Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Gas Phase RDX Decomposition Pathways using Coupled Cluster Theory

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Sections of Supporting Information

1.) NN Homolysis Pathway Sub Reactions

A major part of our study investigated the sub-reactions of the NN homolysis pathway. We began studying these reactions before the results of NN homolysis finished; obviously the conclusion of the NN homolysis barrier negates the value of these sub-reaction barriers. Nonetheless, as these are commonly studied reactions in the literature, we list the results here in the Supplementary Information. We are also open-minded that perhaps an explicitly multi-reference wavefunction methodology might overturn our results. As of today, no such method exists which can reliably capture both static and dynamic correlation consistently as well as CCSD(T), but that day may yet come. Many multi-reference coupled cluster methodologies are in development that even go so far as including perturbative triples (references).

We consider two possibilities: a CN bond scission or a second NN homolysis.

Double NN Homolysis: If one homolysis was good, two might be just fine. In Figure S1, we show the reaction path for a second homolytic nitramine cleavage. Obviously making a diradical structure is undesirable; a concomitant proton transfer allows the formation of a much more stable closed shell species.

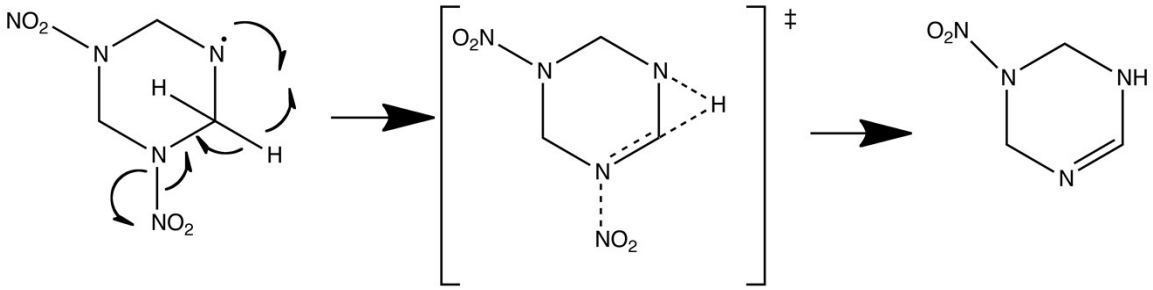

Figure S1: Second NN Homolysis with Concomitant Proton Transfer

Note that the product of the reaction in Figure S1 is similar to the HONO elimination product in making a nitrogenous heterocycloalkene. The barrier to this reaction is rather small; if NN homolysis were the first step at STP conditions, this reaction would be easy to accomplish. Table S1 shows how cheap the reaction is, as well as the usual trend of the MBPT underestimation, CCSD overestimation relative to CCSD(T).

Many-Body Method	AE
$\Delta E^{\neq}$ MBPT(2)	42.2
$\Delta E^{\neq}$CCSD	59.8
$\Delta E^{\neq}$ CCSD(T)	49.1
$\Delta H^{\neq}$ CCSD(T)	44.8
$\Delta G^{\neq}$ CCSD(T)	40.5

Table S1: Electronic Energies, Enthalpies, and Gibbs Energies of Double NN Homolysis, kcal/mol.

In particular, we isolated a transition state structure that is axial/equatorial in nature, and hence this is the only logical comparison.

NN Homolysis into CN Bond Scission: A subsequent CN bond scission results in a compound commonly known in the RDX literature as RDR-o, shown in Figure S2. This isomerization has a very low barrier, as shown in Table S2. The transition state formed is an axial-axial structure, and hence this is the relevant comparison. This provides a clear means of breaking the ringed structure and proceeding to exergonic reactions.

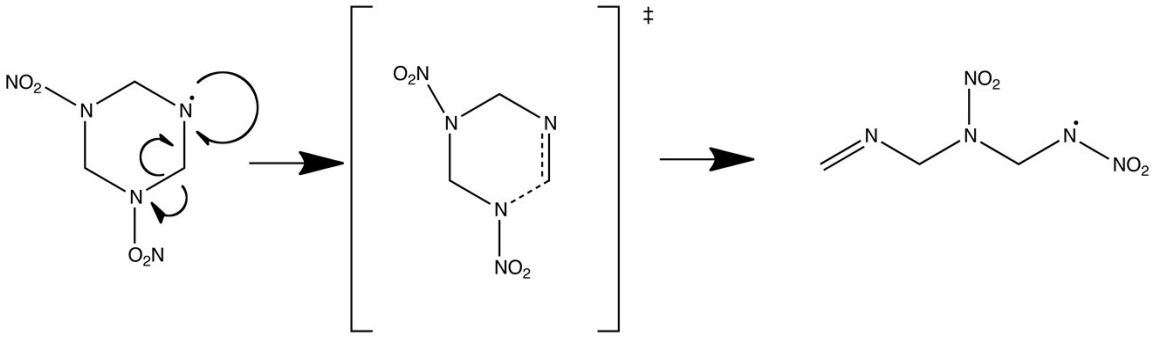

Figure S2: CN Bond Scission Following NN Homolysis

Many-Body Method	AA
$\Delta E^{\neq}$ MBPT(2)	38.2
$\Delta E^{\neq}$CCSD	30.6
$\Delta E^{\neq}$ CCSD(T)	26.5
$\Delta H^{\neq}$ CCSD(T)	24.0
$\Delta G^{\neq}$ CCSD(T)	24.4

Table S2: Electronic Energies, Enthalpies, and Gibbs Energies of Double NN Homolysis, kcal/mol.

2.) Reaction Energies

We list here the energies, enthalpies, and Gibbs energies for the various reactions in this paper. All units are in kcal/mol and are based on CCSD(T)/cc-pVTZ. We do not go through and list the MBPT(2) and CCSD values because none of the reactions have reactants or products which are significantly multi-reference, and thus one is reasonably confident that we need not check for convergence. Consequently, the CCSD(T)/cc-pVTZ value cuts to the chase. The MBPT(2) and CCSD values are available upon request. We list the reaction energies in the order that the occur in the paper.

