_C=4) and its analogues with different lengths of carbon chain (n_C=1-8).



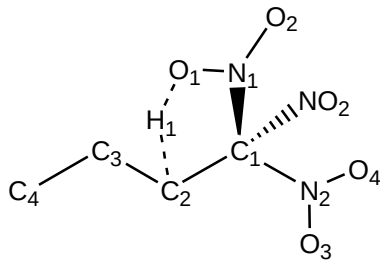
n_C	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Bond lengths (Å)								
N_1-O_1	1.212	1.212	1.213	1.213	1.213	1.214	1.214	1.214
N_1-O_2	1.208	1.209	1.207	1.207	1.207	1.207	1.207	1.207
N_1-C_1	1.508	1.529	1.532	1.532	1.532	1.531	1.532	1.532
C_1-C_2	N.A.	1.497	1.515	1.514	1.513	1.513	1.513	1.513
Angles (°)								
O_1-N_1-C_1	113.4	114.6	113.9	113.8	113.8	113.8	113.8	113.8
O_2-N_1-C_1	117.9	117.4	118.5	118.2	118.2	118.2	118.2	118.2
N_1-C_1-C_2	N.A.	112.2	111.1	111.2	111.2	111.3	111.2	111.2
Dihedral angles (°)								
O_1-N_1-C_1-C_2	N.A.	43.3	46.7	47.4	47.5	47.6	47.8	47.8

Table S3 – Main structural parameters of the radical issued from the C-N breaking (**Rad1**) in 1,1,1-trinitrobutane (n_C=4) and its analogues with different lengths of carbon chain (n_C=1-8).



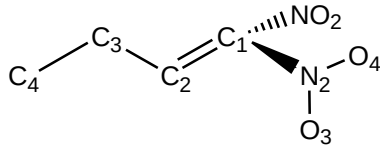
n_C	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Bond lengths (Å)								
N_2-O_3	1.225	1.226	1.225	1.225	1.225	1.225	1.225	1.225
N_2-O_4	1.216	1.221	1.219	1.218	1.219	1.219	1.219	1.219
N_2-C_1	1.425	1.432	1.435	1.436	1.435	1.435	1.435	1.435
C_1-C_2	N.A.	1.468	1.474	1.471	1.471	1.471	1.471	1.471
Angles (°)								
O_3-N_2-C_1	113.9	115.3	115.5	115.5	115.6	115.6	115.6	115.6
O_4-N_2-C_1	118.9	118.2	118.0	118.0	118.0	118.0	118.0	118.0
N_2-C_1-C_2	N.A.	121.7	122.2	122.0	122.1	122.1	122.1	122.1
N_1-C_2-C_3	N.A.	N.A.	112.7	112.9	112.7	112.7	112.7	112.7
Dihedral angles (°)								
O_3-N_2-C_1-C_2	N.A.	20.6	30.2	31.6	30.0	30.1	29.9	29.4
N_2-C_1-C_2-C_3	N.A.	N.A.	-101.9	-99.7	-99.9	-100.0	-99.5	-99.1

Table S4 – Main structural parameters of the transition state issued from the HONO elimination mechanism (**TS2**) in 1,1,1-trinitrobutane (n_C=4) and its analogues with different lengths of carbon chain (n_C=1-8).



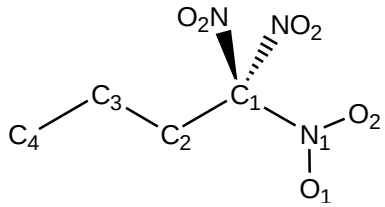
n_C	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Bond lengths (Å)								
N_1-O_1	N.A.	1.260	1.257	1.257	1.257	1.257	1.257	1.257
N_1-O_2	N.A.	1.188	1.189	1.190	1.190	1.190	1.190	1.190
N_1-C_1	N.A.	2.067	2.092	2.096	2.095	2.096	2.095	2.096
C_1-C_2	N.A.	1.381	1.387	1.386	1.386	1.386	1.386	1.386
C_2-H_1	N.A.	1.423	1.386	1.388	1.387	1.386	1.386	1.386
Angles (°)								
O_1-N_1-C_1	N.A.	101.8	101.1	101.0	101.0	101.0	101.0	101.0
N_1-O_1-H_1	N.A.	96.3	95.5	95.5	95.5	95.5	95.5	95.4
O_2-N_1-C_1	N.A.	134.7	135.2	135.4	135.3	135.3	135.3	135.4
C_1-C_2-H_1	N.A.	90.8	89.9	90.0	90.0	90.0	90.0	90.0
C_1-C_2-C_3	N.A.	N.A.	122.2	122.6	122.6	122.6	122.6	122.6
N_2-C_1-C_2	N.A.	122.0	121.9	122.0	121.9	122.0	122.0	122.0
Dihedral angles (°)								
O_1-N_1-C_1-C_2	N.A.	-0.5	0.3	0.1	0.1	-0.0	-0.1	-0.1
O_3-N_2-C_1-C_2	N.A.	-2.5	-9.8	-10.4	-10.5	-10.7	-10.8	-10.9
N_1-C_1-C_2-C_3	N.A.	N.A.	107.4	107.5	107.4	107.5	107.5	107.5

Table S5 – Main structural parameters of the product issued from the HONO elimination mechanism (**Prod1**) in 1,1,1-trinitrobutane (n_C=4) and its analogues with different lengths of carbon chain (n_C=1-8).