NN Homolysis:
cc-pVTZ optimization

AAA Conformer
ΔE=48.4
ΔH=44.6
ΔG=31.3
AAE Conformer
ΔE=47.3
ΔH=43.0
ΔG=29.0

HONO Elimination
AAA Conformer
ΔE=-6.6
ΔH=-9.5
ΔG=-22.8
AAE Conformer
ΔE=-5.4
ΔH=-8.6
ΔG=-22.4
AEE Conformer
ΔE=-6.5
ΔH=-9.8
ΔG=-23.5
EEE Conformer
ΔE=-11.2
ΔH=-14.4
ΔG=-27.8

Triple Whammy
ΔE=55.8
ΔH=48.3
ΔG=18.8

HONO reaction followed by NN Homolysis
ΔE=39.9
ΔH=36.0
ΔG=23.4

HONO reaction followed by HONO Elimination
ΔE=-8.1
ΔH=-11.3
ΔG=-24.4

HONO reaction followed by HONO Elimination followed by HONO Elimination
ΔE=-26.8
ΔH=-29.6
ΔG=-41.8

TAZ Triple Whammy
ΔE=43.5
ΔH=35.1
ΔG=12.3

Double Whammy of Double HONO Elimination Product
ΔE=34.6
ΔH=26.7
ΔG=2.3

Simultaneous NN Homolysis with CN Bond Scission of Double HONO Elimination Product
ΔE=87.2
ΔH=84.5
ΔG=70.1

Simultaneous NN Homolysis with CN Bond Scission of Double HONO Elimination Product
ΔE=
ΔH=
ΔG=

Double NN Homolysis
AA Reaction
ΔE=-31.5
ΔH=-33.4
ΔG=-46.0
AE Reaction
ΔE=-29.3
ΔH=-30.9
ΔG=-43.3
EE Reaction
ΔE=-32.6
ΔH=-30.4
ΔG=-45.9

NN Homolysis into CN Bond Scission
AA
ΔE=
ΔH=
ΔG=
AE
ΔE=
ΔH=
ΔG=

EE
ΔE=
ΔH=
ΔG=

3.) Coordinates of All Structures

All coordinates are given in Å; all compounds are listed in the same order as in the paper.

RDX Conformers
AAA

C	6	-1.16295964	-0.79400080	1.22350859
N	7	0.10716238	-1.40463786	0.85183201
N	7	-1.27102659	0.60968523	0.84754198
H	1	-1.21279742	-0.82635579	2.31583821
H	1	-1.98872437	-1.35966289	0.80130596
C	6	1.26932473	-0.60782338	1.22421070
C	6	-0.10823470	1.40569255	1.21865358
N	7	-1.83587676	0.87750583	-0.43857850
N	7	0.15490138	-2.02494196	-0.43600374
N	7	1.16257744	0.79601652	0.84857657
O	8	-1.60617149	1.98022572	-0.90767827
O	8	-2.56169405	0.01098062	-0.89791944
O	8	1.26708631	-2.21518383	-0.90033261
O	8	-0.91557321	-2.38008550	-0.90155414
H	1	1.32323782	-0.63257121	2.31655519
H	1	2.17173935	-1.04100344	0.80218112
H	1	-0.18420429	2.40192388	0.79214366
H	1	-0.11366417	1.46950918	2.31074875
N	7	1.68170822	1.14774190	-0.43655957
O	8	1.28983846	2.20461162	-0.90371500
O	8	2.52926962	0.40047047	-0.89697593

AAE

C	6	-0.42965060	-1.02081260	-1.17434941
N	7	-0.41099075	-1.09307159	0.28106562
C	6	0.93855612	-1.02081403	0.82632065
N	7	1.54270848	0.21406670	0.40973655
C	6	1.49313198	0.44326638	-1.02111460
N	7	0.17768825	0.21406903	-1.58627093
N	7	-0.69354886	1.33561067	-1.54357151
O	8	-0.16342057	2.42189123	-1.66005607
O	8	-1.88310206	1.09752473	-1.46972800

N	7	1.18693383	1.33561009	1.20616476
O	8	1.48777527	2.42188700	0.75438334
O	8	0.68666802	1.09753034	2.28793514
N	7	-1.18558077	-2.12715093	0.81078644
O	8	-0.88436049	-2.51535139	1.92590848
O	8	-2.11552623	-2.51534467	0.12563181
H	1	0.16195724	-1.82767207	-1.61118877
H	1	-1.44446392	-1.07509703	-1.52816811
H	1	1.56022112	-1.82767418	0.43343369
H	1	0.90021977	-1.07509872	1.90036170
H	1	1.81213024	1.45005197	-1.23926803
H	1	2.16819487	-0.26878595	-1.48277476

AEE

C	6	0.88001330	0.71964661	1.22396750
N	7	-0.47236420	0.35176354	1.54148454
N	7	1.22622534	0.11923046	-0.05622963
H	1	0.91420889	1.80854940	1.17836899
H	1	1.55451781	0.35982412	1.98054444
C	6	-1.41783302	0.71304004	0.52136215
C	6	0.35219667	0.47380483	-1.15631812
N	7	2.58085163	0.20728212	-0.38255790
N	7	-0.59379535	-1.00993912	1.95146864
N	7	-0.98572127	0.11289981	-0.73257891
O	8	2.86398511	0.12124610	-1.56419752
O	8	3.35426069	0.32310896	0.55168612
O	8	-1.68984462	-1.51276578	1.81718446
O	8	0.39257332	-1.50672342	2.45393318
H	1	-1.42643172	1.80182054	0.46270692
H	1	-2.39820044	0.34843327	0.77191911
H	1	0.61961348	-0.10213756	-2.02550387
H	1	0.42096960	1.54360707	-1.39124212
N	7	-1.92664827	0.19429510	-1.76081306
O	8	-1.50008341	0.10863559	-2.89859383
O	8	-3.09087573	0.30454892	-1.41903832

EEE

C	6	1.32329211	0.50222228	0.24904018
N	7	0.21155379	1.31195836	-0.19842602
N	7	1.03129110	-0.83911171	-0.20634193
H	1	1.43411850	0.54044327	1.33985055
H	1	2.22816680	0.84877242	-0.21863143
C	6	-1.09560159	0.89133859	0.25574898
C	6	-0.22311653	-1.39802321	0.24740941

N	7	2.10883188	-1.71617140	-0.04589866
N	7	0.43238660	2.68263538	-0.02942305
N	7	-1.24146538	-0.47353902	-0.19996979
O	8	1.83950367	-2.90327917	-0.00493537
O	8	3.21645621	-1.21138229	-0.00346659
O	8	-0.55871434	3.38892662	0.01854819
O	8	1.59507628	3.04296895	0.01266030
H	1	-1.18299336	0.96151686	1.34709985
H	1	-1.84864860	1.50456242	-0.20738779
H	1	-0.37819012	-2.35395514	-0.22137649
H	1	-0.23894501	-1.51542389	1.33808696
N	7	-2.53880702	-0.96849306	-0.03261272
O	8	-2.65528777	-2.18019725	0.00808032
O	8	-3.43187332	-0.14171742	0.01546727

Boat

C	6	0.37468575	-0.17977823	-1.14072348
N	7	0.23973259	1.04481756	-0.36872309
N	7	0.34434802	-1.33868218	-0.27708769
H	1	-0.46537387	-0.28815167	-1.81929847
H	1	1.29260745	-0.12908512	-1.70761439
C	6	-0.45465973	0.87503051	0.90691117
C	6	-0.91830086	-1.46264174	0.43666585
N	7	1.48484771	-1.45274469	0.54210759
N	7	1.36987993	1.85111467	-0.29743090
N	7	-1.45751639	-0.14042232	0.71951225
O	8	1.40902327	-2.22122462	1.48328536
O	8	2.46045471	-0.80912868	0.19536700
O	8	1.47780044	2.51118523	0.72521726
O	8	2.09821071	1.87094569	-1.27061014
H	1	-0.90563077	1.80478504	1.21288854
H	1	0.21613017	0.52877206	1.69145623
H	1	-0.73274221	-1.99854541	1.35708680
H	1	-1.63829805	-1.99694089	-0.16639291
N	7	-2.52817791	0.26865578	-0.10651687
O	8	-3.19646273	-0.61429075	-0.61386027
O	8	-2.71938785	1.46687484	-0.18141598

Cope

C	6	0.01617568	-1.68950754	0.66822138
C	6	-0.32686644	0.18278015	-0.95680343
C	6	1.78441325	1.21219098	0.06225913
H	1	0.20803619	-2.52819484	-0.00165220
H	1	0.32766867	-0.35298022	-1.63775178

H	1	2.31375333	2.10664537	-0.23162215
H	1	-0.42473242	-2.04612987	1.58612662
H	1	1.79031623	1.12767301	1.14236456
N	7	2.46474475	0.11424715	-0.58182509
N	7	2.12820341	-1.03213530	-0.17521223
O	8	1.21596640	-1.05338177	1.01393404
N	7	-0.85974766	-0.68998675	0.07242240
N	7	0.41211255	1.30089739	-0.44551983
N	7	-2.16897044	-1.12587122	-0.10771964
O	8	-2.89164441	-0.47589455	-0.83882786
O	8	-2.47874148	-2.12485362	0.52607130
O	8	2.44975225	-2.10846822	-0.58168058
N	7	-0.34321172	2.25569370	0.21179340
O	8	0.28697129	3.05184923	0.89300492
O	8	-1.54785853	2.23284038	0.02968684
H	1	-1.17728285	0.55920330	-1.50554441

NONO

H	1	1.48060762	-1.68007696	0.70828861
C	6	0.78212530	-0.95417860	1.08256806
H	1	0.89419435	-0.84079158	2.16067553
C	6	0.10494744	1.30498009	0.98009135
H	1	0.29829468	2.26254538	0.53163956
H	1	0.23578530	1.36041284	2.06071548
N	7	0.98421957	0.30866210	0.39319738
O	8	2.29833909	0.71577880	0.67030131
N	7	2.97957155	0.85077456	-0.70608660
O	8	4.07166750	1.18415178	-0.56409035
N	7	-0.56405220	-1.39370375	0.84665740
N	7	-1.25603448	0.91306306	0.74710620
C	6	-1.56305534	-0.41673730	1.22163182
H	1	-1.56632957	-0.37307208	2.30176725
H	1	-2.52635759	-0.72154720	0.85381913
N	7	-1.74724125	1.22663704	-0.53726519
N	7	-0.76594877	-2.01876665	-0.40145614
O	8	-1.13971741	2.07701441	-1.15862554
O	8	-2.77853357	0.67413350	-0.86606101
O	8	-1.91978457	-2.12380717	-0.76881067
O	8	0.22235425	-2.46366231	-0.95194553

RDR
AA

C	6	1.19188339	1.62317137	0.04331203
N	7	0.00016727	2.02468601	-0.64027111

N	7	1.19497177	0.29216867	0.61174414
H	1	1.31453216	2.31708076	0.87696907
H	1	2.04225302	1.72122414	-0.60702926
C	6	-1.19166661	1.62328643	0.04317190
C	6	-0.00002032	-0.03665085	1.34707068
N	7	1.69112898	-0.72702052	-0.22013088
N	7	-1.19493315	0.29231875	0.61167512
O	8	1.47631855	-1.86742881	0.14342459
O	8	2.35220017	-0.37919080	-1.18138245
H	1	-1.31430825	2.31722501	0.87679984
H	1	-2.04194371	1.72140455	-0.60729311
H	1	-0.00008881	-1.08241252	1.59572575
H	1	0.00001528	0.56261198	2.24704336
N	7	-1.69121468	-0.72683518	-0.22012474
O	8	-1.47661093	-1.86724041	0.14354654
O	8	-2.35220075	-0.37896730	-1.18142970

AE

C	6	0.74741509	1.52327876	-0.40160183
N	7	0.86359346	0.09288649	-0.08536494
C	6	0.06379346	-0.37111579	1.04096294
N	7	-1.31006185	-0.03147087	0.76495248
C	6	-1.49677100	1.39872346	0.55615059
N	7	-0.57819361	2.05352200	-0.33220989
N	7	-1.87832222	-0.84257073	-0.25994960
O	8	-2.82319079	-0.36794173	-0.86875445
O	8	-1.41185314	-1.96218788	-0.38274865
N	7	2.17648369	-0.37081232	-0.09506899
O	8	2.40835331	-1.39033440	0.54194124
O	8	2.97195264	0.26817637	-0.77302593
H	1	1.36196602	2.11973350	0.29254367
H	1	1.14380532	1.68891621	-1.39820487
H	1	0.33779188	0.13321934	1.97252767
H	1	0.18311938	-1.43851783	1.15075226
H	1	-2.51020360	1.57285735	0.21567088
H	1	-1.38485802	1.87334507	1.53819643

EE

C	6	0.90559875	0.70544127	1.20984165
N	7	-0.47352230	0.67478164	1.54222460
N	7	1.22295656	0.13537497	-0.09466203
H	1	1.22398142	1.75643078	1.25737531
H	1	1.46296083	0.17074798	1.96615902
C	6	-1.43106605	0.69874517	0.49535362

C	6	0.35783558	0.53832381	-1.17539760
N	7	2.57390438	0.19253336	-0.41219759
N	7	-0.96160624	0.12908046	-0.76262305
O	8	2.86832072	0.13419803	-1.59411413
O	8	3.34496051	0.25879874	0.53171338
H	1	-1.72709150	1.74797411	0.35500210
H	1	-2.31327845	0.15993255	0.81149723
H	1	0.63373220	0.01170556	-2.07274797
H	1	0.40947016	1.62006170	-1.35445711
N	7	-1.90423936	0.17962202	-1.78148055
O	8	-1.48698601	0.12157265	-2.92583101
O	8	-3.07168152	0.24030299	-1.43034954