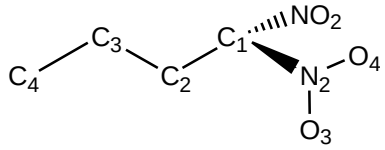
n_C	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Bond lengths (Å)								
N_2-O_3	N.A.	1.218	1.219	1.219	1.219	1.219	1.219	1.219
N_2-O_4	N.A.	1.214	1.216	1.217	1.217	1.217	1.217	1.217
N_2-C_1	N.A.	1.467	1.461	1.461	1.460	1.460	1.460	1.460
C_1-C_2	N.A.	1.323	1.331	1.331	1.331	1.331	1.331	1.331
Angles (°)								
O_3-N_2-C_1	N.A.	116.5	116.9	117.0	117.0	117.0	117.0	117.0
O_4-N_2-C_1	N.A.	116.4	116.7	116.7	116.7	116.7	116.7	116.7
N_2-C_1-C_2	N.A.	122.3	122.3	122.4	122.5	122.5	122.5	122.5
N_1-C_2-C_3	N.A.	N.A.	127.0	127.3	127.2	127.2	127.3	127.2
Dihedral angles (°)								
O_3-N_2-C_1-C_2	N.A.	32.6	13.3	13.2	12.3	12.3	12.5	12.2
N_2-C_1-C_2-C_3	N.A.	N.A.	177.9	178.1	178.6	178.6	178.6	178.8

Table S6 – Main structural parameters of 1,1,1-trinitrobutane and its analogues with double bonds (**1=2**, **2=3** and **1=2=3**).



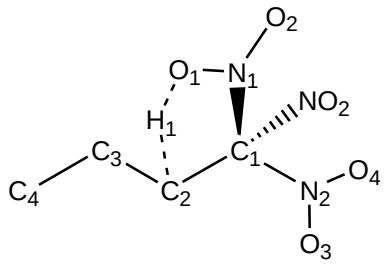
	1,1,1-trinitrobutane	**1=2**	**2=3**	**1=2=3**
Bond lengths (Å)				
N_1-O_1	1.213	1.214	1.212	1.212
N_1-O_2	1.207	1.206	1.207	1.207
N_1-C_1	1.532	1.530	1.538	1.533
C_1-C_2	1.514	1.520	1.477	1.480
Angles (°)				
O_1-N_1-C_1	113.8	113.8	114.5	114.6
O_2-N_1-C_1	118.2	118.2	117.5	117.3
N_1-C_1-C_2	111.2	111.1	112.1	111.6
Dihedral angles (°)				
O_1-N_1-C_1-C_2	47.4	46.7	41.6	42.1

Table S7 – Main structural parameters of the radical issued from the C-N breaking (**Rad1**) in 1,1,1-trinitrobutane and its analogues with double bonds (**1=2**, **2=3** and **1=2=3**).



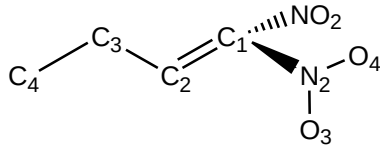
	1,1,1-trinitrobutane	**1=2**	**2=3**	**1=2=3**
Bond lengths (Å)				
N_2-O_3	1.225	1.224	1.225	1.226
N_2-O_4	1.218	1.218	1.221	1.223
N_2-C_1	1.436	1.437	1.438	1.429
C_1-C_2	1.471	1.479	1.386	1.395
Angles (°)				
O_3-N_2-C_1	115.5	115.8	116.7	116.6
O_4-N_2-C_1	118.0	117.6	117.3	117.3
N_2-C_1-C_2	122.0	122.0	121.7	122.0
N_1-C_2-C_3	112.9	111.0	126.1	124.3
Dihedral angles (°)				
O_3-N_2-C_1-C_2	31.6	33.8	13.3	8.7
N_2-C_1-C_2-C_3	-99.7	-111.9	177.6	179.5

Table S8 – Main structural parameters of the transition state issued from the HONO elimination mechanism (**TS2**) in 1,1,1-trinitrobutane and its analogues with double bonds (**1=2**, **2=3** and **1=2=3**).



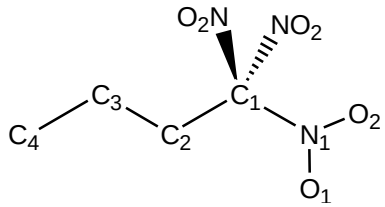
	1,1,1-trinitrobutane	**1=2**	**2=3**	**1=2=3**
Bond lengths (Å)				
N_1-O_1	1.257	1.253	1.266	1.265
N_1-O_2	1.190	1.188	1.188	1.184
N_1-C_1	2.096	2.033	2.136	2.025
C_1-C_2	1.386	1.399	1.358	1.368
C_2-H_1	1.388	1.381	1.432	1.459
Angles (°)				
O_1-N_1-C_1	101.0	102.4	101.3	103.7
N_1-O_1-H_1	95.5	95.5	96.4	97.0
O_2-N_1-C_1	135.4	133.0	136.1	132.9
C_1-C_2-H_1	90.0	89.6	93.8	93.2
C_1-C_2-C_3	122.6	123.1	145.2	147.4
N_2-C_1-C_2	122.0	120.7	123.6	122.6
Dihedral angles (°)				
O_1-N_1-C_1-C_2	0.1	1.0	-2.1	-2.0
O_3-N_2-C_1-C_2	-10.4	-9.0	-2.1	- 1.8
N_1-C_1-C_2-C_3	107.5	-153.6	180.0	-177.8

Table S9 – Main structural parameters of the product issued from the HONO elimination mechanism (**Prod1**) in 1,1,1-trinitrobutane and its analogues with double bonds (**1=2**, **2=3** and **1=2=3**).



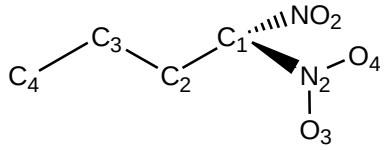
	1,1,1-trinitrobutane	**1=2**	**2=3**	**1=2=3**
Bond lengths (Å)				
N_2-O_3	1.219	1.221	1.217	1.217
N_2-O_4	1.217	1.217	1.214	1.215
N_2-C_1	1.461	1.456	1.472	1.468
C_1-C_2	1.331	1.341	1.305	1.313
Angles (°)				
O_3-N_2-C_1	117.0	116.8	116.6	116.6
O_4-N_2-C_1	116.7	116.9	116.5	116.4
N_2-C_1-C_2	122.4	121.5	122.1	122.0
N_1-C_2-C_3	127.3	127.1	179.8	180.0
Dihedral angles (°)				
O_3-N_2-C_1-C_2	13.2	15.7	32.0	32.5
N_2-C_1-C_2-C_3	178.1	177.6	-121.8	-118.8

Table S10 – Main structural parameters of 1,1,1-trinitrobutane (**-H**) and its analogues by substitution on carbon 2 (**-CH_3**, **-Cl**, **-CN**, **-NH_2**, **-NO_2**, **-OH**).



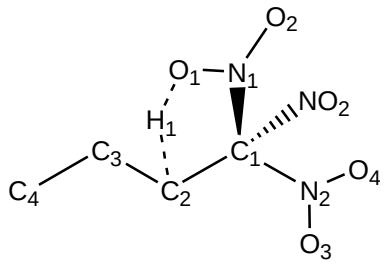
	-H	-CH_3	-Cl	-CN	-NH_2	-NO_2	OH
Bond lengths (Å)							
N_1-O_1	1.213	1.209	1.208	1.209	1.212	1.210	1.216
N_1-O_2	1.207	1.210	1.210	1.208	1.209	1.208	1.207
N_1-C_1	1.532	1.542	1.541	1.537	1.536	1.536	1.534
C_1-C_2	1.514	1.532	1.534	1.536	1.550	1.530	1.553
Angles (°)							
O_1-N_1-C_1	113.8	117.2	117.2	115.9	116.7	115.6	116.3
O_2-N_1-C_1	118.2	115.1	114.7	115.7	115.9	116.1	116.5
N_1-C_1-C_2	111.2	113.7	113.3	112.4	111.9	112.0	111.5
Dihedral angles (°)							
O_1-N_1-C_1-C_2	47.4	15.0	14.1	25.8	19.0	29.0	23.4

Table S11 – Main structural parameters of the radical issued from the C-N breaking (**Rad1**) in 1,1,1-trinitrobutane (**-H**) and its analogues by substitution on carbon 2 (**-CH_3**, **-Cl**, **-CN**, **-NH_2**, **-NO_2**, **-OH**).



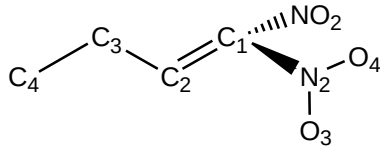
	-H	**-CH_3**	**-Cl**	**-CN**	**-NH_2**	**-NO_2**	**OH**
Bond lengths (Å)							
N_2-O_3	1.225	1.219	1.219	1.220	1.223	1.219	1.230
N_2-O_4	1.218	1.215	1.212	1.212	1.213	1.211	1.214
N_2-C_1	1.436	1.450	1.448	1.446	1.441	1.448	1.432
C_1-C_2	1.471	1.480	1.479	1.486	1.493	1.477	1.500
Angles (°)							
O_3-N_2-C_1	115.5	115.9	115.6	115.2	115.0	115.7	114.9
O_4-N_2-C_1	118.0	117.1	116.9	117.2	118.0	116.8	118.7
N_2-C_1-C_2	122.0	121.5	122.0	122.3	121.0	123.6	121.5
N_1-C_2-C_3	112.9	110.0	114.1	112.2	110.4	115.6	110.8
Dihedral angles (°)							
O_3-N_2-C_1-C_2	31.6	62.7	60.4	52.6	51.1	62.1	37.1
N_2-C_1-C_2-C_3	-99.7	-94.8	-73.4	-90.6	-104.1	-53.3	-100.3

Table S12 – Main structural parameters of the transition state issued from the HONO elimination mechanism (**TS2**) in 1,1,1-trinitrobutane (**-H**) and its analogues by substitution on carbon 2 (**-CH_3**, **-Cl**, **-CN**, **-NH_2**, **-NO_2**, **-OH**).



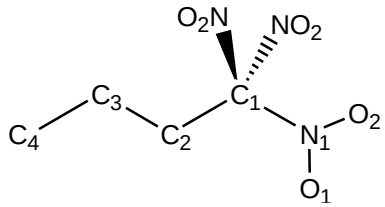
	-H	-CH_3	-Cl	-CN	-NH_2	-NO_2	OH
Bond lengths (Å)							
N_1-O_1	1.257	1.256	1.257	1.261	1.244	1.269	1.243
N_1-O_2	1.190	1.190	1.187	1.183	1.193	1.178	1.192
N_1-C_1	2.096	2.090	2.055	1.953	2.127	1.887	2.115
C_1-C_2	1.386	1.401	1.407	1.167	1.423	1.414	1.424
C_2-H_1	1.388	1.371	1.405	1.471	1.303	1.554	1.323
Angles (°)							
O_1-N_1-C_1	101.0	101.8	102.1	104.2	101.3	105.2	101.4
N_1-O_1-H_1	95.5	94.7	95.5	96.1	94.0	97.2	94.7
O_2-N_1-C_1	135.4	135.2	134.0	131.6	133.7	131.6	133.3
C_1-C_2-H_1	90.0	88.7	89.4	88.0	88.7	86.3	89.0
C_1-C_2-C_3	122.6	122.6	124.8	119.4	117.2	125.3	120.0
N_2-C_1-C_2	122.0	118.4	120.2	122.4	125.9	122.1	124.7
Dihedral angles (°)							
O_1-N_1-C_1-C_2	0.1	-1.6	-5.1	-1.4	-7.4	-7.5	-9.2
O_3-N_2-C_1-C_2	-10.4	76.4	76.5	-45.0	-22.0	-47.6	-17.6
N_1-C_1-C_2-C_3	107.5	110.3	117.0	104.7	112.0	120.8	115.1

Table S13 – Main structural parameters of the product issued from the HONO elimination mechanism (**Prod1**) in 1,1,1-trinitrobutane (**-H**) and its analogues by substitution on carbon 2 (**-CH_3**, **-Cl**, **-CN**, **-NH_2**, **-NO_2**, **-OH**).