Twist

C	6	-0.25445194	-1.25546162	0.13797648
N	7	0.93283628	-0.42353061	0.11946910
N	7	-1.43377156	-0.44474179	0.32311866
H	1	-0.38045745	-1.74731227	-0.82014253
H	1	-0.14509350	-1.99409971	0.91702203
C	6	0.73367951	0.98299800	-0.24137230
C	6	-1.56629065	0.51482933	-0.76229391
N	7	-1.50882550	0.12952994	1.60630667
N	7	1.80668546	-0.60678011	1.18706263
N	7	-0.35271932	1.16448599	-1.15473204
O	8	-2.26538887	1.07454390	1.74043195
O	8	-0.84749957	-0.40922614	2.47793797
O	8	2.47066198	0.36913420	1.50566861
O	8	1.87763488	-1.72857222	1.65665278
H	1	1.64587134	1.36469723	-0.67723728
H	1	0.52460212	1.58137765	0.65431766
H	1	-2.29097890	1.26915571	-0.47070601
H	1	-1.96844904	-0.01087422	-1.62432606

Transition state of NN Homolysis

C	6	0.14711186	-1.49836794	1.14314592
N	7	-0.78330083	-0.55990558	0.60538081
C	6	-0.63460018	0.65752251	1.34230488
N	7	0.65430135	1.23826036	0.97096517
C	6	1.74954142	0.32102729	1.21466632
N	7	1.48953997	-1.03617730	0.78522269
N	7	1.87826716	-1.33304574	-0.53635853
O	8	2.83428693	-0.71576510	-0.96906958
O	8	1.28383359	-2.23826796	-1.09105376
N	7	0.65313032	1.84225481	-0.30142745

O	8	1.73880197	2.00602222	-0.82638859
O	8	-0.42512248	2.22342429	-0.72160537
N	7	-3.33391736	-0.35935325	-0.13878616
O	8	-3.26216686	0.76945034	-0.48761311
O	8	-3.77538150	-1.39926730	-0.49257400
H	1	0.15286153	-1.54513489	2.23597907
H	1	0.00894458	-2.48381213	0.73117941
H	1	-0.57346486	0.51920875	2.42504957
H	1	-1.40882765	1.36991920	1.10505516
H	1	2.64110834	0.68495189	0.73532366
H	1	1.88338060	0.28773229	2.28683092

Transition State of HONO Elimination

C	6	-0.36234027	-1.20642769	1.04063193
N	7	0.87766756	-0.83523771	1.39522598
C	6	1.18336079	0.57292224	1.54547701
N	7	0.28379529	1.48790063	0.84095866
C	6	-1.10424268	1.14691825	1.10294758
N	7	-1.38182894	-0.23529985	0.77252509
N	7	1.80240525	-1.21609875	-0.26811327
N	7	0.57202370	1.59782854	-0.54535734
N	7	-2.20144257	-0.48437557	-0.34001975
O	8	0.97641809	-1.87396213	-0.94785563
O	8	2.96958660	-1.10326186	-0.51762429
O	8	1.75400141	1.61299461	-0.85218767
O	8	-0.38496191	1.72245825	-1.29680703
O	8	-3.02615308	0.36795121	-0.61939156
O	8	-2.05235114	-1.57866398	-0.87339976
H	1	0.02586320	-1.70886763	-0.16655428
H	1	-0.72794527	-2.13511634	1.47220143
H	1	1.09277670	0.81573605	2.60487513
H	1	2.20286700	0.76381554	1.22907925
H	1	-1.24888337	1.29502431	2.17148867
H	1	-1.78057253	1.78000243	0.54330523

Product of HONO Elimination

C	6	1.13898746	1.49227684	0.00715182
C	6	-1.19577132	1.52997615	0.16856922
C	6	-0.01506676	-0.62312783	0.36496404
H	1	2.10777037	1.95617615	-0.05880426
H	1	-1.62053034	1.64403218	1.16717004
H	1	-1.85616971	2.02074647	-0.53233037
H	1	-0.08083121	-0.67992813	1.45433998
H	1	0.00899419	-1.61757452	-0.04863453

N	7	0.08144463	2.18202358	0.13207747
N	7	1.15861628	0.10522553	-0.04529824
N	7	-1.11311338	0.11947590	-0.20812103
N	7	2.37421381	-0.56781478	-0.02444210
O	8	3.36199198	0.08101215	-0.31089184
O	8	2.31767604	-1.75050195	0.26316629
N	7	-2.32339724	-0.55684545	-0.15481854
O	8	-2.27535525	-1.77128840	-0.04367875
O	8	-3.32558544	0.13024270	-0.26214833

Triple Whammy TS

C	6	0.66883605	-1.51130183	1.41433790
N	7	1.58193765	0.26784290	0.97972823
C	6	0.97483724	1.33787852	1.41224276
N	7	-1.02287228	1.23951024	0.97717615
C	6	-1.64616680	0.18028890	1.41299298
N	7	-0.56130708	-1.50263328	0.98133236
N	7	2.02256654	0.39988096	-0.38963564
N	7	-1.35631145	1.54926550	-0.39384754
N	7	-0.66633594	-1.95026984	-0.38800066
O	8	1.86199207	-0.60189398	-1.06801109
O	8	2.55406433	1.44329646	-0.71638751
O	8	-0.40685292	1.90422921	-1.07410227
O	8	-2.52584847	1.48944323	-0.72046536
O	8	-1.45557886	-1.31221840	-1.06611730
O	8	-0.02606459	-2.93051590	-0.71545271
H	1	1.42664354	-2.07310209	0.88630241
H	1	0.80479637	-1.31726084	2.46946456
H	1	0.73826923	1.35903063	2.46724016
H	1	1.08310384	2.27481334	0.88391833
H	1	-1.54588214	-0.03227993	2.46852849
H	1	-2.51122750	-0.19672968	0.88556446

Product of Triple Whammy

C	6	-1.71081465	-0.00828818	0.38642361
H	1	-2.72376781	-0.36568194	0.26553016
H	1	-1.48817130	0.78194617	1.09616992
N	7	-0.82243942	-0.55295747	-0.34666916
N	7	0.50104313	0.00288573	-0.06572016
O	8	0.60768071	1.21454427	0.00460036
O	8	1.37276072	-0.83768344	0.02169711

NONO Isomerization TS

C	6	-0.84828197	-1.21642926	1.28103843
N	7	0.55552357	-1.33668085	1.00969911
C	6	1.31038714	-0.13716931	1.29188394
N	7	0.85587992	-2.12112419	-0.54508143
O	8	1.93710580	-2.44487443	-0.88629062
O	8	0.44605914	-0.82199369	-0.89090467
H	1	-1.37489564	-2.04270271	0.83496619
H	1	-0.92265458	-1.28421289	2.36507278
H	1	2.29066329	-0.20597728	0.84755966
H	1	1.40925781	-0.15334428	2.37706873
N	7	0.69579976	1.09351167	0.90980915
N	7	-1.46351766	0.01436471	0.87243961
C	6	-0.71130547	1.19829836	1.20264148
H	1	-0.80702866	1.33907706	2.27160667
H	1	-1.12022820	2.04383358	0.67830765
N	7	1.18405110	1.72376309	-0.24660956
N	7	-2.08283055	-0.00844421	-0.39337439
O	8	2.32459786	1.44984125	-0.56240252
O	8	0.44729703	2.53231358	-0.77338459
O	8	-2.51289217	-1.08386480	-0.75836359
O	8	-2.19880824	1.05978472	-0.95869006