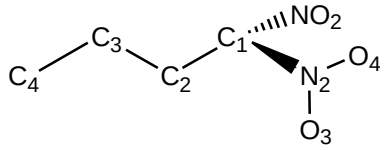
	-H	**-CH_3**	**-Cl**	**-CN**	**-NH_2**	**-NO_2**	**OH**
Bond lengths (Å)							
N_2-O_3	1.219	1.221	1.214	1.216	1.244	1.215	1.256
N_2-O_4	1.217	1.219	1.215	1.217	1.218	1.215	1.210
N_2-C_1	1.461	1.453	1.473	1.457	1.416	1.465	1.416
C_1-C_2	1.331	1.344	1.344	1.341	1.385	1.333	1.385
Angles (°)							
O_3-N_2-C_1	117.0	117.6	117.0	116.9	117.3	117.0	**116.5**
O_4-N_2-C_1	116.7	116.5	115.7	116.1	119.2	115.7	120.5
N_2-C_1-C_2	122.4	125.7	122.5	126.1	124.8	125.1	122.7
N_1-C_2-C_3	127.3	121.3	127.9	123.3	121.9	128.6	123.8
Dihedral angles (°)							
O_3-N_2-C_1-C_2	13.2	-27.7	-77.1	-12.2	7.5	-33.9	-5.4
N_2-C_1-C_2-C_3	178.1	-178.5	179.6	-177.4	-179.9	-179.3	-177.4

Table S14 – Main structural parameters of 1,1,1-trinitrobutane (**-H**) and its analogues by substitution on carbon 3 (**-CH_3**, **-Cl**, **-CN**, **-NH_2**, **-NO_2**, **-OH**).



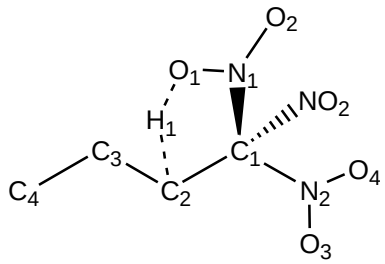
	-H	**-CH_3**	**-Cl**	**-CN**	**-NH_2**	**-NO_2**	**OH**
Bond lengths (Å)							
N_1-O_1	1.213	1.215	1.214	1.214	1.214	1.210	1.214
N_1-O_2	1.207	1.205	1.205	1.205	1.206	1.209	1.206
N_1-C_1	1.532	1.537	1.538	1.535	1.536	1.534	1.535
C_1-C_2	1.514	1.518	1.523	1.519	1.516	1.511	1.515
Angles (°)							
O_1-N_1-C_1	113.8	113.4	113.5	113.5	113.5	114.9	113.6
O_2-N_1-C_1	118.2	118.6	118.5	118.3	118.6	117.0	118.4
N_1-C_1-C_2	111.2	111.0	110.4	110.5	109.8	110.1	110.5
Dihedral angles (°)							
O_1-N_1-C_1-C_2	47.4	46.5	48.0	46.3	54.2	42.4	50.9

Table S15 – Main structural parameters of the radical issued from the C-N breaking (**Rad1**) in 1,1,1-trinitrobutane (**-H**) and its analogues by substitution on carbon 3 (**-CH_3**, **-Cl**, **-CN**, **-NH_2**, **-NO_2**, **-OH**).



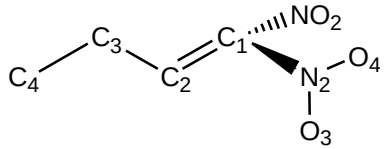
	-H	**-CH_3**	**-Cl**	**-CN**	**-NH_2**	**-NO_2**	**OH**
Bond lengths (Å)							
N_2-O_3	1.225	1.225	1.222	1.222	1.226	1.223	1.228
N_2-O_4	1.218	1.221	1.219	1.218	1.219	1.218	1.217
N_2-C_1	1.436	1.433	1.439	1.441	1.437	1.440	1.436
C_1-C_2	1.471	1.471	1.476	1.477	1.477	1.477	1.468
Angles (°)							
O_3-N_2-C_1	115.5	116.0	115.9	115.6	115.8	115.5	115.6
O_4-N_2-C_1	118.0	117.7	117.4	117.5	118.0	117.8	118.2
N_2-C_1-C_2	122.0	123.3	121.8	121.6	121.4	120.6	121.1
N_1-C_2-C_3	112.9	113.9	114.7	114.9	110.2	114.9	112.4
Dihedral angles (°)							
O_3-N_2-C_1-C_2	31.6	28.4	35.1	39.3	33.9	37.0	29.8
N_2-C_1-C_2-C_3	-99.7	-116.2	-133.7	114.9	-114.1	-126.8	-101.6

Table S16 – Main structural parameters of the transition state issued from the HONO elimination mechanism (**TS2**) in 1,1,1-trinitrobutane (**-H**) and its analogues by substitution on carbon 3 (**-CH_3**, **-Cl**, **-CN**, **-NH_2**, **-NO_2**, **-OH**).



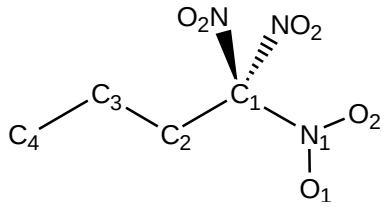
	-H	**-CH_3**	**-Cl**	**-CN**	**-NH_2**	**-NO_2**	**OH**
Bond lengths (Å)							
N_1-O_1	1.257	1.257	1.260	1.258	1.263	1.254	1.260
N_1-O_2	1.190	1.190	1.187	1.187	1.189	1.187	1.188
N_1-C_1	2.096	2.098	2.069	2.053	2.103	2.004	2.087
C_1-C_2	1.386	1.387	1.390	1.388	1.386	1.390	1.384
C_2-H_1	1.388	1.380	1.411	1.421	1.398	1.438	1.403
Angles (°)							
O_1-N_1-C_1	101.0	101.0	101.7	101.9	100.8	102.8	101.1
N_1-O_1-H_1	95.5	95.4	95.7	96.0	95.6	97.5	95.9
O_2-N_1-C_1	135.4	135.3	134.6	134.1	136.3	132.6	135.5
C_1-C_2-H_1	90.0	90.0	89.9	89.7	90.2	90.3	90.1
C_1-C_2-C_3	122.6	123.5	123.4	122.0	121.3	121.8	121.7
N_2-C_1-C_2	122.0	122.0	120.8	121.3	120.1	121.1	122.4
Dihedral angles (°)							
O_1-N_1-C_1-C_2	0.1	-0.8	1.3	0.1	0.1	-1.5	-2.9
O_3-N_2-C_1-C_2	-10.4	-8.9	-3.2	-7.8	-27.8	-9.7	-22.1
N_1-C_1-C_2-C_3	107.5	109.3	105.0	109.2	107.2	111.9	112.1

Table S17 – Main structural parameters of the product issued from the HONO elimination mechanism (**Prod1**) in 1,1,1-trinitrobutane (**-H**) and its analogues by substitution on carbon 3 (**-CH_3**, **-Cl**, **-CN**, **-NH_2**, **-NO_2**, **-OH**).



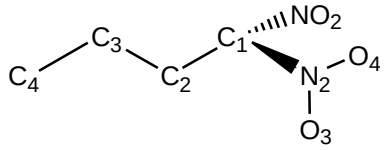
	-H	**-CH_3**	**-Cl**	**-CN**	**-NH_2**	**-NO_2**	**OH**
Bond lengths (Å)							
N_2-O_3	1.219	1.219	1.218	1.217	1.219	1.217	1.218
N_2-O_4	1.217	1.217	1.216	1.215	1.216	1.215	1.216
N_2-C_1	1.461	1.460	1.464	1.466	1.462	1.468	1.466
C_1-C_2	1.331	1.330	1.329	1.328	1.331	1.330	1.329
Angles (°)							
O_3-N_2-C_1	117.0	117.0	116.8	116.8	117.0	116.7	117.0
O_4-N_2-C_1	116.7	116.7	116.5	116.4	116.7	116.3	116.6
N_2-C_1-C_2	122.4	122.6	122.1	121.9	122.1	121.3	121.6
N_1-C_2-C_3	127.3	127.4	126.2	126.1	127.5	126.1	129.7
Dihedral angles (°)							
O_3-N_2-C_1-C_2	13.2	12.4	13.4	15.5	18.0	23.3	11.6
N_2-C_1-C_2-C_3	178.1	177.8	178.9	-180.0	177.8	174.3	178.7

Table S18 – Main structural parameters of 1,1,1-trinitrobutane (**-H**) and its analogues by substitution on carbon 4 (**-CH_3**, **-Cl**, **-CN**, **-NH_2**, **-NO_2**, **-OH**).



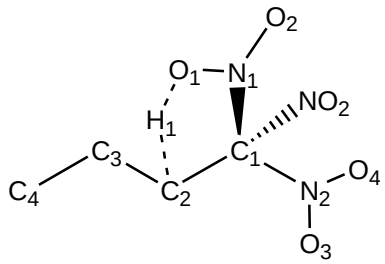
	-H	**-CH_3**	**-Cl**	**-CN**	**-NH_2**	**-NO_2**	**OH**
Bond lengths (Å)							
N_1-O_1	1.213	1.213	1.213	1.213	1.213	1.213	1.214
N_1-O_2	1.207	1.207	1.206	1.206	1.207	1.206	1.206
N_1-C_1	1.532	1.532	1.533	1.533	1.533	1.532	1.532
C_1-C_2	1.514	1.513	1.514	1.514	1.513	1.515	1.513
Angles (°)							
O_1-N_1-C_1	113.8	113.8	113.8	113.9	113.9	113.8	113.8
O_2-N_1-C_1	118.2	118.2	118.0	118.0	118.1	118.0	118.2
N_1-C_1-C_2	111.2	111.2	110.9	110.8	111.1	110.9	111.1
Dihedral angles (°)							
O_1-N_1-C_1-C_2	47.4	47.5	46.8	46.4	47.6	46.3	47.2

Table S19 – Main structural parameters of the radical issued from the C-N breaking (**Rad1**) in 1,1,1-trinitrobutane (**-H**) and its analogues by substitution on carbon 4 (**-CH_3**, **-Cl**, **-CN**, **-NH_2**, **-NO_2**, **-OH**).



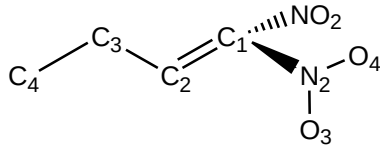
	-H	**-CH_3**	**-Cl**	**-CN**	**-NH_2**	**-NO_2**	**OH**
Bond lengths (Å)							
N_2-O_3	1.225	1.225	1.225	1.225	1.226	1.225	1.225
N_2-O_4	1.218	1.219	1.218	1.217	1.220	1.217	1.219
N_2-C_1	1.436	1.435	1.436	1.437	1.433	1.437	1.435
C_1-C_2	1.471	1.471	1.472	1.474	1.471	1.474	1.472
Angles (°)							
O_3-N_2-C_1	115.5	115.6	115.4	115.2	115.5	115.2	115.5
O_4-N_2-C_1	118.0	118.0	118.0	118.0	118.1	118.0	118.0
N_2-C_1-C_2	122.0	122.1	121.8	121.6	122.2	121.6	122.2
N_1-C_2-C_3	112.9	112.7	112.3	112.6	112.5	112.3	112.5
Dihedral angles (°)							
O_3-N_2-C_1-C_2	31.6	30.0	31.5	34.2	25.1	33.5	28.6
N_2-C_1-C_2-C_3	-99.7	-99.9	-100.0	-100.9	-95.7	-100.6	-100.9

Table S20– Main structural parameters of the transition state issued from the HONO elimination mechanism (**TS2**) in 1,1,1-trinitrobutane (**-H**) and its analogues by substitution on carbon 4 (**-CH_3**, **-Cl**, **-CN**, **-NH_2**, **-NO_2**, **-OH**).