NONO Cleavage TS

C	6	-1.25846772	-0.12186692	-1.41931196
C	6	0.91751132	-0.88008244	-0.66806586
C	6	0.39770312	1.42744080	-0.64028002
H	1	1.39603071	-1.69569332	-0.16272298
H	1	-0.96641308	-0.04285959	-2.45700059
H	1	-2.30401088	-0.35886954	-1.34088843
H	1	0.53987178	2.35000218	-0.10695563
H	1	0.83539812	1.49525309	-1.63576023
H	1	1.34669955	-0.74925447	-1.66194869
N	7	-0.47313187	-1.18208450	-0.83553925
N	7	-0.99731834	1.16015536	-0.80816512
N	7	1.00583720	0.34320354	0.12521708
N	7	-1.06784136	-1.85489025	0.25424971
N	7	-1.79997034	1.47632990	0.31079938
O	8	2.36120030	0.79899450	0.25966768
N	7	3.31776798	-0.26486999	0.07308288
O	8	4.39426197	0.13526232	0.29330409
O	8	-2.28217867	-1.89000758	0.26095840
O	8	-0.31243486	-2.39833835	1.03571425
O	8	-2.91289835	0.98951826	0.32395934
O	8	-1.33109746	2.26446916	1.10759514

2-Nitramine Propane

C	6	1.32065371	-1.26705448	0.04582275
H	1	0.92199761	-2.01237490	-0.63753946
H	1	2.37653891	-1.11824775	-0.16516103
H	1	1.20545156	-1.64156819	1.06646835
N	7	0.65479708	-0.00001840	-0.14830508
N	7	-0.70599243	-0.00003941	-0.02002159
C	6	1.32045522	1.26710553	0.04589523
H	1	2.37642752	1.11838225	-0.16469326
H	1	0.92195819	2.01231210	-0.63769680
H	1	1.20484409	1.64172483	1.06645283
O	8	-1.25201137	1.08283546	0.02260358
O	8	-1.25216743	-1.08283754	0.02269292

2-Nitramine Propane HONO Elimination TS

C	6	-1.36782357	-1.12326593	0.08479736
N	7	-1.02230851	0.11341334	0.47861349
C	6	-1.44285753	1.22078016	-0.34501768
N	7	0.85727528	0.06641497	-0.00289166
O	8	1.08522335	-1.13757346	-0.27774092
O	8	1.69443066	0.90727302	0.16865527
H	1	-0.10218683	-1.49573574	-0.22279406
H	1	-1.58043686	-1.82761453	0.88757077
H	1	-2.41873335	1.54095542	0.02731703
H	1	-0.75348809	2.05610333	-0.23300838
H	1	-1.55032443	0.96272142	-1.40594255
H	1	-1.95061701	-1.24107783	-0.83331992

2-Nitramine Propane NN Homolysis TS

C	6	-1.43291495	-1.20203190	-0.16036369
N	7	-0.97831755	0.00000825	0.47145775
C	6	-1.43290872	1.20203510	-0.16039513
N	7	0.92054718	-0.00000148	0.03038669
O	8	1.39769564	-1.08099936	-0.04257673
O	8	1.39771110	1.08099064	-0.04254468
H	1	-2.44144828	-1.40725883	0.21404012
H	1	-0.80330972	-2.03825315	0.14160509
H	1	-2.44142654	1.40729817	0.21402830
H	1	-0.80327771	2.03825385	0.14152855
H	1	-1.47506376	1.14692347	-1.25693584
H	1	-1.47504198	-1.14695753	-1.25690817

HONO Elimination to NN Homolysis Transition State

C	6	-0.01463842	-0.48644110	0.63999762
C	6	-0.13549271	1.43243977	-0.64691700
C	6	1.59383822	1.25100862	0.91036878
H	1	-0.12687611	-1.54927281	0.50321163
H	1	-0.48819009	-0.21033625	1.58117422
H	1	-0.61724587	2.01301567	-1.42072934
H	1	2.64927128	1.45610596	0.84110738
H	1	1.25889485	1.53452235	1.90674298
N	7	0.88593750	2.04491528	-0.05360535
N	7	1.39057633	-0.17984059	0.79958181
N	7	-0.62121624	0.22234414	-0.45979488
N	7	2.19295866	-0.78661465	-0.18190344
N	7	-3.17414820	-0.12358969	0.08070506
O	8	-3.76486184	0.16648886	-0.89838865
O	8	1.79286676	-1.84253863	-0.64041465
O	8	3.25743318	-0.24835099	-0.43387090
O	8	-3.12732778	-0.95889923	0.91796821

Product of HONO Elimination to NN Homolysis

C	6	-0.53476070	1.18510923	0.75175835
C	6	-1.79972433	-0.00000013	-0.80444053
C	6	-0.53476131	-1.18511079	0.75175692
H	1	-1.07949419	1.26813926	1.68818063
H	1	0.09845238	2.05015339	0.65280040
H	1	-2.46395000	0.00000068	-1.65071315
H	1	-1.07949671	-1.26814030	1.68817812
H	1	0.09845159	-2.05015519	0.65280032
N	7	-1.48345443	-1.17372455	-0.32063223
N	7	-1.48345630	1.17372391	-0.32062853
N	7	0.28528076	-0.00000103	0.83547586
N	7	1.35565028	0.00000058	-0.08126874
O	8	1.79617568	1.08714452	-0.40717633
O	8	1.79618046	-1.08714216	-0.40717389

Double HONO Elimination TS

C	6	0.78873544	1.45205160	-0.39731888
N	7	-0.23477693	2.17369023	-0.12125017
C	6	-1.27680537	1.52433214	0.60029769
N	7	-1.16761405	0.31408626	1.17929001
C	6	0.14060444	-0.29276404	1.20012237
N	7	0.92361487	0.13270834	0.03364416
N	7	-1.93558435	-0.76797833	-0.24885196

N	7	2.14555911	-0.50571592	-0.17919351
O	8	-2.52666927	0.05631682	-0.98851197
O	8	-2.01221120	-1.96206291	-0.35633451
O	8	2.37575657	-1.46015293	0.55234008
O	8	2.84463481	-0.07699521	-1.08513369
H	1	1.61266947	1.83119912	-0.98503531
H	1	-1.99588716	2.19912108	1.05460273
H	1	-2.09145438	1.05350397	-0.38030339
H	1	0.64178229	0.00964082	2.12536126
H	1	0.05622819	-1.37428843	1.18474250