	-H	-CH_3	-Cl	-CN	-NH_2	-NO_2	OH
Bond lengths (Å)							
N_1-O_1	1.257	1.257	1.259	1.260	1.258	1.261	1.258
N_1-O_2	1.190	1.190	1.188	1.187	1.189	1.187	1.189
N_1-C_1	2.096	2.095	2.081	2.077	2.092	2.077	2.090
C_1-C_2	1.386	1.386	1.387	1.387	1.386	1.387	1.386
C_2-H_1	1.388	1.387	1.405	1.410	1.391	1.411	1.394
Angles (°)							
O_1-N_1-C_1	101.0	101.0	101.3	101.3	101.1	101.4	101.1
N_1-O_1-H_1	95.5	95.5	95.6	95.5	95.5	95.5	95.5
O_2-N_1-C_1	135.4	135.3	135.1	135.0	135.3	135.0	135.3
C_1-C_2-H_1	90.0	90.0	89.6	89.6	89.9	89.5	89.8
C_1-C_2-C_3	122.6	122.6	122.1	122.0	122.3	121.9	122.3
N_2-C_1-C_2	122.0	121.9	121.6	121.5	121.8	121.5	121.7
Dihedral angles (°)							
O_1-N_1-C_1-C_2	0.1	0.1	0.3	0.5	0.2	0.3	0.2
O_3-N_2-C_1-C_2	-10.4	-10.5	-10.1	-9.7	-11.1	-9.6	-10.4
N_1-C_1-C_2-C_3	107.5	107.4	107.8	107.6	107.4	108.0	107.7

Table S21 – Main structural parameters of the product issued from the HONO elimination mechanism (**Prod1**) in 1,1,1-trinitrobutane (**-H**) and its analogues by substitution on carbon 4 (**-CH_3**, **-Cl**, **-CN**, **-NH_2**, **-NO_2**, **-OH**).



	-H	**-CH_3**	**-Cl**	**-CN**	**-NH_2**	**-NO_2**	**OH**
Bond lengths (Å)							
N_2-O_3	1.219	1.219	1.219	1.218	1.219	1.218	1.219
N_2-O_4	1.217	1.217	1.216	1.215	1.216	1.215	1.216
N_2-C_1	1.461	1.460	1.463	1.465	1.460	1.464	1.461
C_1-C_2	1.331	1.331	1.329	1.330	1.330	1.330	1.330
Angles (°)							
O_3-N_2-C_1	117.0	117.0	116.8	116.7	117.0	116.8	116.9
O_4-N_2-C_1	116.7	116.7	116.6	116.6	116.7	116.6	116.7
N_2-C_1-C_2	122.4	122.5	122.3	122.2	122.4	122.0	122.4
N_1-C_2-C_3	127.3	127.2	126.8	126.4	127.1	126.9	127.0
Dihedral angles (°)							
O_3-N_2-C_1-C_2	13.2	12.3	12.7	16.3	13.1	13.9	12.4
N_2-C_1-C_2-C_3	178.1	178.6	177.6	176.8	177.7	176.8	177.4

Annex S1 – XYZ structures for the stationary points and transition states along the decomposition mechanisms of 1,1,1-trinitrobutane

S0

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.52475504
H	1.02415246	0.00000000	-0.38294629
H	-0.50414379	-0.88649235	-0.39911471
H	-0.50538692	0.88505713	-0.40157551
C	-1.43576014	0.02502967	2.05586480
H	0.52202454	-0.88436612	1.89795609
H	0.54105396	0.88165590	1.88665989
C	-1.59196085	0.00262548	3.56121167
H	-1.93660905	0.93704488	1.71254404
H	-2.01132614	-0.82276852	1.67222332
N	-3.01200423	0.39905704	3.97800391
O	-3.88314177	-0.16955934	3.35335635
O	-3.14061811	1.20144798	4.86988517
N	-0.62657910	0.96962061	4.23130317
O	-0.69354243	2.10614016	3.81787591
O	0.13067367	0.52377434	5.06293360
N	-1.37869892	-1.37513507	4.19832788
O	-1.94049717	-1.56843182	5.25195919
O	-0.66358870	-2.14011204	3.59028282

Rad1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.52219789
H	1.02459248	0.00000000	-0.38318436
H	-0.50457368	-0.88655294	-0.39850421
H	-0.50590746	0.88555936	-0.39915616
C	-1.44294887	0.00093718	2.07729419
H	0.52125785	-0.88309934	1.90603793
H	0.52905443	0.88338545	1.89802175
C	-1.49125775	0.01921394	3.54766418
H	-1.97136586	0.88964879	1.71465721
H	-1.97021967	-0.89230165	1.72994414
N	-1.71703383	-1.17227578	4.31687439
O	-1.28529992	-2.20755743	3.82472654
O	-2.35404992	-1.07274763	5.35080559
N	-1.18654022	1.21098060	4.29274061
O	-1.49442701	2.26677274	3.75408349
O	-0.60782733	1.08557517	5.35899896

TS1 a

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.52431388
H	1.02315139	0.00000000	-0.38527021
H	-0.50718544	-0.88477381	-0.39887865
H	-0.50615421	0.88583760	-0.39808952
C	-1.42706110	0.02289785	2.07041204
H	0.53016982	-0.88678117	1.89223016
H	0.55235273	0.87163576	1.89192588
C	-1.54696835	-0.10846446	3.55505073
H	-1.95572060	0.93586490	1.78395962
H	-2.00131670	-0.81788334	1.66072006
N	-0.31117083	0.98547804	4.30685238
O	-1.44783837	1.59097521	4.22115946
O	0.61395864	1.50721459	4.82924368
N	-0.96081619	-1.47039207	4.06034861
O	-0.03213580	-1.49230581	4.82207937
O	-1.54720165	-2.41033651	3.56106812
N	-3.00933343	-0.20006153	4.06563612
O	-3.15146699	-0.61529130	5.19387205
O	-3.86282255	0.19766462	3.30685199

TS1 b

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H	1.02515322	0.00000000	-0.38045998
H	-0.50343352	-0.88672681	-0.39903194
H	-0.50461956	0.88505324	-0.40263616
C	-1.44111943	0.01734498	2.05055741
H	0.51823471	-0.88725763	1.90003965
H	0.54900699	0.87436159	1.89061973
C	-1.60173457	-0.09899684	3.53727228
H	-1.93325322	0.94901319	1.75065048
H	-2.01032757	-0.81210527	1.62180698
N	-3.10164190	0.83433568	4.06204474
O	-3.40593482	-0.35739160	3.66285212
O	-3.93330719	1.53897365	4.52251945
N	-0.54622079	0.81059657	4.26743996
O	-0.80693786	1.96693013	4.47102837
O	0.50586583	0.23469438	4.45379463
N	-1.36269787	-1.47658228	4.16103079
O	-1.46735515	-1.53496698	5.36486097
O	-1.14409470	-2.38308127	3.38784603

LM1 a

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C	0.00000000	0.00000000	1.52419970
H	1.02278900	0.00000000	-0.38757672
H	-0.50699883	-0.88528249	-0.39923944
H	-0.50681780	0.88538116	-0.39864570
C	-1.42543482	-0.00467962	2.07398027
H	0.53636963	-0.87754455	1.90004395
H	0.53180678	0.88515423	1.89086899
C	-1.49124988	-0.03490516	3.58855420
H	-1.97763948	0.87500305	1.72949237
H	-1.95944267	-0.89976203	1.73558368
N	-2.99565840	-0.10037341	4.00265270
O	-3.48317651	-1.20966253	3.98803293
O	-3.55653632	0.94602427	4.24171793
N	-0.98956271	1.30412211	4.21508855
O	-1.03027988	2.29476500	3.52098791
O	-0.57809720	1.23027810	5.35569801
N	-1.16147685	-1.31235414	5.61235090
O	-0.42193733	-2.06507885	6.04646313
O	-0.79827531	-1.06419898	4.10474185

LM1 b

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.52439704
H	1.02310401	0.00000000	-0.38640535
H	-0.50517270	-0.88689992	-0.39762605
H	-0.50748968	0.88398131	-0.40203323
C	-1.43000935	0.03178933	2.06299416
H	0.52043669	-0.88561643	1.89849345
H	0.55120284	0.87683450	1.88516692
C	-1.60845475	-0.02393306	3.57280458
H	-1.92642409	0.95923190	1.75787434
H	-2.01219706	-0.80059527	1.65371987
N	-2.94482172	0.72794435	5.44956614
O	-2.84772319	0.37645409	3.92159234
O	-4.04461425	0.85892323	5.72431603
N	-0.51568883	0.85365459	4.24305815
O	-0.73339091	2.04570165	4.22785723
O	0.47791263	0.29177512	4.64869144
N	-1.36241681	-1.44765469	4.15821377
O	-1.78777730	-1.63115022	5.28050331
O	-0.80853323	-2.25992334	3.45130621

Rad2 a

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.52562238
H	1.02443902	0.00000000	-0.38264774
H	-0.50621417	-0.88491367	-0.39980576
H	-0.50444274	0.88605030	-0.39997422
C	-1.42769651	0.00188733	2.05562614
H	0.53476986	-0.87776335	1.90275545
H	0.54208213	0.88037576	1.88982477
C	-1.51851403	0.05179725	3.60178264
H	-1.98747408	0.88287821	1.72012167
H	-1.97755555	-0.89219862	1.75267397
N	-3.02733011	0.19083636	4.05424515
O	-3.87088974	-0.21097671	3.28631706
O	-3.18425530	0.61719636	5.17522874
N	-0.86352039	1.41045112	4.06635246
O	-1.44328572	2.40829949	3.69179126
O	0.16014967	1.33339313	4.69699593
O	-0.98376216	-0.98167653	4.15057152

Rad2 b

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.52619416
H	1.02787129	0.00000000	-0.37465423
H	-0.50063238	-0.88805204	-0.39897770
H	-0.50266648	0.88505043	-0.40445003
C	-1.44081583	0.03647440	2.03468519
H	0.50849924	-0.89231264	1.90045255
H	0.55177021	0.87164874	1.89391834
C	-1.60969136	-0.13979682	3.56731135
H	-1.91867471	0.98875778	1.78527988
H	-2.03368501	-0.77223315	1.59823984
O	-2.80618292	0.20867181	3.91271160
N	-0.50985996	0.74129876	4.28099121
O	-0.80865400	1.89530347	4.46192572
O	0.54082453	0.18820873	4.51623592
N	-1.31343545	-1.60254368	4.03941948
O	-1.43902915	-1.77943590	5.23020766
O	-1.05936482	-2.43323049	3.19388917

TS2 a

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.52487595
H	1.02402159	0.00000000	-0.38293485
H	-0.50479203	-0.88668055	-0.39745945
H	-0.50570618	0.88427257	-0.40177408
C	-1.40709453	-0.06156803	2.09236252
H	0.56086454	-0.86909092	1.89391762
H	0.52024574	0.88976307	1.89627988
C	-1.69857467	0.28209751	3.40325667
H	-2.03898652	1.09135062	1.64886167
H	-2.07505404	-0.82900201	1.69558310
N	-2.85098939	-0.30175868	4.13035644
O	-2.93779173	-0.04869471	5.31315510
O	-3.63684531	-0.94388098	3.45797102
N	-2.67479018	2.10282959	3.05103256
O	-2.61535702	2.16861082	1.79686848
O	-3.18527284	2.93483951	3.73098190
N	-0.61563628	0.72756210	4.30943611
O	-0.24164442	1.87947486	4.23744444
O	-0.14362160	-0.15938646	4.99191761

TS2 b

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.52545036
H	1.02354705	0.00000000	-0.38419505
H	-0.50717647	-0.88615927	-0.39523739
H	-0.50482217	0.88636887	-0.39905656
C	-1.38488117	0.01888120	2.08293497
H	0.55024230	-0.86427126	1.91288538
H	0.55416660	0.88148102	1.89160042
C	-1.67008259	-0.03993951	3.46995539
H	-2.12101140	0.58493064	1.50896003
H	-3.12084518	-0.96224542	2.10565456
N	-3.13292728	0.00512664	3.64568478
O	-3.83106223	-0.68894454	2.75657173
O	-3.69494414	0.49469763	4.57483161
N	-1.20382303	1.27550097	4.44691336
O	-1.27489388	2.34240539	3.88131290
O	-0.79923529	1.04477080	5.56091965
N	-1.04057742	-1.20452522	4.25831484
O	-1.82134080	-1.94832243	4.82253111
O	0.16063280	-1.33170911	4.16598885