Product of Double HONO Elimination

C	6	-2.51457588	-0.40668806	0.14985405
N	7	-1.41899864	-0.62317971	0.76431679
C	6	-0.85761804	0.45128897	1.53889570
C	6	-2.66458954	1.80347321	0.57541311
N	7	-3.27306479	0.77423960	0.11759636
H	1	0.21490994	0.47939590	1.40110472
H	1	-3.10524454	2.78553538	0.55476583
N	7	-1.40455628	1.73574869	1.11062811
N	7	-0.80290990	2.89305091	1.58714534
O	8	-1.28651699	3.95455047	1.24206066
O	8	0.16860243	2.71179532	2.30148055
H	1	-2.93892296	-1.21648388	-0.42029686
H	1	-1.05705918	0.28604502	2.59788516

Triple HONO Elimination TS

C	6.0	0.7168356571	1.2859248633	0.4609453559
N	7.0	1.7164890303	1.1882253039	-0.3919624274
C	6.0	2.0266700601	-0.0954734304	-0.7515026478
N	7.0	1.5721837486	-1.1991482943	-0.2090244960
C	6.0	0.5880278180	-0.9990197724	0.7576928336
N	7.0	0.0497751259	0.2554268913	1.0396458643
N	7.0	-1.5712306971	0.0430953970	-0.1471585589
O	8.0	-1.6630569917	-1.1831501936	-0.3163742662
O	8.0	-2.3876164372	0.8691640984	-0.4585206453
H	1.0	0.3939312507	2.2815768670	0.7427174541
H	1.0	2.7700448864	-0.1964548897	-1.5320739981
H	1.0	-0.4532983135	-1.4863942814	0.2290477660
H	1.0	0.6432369916	-1.6732025057	1.6120185884

Product of Triple HONO Elimination TS

C	6	-5.09598590	0.32831342	-0.00000487

N	7	-3.76587142	0.34011836	-0.00000810
C	6	-3.23234159	1.55851654	-0.00000937
C	6	-5.22961163	2.55737463	-0.00000693
N	7	-5.88441915	1.39962943	-0.00000370
H	1	-2.15685212	1.62280702	-0.00001127
H	1	-5.57790461	-0.63530824	-0.00000265
H	1	-5.82331146	3.45644720	-0.00000624
N	7	-3.90768225	2.70438912	-0.00000995

Triple Whammy of TAZ TS

C	6.0	0.1327926085	1.5277091689	-0.0000409843
N	7.0	1.5625368641	0.2792621705	-0.0010457899
C	6.0	1.2566101254	-0.8788457260	-0.0002793789
N	7.0	-0.5394337311	-1.4928214633	0.0013254400
C	6.0	-1.3894524562	-0.6488195895	0.0002766654
N	7.0	-1.0231219997	1.2135909580	-0.0003200483
H	1.0	0.7449071982	2.4059066353	0.0006149265
H	1.0	1.7111285575	-1.8480172112	0.0000372348
H	1.0	-2.4560563962	-0.5578148644	-0.0006890795

Products of Triple Whammy of TAZ

C	6	-1.71081465	-0.00828818	0.38642361
H	1	-2.72376781	-0.36568194	0.26553016
H	1	-1.48817130	0.78194617	1.09616992
N	7	-0.82243942	-0.55295747	-0.34666916
N	7	0.50104313	0.00288573	-0.06572016
O	8	0.60768071	1.21454427	0.00460036
O	8	1.37276072	-0.83768344	0.02169711

Double Whammy of Double HONO Elimination Product TS

C	6	-0.68941918	1.59638356	0.30812463
N	7	-1.74783246	1.41042844	-0.18736930
C	6	-2.13506136	-0.47864572	-0.60133729
N	7	-1.43031592	-1.29854592	-0.12549604
C	6	-0.20058080	-1.34950844	0.81633904
N	7	0.46110754	-0.12862617	0.91158646
N	7	1.34697766	0.03076322	-0.13754535
O	8	1.40852295	-0.80626122	-1.04823209
O	8	2.02196038	1.06412334	-0.09499502
H	1	0.16821845	2.16064034	0.61824474
H	1	-2.97896883	-0.29117089	-1.23032243
H	1	-0.64970692	-1.60088947	1.77248117
H	1	0.38830810	-2.16561478	0.41097750

Product of Aforementioned

2HCN molecules and what is called MN in the literature:

C	6	-1.71081465	-0.00828818	0.38642361
H	1	-2.72376781	-0.36568194	0.26553016
H	1	-1.48817130	0.78194617	1.09616992
N	7	-0.82243942	-0.55295747	-0.34666916
N	7	0.50104313	0.00288573	-0.06572016
O	8	0.60768071	1.21454427	0.00460036
O	8	1.37276072	-0.83768344	0.02169711

HONO Elimination into Simultaneous CN Bond Scission AND NN Homolysis TS

C	6	-2.62972527	-0.17189278	-0.41797322
C	6	-0.97889292	1.25845797	0.18976208
C	6	-0.70760371	-1.00509290	0.50252239
H	1	-3.59929289	-0.31368340	-0.87429937
H	1	0.07427319	-1.69991704	0.18815261
H	1	-0.93825255	-1.27177919	1.54044955
H	1	-0.62813823	2.28043586	0.14773863
N	7	-0.15405028	0.33518639	0.48700157
N	7	-2.33511106	1.08742690	-0.06057196
N	7	-1.88222342	-1.24444343	-0.27997107
N	7	2.29481686	0.01965928	-0.20575273
O	8	2.38824136	-1.15336086	-0.03625416
O	8	2.98873414	0.98236426	-0.18077217

Product of Aforementioned

H	1	-2.09766206	1.82293174	-0.34966180
C	6	-1.49866332	1.07738176	0.14628000
H	1	-0.99531412	1.34844649	1.06454521
N	7	-1.42364122	-0.07524635	-0.36651117
C	6	-0.61489704	-1.03828516	0.20069804
H	1	-1.14412224	-1.88323429	0.61280790
N	7	0.64786411	-1.07827248	0.17978080
C	6	1.35678916	-0.00973078	-0.36477666
H	1	1.77640494	-0.19242775	-1.35011325
N	7	1.60139627	1.04949307	0.20359673

HONO Elimination into CN Bond Scission TS

C	6	1.34535995	-1.97124466	0.08027635
C	6	-0.97276142	-1.40360083	0.12203394

C	6	0.03748825	0.79451376	0.36177789
H	1	-1.85317275	-1.99419601	-0.05402296
H	1	2.11011377	-2.25031789	0.78597897
H	1	1.61184031	-1.76325531	-0.94232844
H	1	0.38527666	0.60613102	1.37664169
H	1	-0.33133718	1.80845677	0.30482831
N	7	2.22133182	0.63585896	-0.16336972
N	7	0.99659871	0.41204343	-0.62521767
N	7	0.14121642	-1.96081227	0.47143609
N	7	-1.10703241	-0.09254319	0.11995603
N	7	-2.43601398	0.42967688	-0.09201068
O	8	3.15949855	0.12127899	-0.79903643
O	8	2.39485927	1.30602733	0.87841840
O	8	-2.52448694	1.62888471	-0.03436240
O	8	-3.29768426	-0.38984823	-0.30772162

Product of Aforementioned

Double NN Homolysis TS

C	6	-0.74037822	1.44911609	-0.51893778
N	7	-0.83316044	0.11323380	0.06344721
C	6	-0.23580686	-0.10512143	1.38662982
N	7	1.12150842	0.38930946	1.47078959
C	6	1.32356168	1.52217408	0.64357916
N	7	0.51834196	2.10286982	-0.26979744
N	7	-2.07355194	-0.47356903	-0.10520582
N	7	1.87612228	-1.27159242	-0.74983462
O	8	-2.77160025	-0.02461176	-1.01136457
O	8	-2.35485354	-1.40923067	0.63626960
O	8	2.75915775	-2.04552535	-0.48430106
O	8	1.80319796	-0.34679282	-1.52627524
H	1	-0.83603971	1.35944867	-1.59979959
H	1	-1.55999546	2.09029809	-0.17629772
H	1	-0.86792995	0.35238528	2.16020971
H	1	-0.21641769	-1.17341727	1.57525580
H	1	0.90719277	1.92830449	1.64467760
H	1	2.35711924	1.85900197	0.61935236

Product of Aforementioned

C	6	-1.01790356	-0.72713342	-0.14106582
C	6	-0.40718988	1.25768904	1.08119512
C	6	-2.62887882	0.23150295	1.25153135

H	1	-0.69951893	-1.48502574	-0.84882103
H	1	-0.09892561	0.93006413	2.07986041
H	1	0.09349057	2.18873738	0.84852663
H	1	-3.66008401	0.44918316	0.99780063
N	7	-0.08585452	0.25312322	0.10341951
H	1	0.50927269	0.52043532	-0.66172384
N	7	-2.16619376	-0.84463911	0.40944732
N	7	-1.85385986	1.46960762	1.05755124
N	7	-2.26113979	2.51209076	1.88129479
O	8	-3.42515914	2.48977582	2.26348148
O	8	-1.43415889	3.38763854	2.11927517
H	1	-2.59627355	-0.07408117	2.30298371

NN Homolysis into CN Bond Scission TS

C	6	-0.36160164	-1.61082690	-0.98499115
N	7	0.96147185	-1.00502706	0.48029729
C	6	0.08480403	-0.26784851	1.39005220
N	7	-1.16601709	0.20124239	0.80809211
C	6	-2.06045473	-0.87565173	0.41378096
N	7	-1.37303134	-1.97299124	-0.24968177
N	7	1.92662146	-0.14657518	-0.13416094
N	7	-1.04358296	1.27894243	-0.08180801
O	8	2.10135297	-0.27344898	-1.33394825
O	8	2.57622764	0.53139597	0.64667866
O	8	-0.00017401	1.91580117	-0.01770436
O	8	-2.00705205	1.51795387	-0.79609003
H	1	-0.23287142	-0.59747548	-1.36442292
H	1	0.20228018	-2.38301688	-1.48907866
H	1	-0.21307147	-0.97370634	2.16268092
H	1	0.63574792	0.56345485	1.82059231
H	1	-2.51878295	-1.26679255	1.31856594
H	1	-2.83874299	-0.46265703	-0.22569282

Product of Aforementioned

C	6	2.15486903	2.15182645	-0.20565153
H	1	2.45026634	2.24501790	0.84388555
H	1	2.91519533	2.30766141	-0.96173263
N	7	0.97103160	1.86400389	-0.57494761
C	6	0.01201082	1.68103910	0.49555248
H	1	-0.73715936	2.46760044	0.42199463
H	1	0.47919523	1.70211799	1.48779212
N	7	-0.64264065	0.39199029	0.38277894
N	7	-1.77556286	0.32967531	-0.43735369
C	6	-0.49941793	-0.61048318	1.39954793

H	1	-0.53353046	-0.17428190	2.39786003
H	1	-1.32148478	-1.32089037	1.28586537
N	7	0.73601709	-1.37417854	1.34479751
N	7	1.08777306	-1.59989921	-0.01815230
O	8	2.11697467	-1.06285360	-0.37809171
O	8	0.34948944	-2.34477113	-0.63563948
O	8	-1.99061490	1.31997750	-1.11750610
O	8	-2.42512375	-0.70621238	-0.41475448

Sulfamine RDX

C	6	0.44043500	0.08817200	-1.14175600
C	6	-0.07887100	-1.98324500	0.00885900
C	6	-0.44869500	0.12909500	1.14243400
H	1	-0.60986000	-2.60928500	-0.70871900
H	1	1.19468800	0.62754900	-1.71060000
H	1	-0.40522300	-0.13552600	-1.80325500
H	1	-1.16709000	0.72369900	1.70284700
H	1	0.37480800	-0.15149800	1.81027200
H	1	0.40774800	-2.63306300	0.73688300
N	7	0.94397800	-1.16832200	-0.64480600
N	7	-1.04116100	-1.08952800	0.64980800
N	7	0.02744500	0.89075300	-0.00152500
N	7	0.09336300	2.23030900	0.00054200
N	7	2.23769200	-1.19606200	-0.11631800
N	7	-2.33112000	-1.02297300	0.11449800
S	16	0.28517300	2.99789000	-1.45673100
S	16	3.11939700	0.19431100	-0.07409200
S	16	-3.00756300	-2.44706300	-0.37305100
S	16	-3.10597300	0.42977100	0.06375000
S	16	-0.02247900	3.00739900	1.46076700
S	16	2.80746500	-2.66576100	0.37310500

Sulfamine RDX HONO TS

C	6	0.56819100	0.12792400	-1.10108200
C	6	-0.17778500	-1.95541300	-0.09830000
C	6	-0.48815700	0.13835700	1.09836900
H	1	-0.73046300	-2.46422600	-0.88920100
H	1	1.35139200	1.62130600	-1.68817600
H	1	-0.01281700	0.13317500	-2.02243600
H	1	-1.19526000	0.76580600	1.63680300
H	1	0.33445500	-0.14098500	1.76574900
H	1	0.22473800	-2.71201500	0.57752300
N	7	0.91118200	-1.15469800	-0.63624300