Prod 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.53090881
H	1.02726035	0.00000000	-0.37379948
H	-0.50355955	-0.88667767	-0.39570060
H	-0.50448401	0.88474827	-0.40118185
C	-1.38216951	0.06859636	2.07793456
H	0.54071587	-0.86385322	1.92550403
H	0.53253208	0.89044536	1.89396614
C	-1.93372450	-0.73897995	2.98044951
H	-2.04398575	0.84702889	1.70051065
N	-3.29556190	-0.54861553	3.47344615
O	-4.00405166	0.22682841	2.85448151
O	-3.60012092	-1.15047791	4.48581287
N	-1.24864928	-1.89310418	3.56490005
O	-0.21345994	-1.67396106	4.16973022
O	-1.74978355	-2.98020660	3.35438509

S0'

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.52362830
H	1.02955639	0.00000000	-0.36889673
H	-0.50083746	-0.88382766	-0.40770517
H	-0.48414148	0.89054231	-0.41156002
C	-1.35696172	-0.20252793	2.20684024
H	0.61741304	-0.83134091	1.88435206
H	0.47224606	0.91334202	1.89691655
C	-2.46513282	0.79957416	1.96181458
H	-1.78554524	-1.16747543	1.91305683
H	-1.22736067	-0.23197947	3.29295452
N	-3.70073808	0.47323295	2.83026963
O	-3.47261447	-0.01404467	3.91368014
O	-4.77791054	0.74765522	2.35414266
N	-2.99698348	0.78333346	0.52616164
O	-3.18920309	-0.32887933	0.08311130
O	-3.20177609	1.84285299	-0.01531884
N	-2.07359931	2.22910274	2.30467064
O	-2.69411152	2.78098000	3.18648034
O	-1.14108179	2.66944991	1.66948046

TS3

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.49174372
H	0.95969888	0.00000000	-0.51407075
H	-0.79114083	-0.52450486	-0.52360677
H	0.41227487	1.77495417	0.10408615
C	-0.94821632	0.96444958	2.31169104
H	-0.29808694	-1.00871307	1.81294003
H	1.01505509	0.17655198	1.85036612
C	-1.47759455	2.17801462	1.58488410
H	-1.83379401	0.42131716	2.65022857
H	-0.40699733	1.31097698	3.19345739
N	-2.53087727	2.94996670	2.38174243
O	-2.23258186	3.14644213	3.54416521
O	-3.53391651	3.29144794	1.80653344
N	-2.18029866	1.61211254	0.28949162
O	-2.98215012	0.70534916	0.46725627
O	-1.37903929	1.65221731	-0.67233068
N	-0.49342238	3.09200695	1.14218800
O	-0.79376846	4.22371180	0.77658330
O	0.65586433	2.52157102	0.79321339

Prod2

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.49636263
H	0.99350826	0.00000000	-0.45854639
H	-0.62008031	-0.74565259	-0.48996396
C	-1.36368121	0.12403881	2.19255004
H	0.47737434	-0.93897318	1.81235737
H	0.62722061	0.83108137	1.83908508
C	-2.64320833	0.26071145	1.39378852
H	-1.52904571	-0.75264081	2.83707212
H	-1.33832293	1.00454436	2.84186048
N	-3.84721419	0.07383632	2.27926370
O	-3.77302318	0.63955572	3.35544377
O	-4.78757498	-0.55973942	1.85314950
N	-2.81846967	-0.67826230	0.22467162
O	-2.62964173	-1.85335752	0.47354362
O	-2.99125639	-0.19203215	-0.87103481

Rad3 a

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.52419464
H	1.02300104	0.00000000	-0.38636491
H	-0.50549873	-0.88735348	-0.39580981
H	-0.50776242	0.88360488	-0.40209843
C	-1.43367067	0.02108255	2.06272118
H	0.52143079	-0.88639070	1.89627775
H	0.54681689	0.87770190	1.88835844
C	-1.55931796	-0.04872563	3.57079743
H	-1.92522553	0.95150254	1.75390495
H	-2.02108289	-0.80618974	1.65150516
N	-2.94304525	0.38667722	4.01574456
O	-3.86534156	-0.23198263	3.52776610
O	-3.00831162	1.31039778	4.79764878
N	-0.59482853	0.96805998	4.19131963
O	0.22819521	0.50205308	4.90723901
N	-1.35779987	-1.41706137	4.16554337
O	-1.72608420	-1.54900151	5.31514745
O	-0.77631374	-2.23791596	3.48470487

Rad3 b

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.52424445
H	1.02383412	0.00000000	-0.38442189
H	-0.50419061	-0.88640440	-0.39995886
H	-0.50566563	0.88512397	-0.40138813
C	-1.43253376	0.01846367	2.06394238
H	0.52363264	-0.88234921	1.90057554
H	0.53567479	0.88308914	1.88971233
C	-1.59083837	0.01980584	3.56880626
H	-1.94912477	0.91664038	1.70296254
H	-1.99719849	-0.84538792	1.69505334
N	-3.10232676	0.29856871	3.85832085
O	-3.33271114	1.31114171	4.41762116
N	-0.72569832	1.02513833	4.25420866
O	-0.78272257	2.13796000	3.76607318
O	-0.10422346	0.68890165	5.24196856
N	-1.37489476	-1.32112510	4.23063390
O	-2.04334194	-1.51619276	5.22648730
O	-0.58556662	-2.08742932	3.72077441

Rad4

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.48817710
C	1.41445322	0.00000000	2.09340145
H	0.08030572	0.92858717	-0.55714883
H	0.08011519	-0.92863384	-0.55706900
H	-0.53964708	-0.88010476	1.86108187
H	-0.53969617	0.88004924	1.86115081
H	1.97676762	-0.88382467	1.77537542
H	1.36904842	-0.00079871	3.18810569
H	1.97632929	0.88454127	1.77661184