N	7	-1.10698800	-1.05361500	0.60262800
N	7	0.03415100	0.89196900	-0.05322000
N	7	0.18708800	2.19929800	0.03247900
N	7	2.18139800	-1.32195100	-0.03192700
N	7	-2.39070200	-0.93201000	0.06430700
S	16	0.89263400	2.92610000	-1.36371300
S	16	3.12095200	0.00689700	0.20134400
S	16	-3.12875400	-2.33834700	-0.37522800
S	16	-3.09309100	0.55562600	-0.04465700
S	16	-0.30386200	3.11740100	1.31688500
S	16	2.63096900	-2.85962800	0.35159700

Aminated RDX

C	6	1.51263600	0.24187500	0.59068300
N	7	0.56443400	1.25819900	0.13842800
C	6	-0.78870000	1.14935200	0.61279600
N	7	-1.28152600	-0.20314300	0.35003800
C	6	-0.43648700	-1.27003600	0.88542000
N	7	0.90623300	-1.10386100	0.39323100
N	7	0.72597400	1.72687200	-1.19152300
N	7	-2.65393500	-0.38304500	0.52019600
N	7	1.17530200	-1.73110700	-0.85510900
O	8	1.83479800	1.62208600	-1.66643200
O	8	-0.24341600	2.24410000	-1.70230600
O	8	-3.34296100	0.61568000	0.45200000
O	8	-3.03274400	-1.52429000	0.69685600
O	8	0.38318000	-2.56870300	-1.22756100
O	8	2.21338200	-1.41621200	-1.39575300
H	1	2.38307400	0.28834100	-0.06479100
H	1	-1.41887400	1.87420200	0.10102700
H	1	-0.40267800	-1.22964100	1.98647200
H	1	-0.83101200	-2.23680700	0.57909300
H	1	-0.79489100	1.37041300	1.69267400
N	7	1.89935500	0.49553700	1.93601400
H	1	1.15076000	0.37592900	2.60982500
H	1	2.67295800	-0.10279800	2.20152300

Aminated RDX HONO TS

C	6	1.27463900	0.26474400	0.87493500
N	7	0.34449200	1.22304900	1.05044600
C	6	-1.06186600	0.97969600	0.96507900
N	7	-1.37372100	-0.19709600	0.15597700
C	6	-0.61717800	-1.37795500	0.55754900
N	7	0.78249700	-1.05726000	0.45464000

N	7	0.56276700	2.16234600	-0.68561200
N	7	-2.73182900	-0.41693600	-0.08466600
N	7	1.51528800	-1.68865300	-0.55078100
O	8	1.61175500	1.69254500	-1.16229100
O	8	-0.06240400	3.07230500	-1.13109900
O	8	-3.45565400	0.55635500	-0.00876700
O	8	-3.05677900	-1.55069500	-0.37756700
O	8	1.04487800	-2.68575000	-1.05654500
O	8	2.61059100	-1.20149100	-0.78659800
H	1	1.74828700	0.81570400	-0.26000700
H	1	-1.56873400	1.85270200	0.54786900
H	1	-0.85189200	-1.65140000	1.59912900
H	1	-0.85079900	-2.21603000	-0.09848200
H	1	-1.42336800	0.84322200	2.00135500
N	7	2.40343900	0.31217000	1.72567300
H	1	2.20930800	-0.01972300	2.66383500
H	1	3.18653400	-0.18886400	1.32393100

Methylated RDX

C	6	-2.56026900	-0.72515200	0.20260600
C	6	-2.63366100	1.52346100	1.23106800
C	6	-4.68196900	0.22444400	1.04801400
H	1	-2.19657400	-1.17906800	-0.72016200
H	1	-2.56509500	0.98762100	2.18842800
H	1	-4.31786600	-0.18112800	2.00154500
N	7	-4.09709100	1.57731900	1.03331700
N	7	-4.02401700	-0.65534900	0.07203200
N	7	-1.95920600	0.61383500	0.29210000
N	7	-1.41664500	1.12701600	-0.91720800
N	7	-4.47791100	-0.66209000	-1.27135100
N	7	-4.53984600	2.37391700	-0.07475000
O	8	-0.81879100	2.17470400	-0.83173100
O	8	-1.52694000	0.43773200	-1.90984100
O	8	-3.92938900	-1.44886900	-2.00966300
O	8	-5.40707000	0.06921200	-1.54806300
O	8	-5.69589800	2.72018200	-0.03601500
O	8	-3.71599500	2.65662900	-0.92164100
C	6	-2.03061100	2.88934500	1.48203800
H	1	-0.97231000	2.78546200	1.72910400
H	1	-2.11494500	3.56103700	0.62959900
H	1	-2.55926800	3.31870600	2.33879200
C	6	-6.19101000	0.13930500	1.12783100
H	1	-6.46683300	-0.91644000	1.21280900
H	1	-6.51138400	0.66243500	2.03292900
H	1	-6.70296500	0.57427400	0.27406100

C	6	-2.14246000	-1.58800500	1.37804400
H	1	-2.57867500	-2.58392400	1.26272100
H	1	-1.05298900	-1.67663000	1.38896100
H	1	-2.45341400	-1.19327500	2.35131600

Methylated RDX Double Whammy TS

C	6	1.07006867	-1.28376519	-0.83940096
N	7	-0.45880553	-1.39436225	-0.51529106
C	6	-1.37558276	-0.77434835	-1.22225984
N	7	-1.05934821	1.34409975	-0.78567565
C	6	0.09111735	1.80469255	-1.18155894
N	7	1.53322443	0.01760331	-0.57797726
N	7	-0.79614285	-1.84307186	0.85086098
N	7	-1.44257940	1.72805877	0.53348054
N	7	2.43044055	0.07550130	0.44454717
O	8	0.08461544	-1.72541463	1.65025988
O	8	-1.89423097	-2.32344786	0.97828790
O	8	-1.61351062	0.80295949	1.30395718
O	8	-1.62943405	2.90252133	0.74978836
O	8	2.75404090	1.20428116	0.80958818
O	8	2.92307541	-0.94980555	0.92119649
H	1	1.52451835	-2.02149559	-0.16782291
H	1	-1.01510919	-0.53078895	-2.22213456
H	1	0.35632545	1.47951509	-2.18861336
C	6	1.24584822	-1.69805191	-2.28609363
H	1	0.74039941	-2.64142922	-2.52085477
H	1	0.91690922	-0.92011679	-2.98656178
H	1	2.31958683	-1.82778085	-2.44922355
C	6	0.89304746	2.90548850	-0.60317501
H	1	0.42709318	3.85246499	-0.90535955
H	1	0.93486387	2.86621947	0.48653965
H	1	1.91419689	2.84810716	-0.97926543
C	6	-2.84664001	-0.78251480	-1.03439106
H	1	-3.22101311	-1.78984690	-1.25143214
H	1	-3.13710778	-0.53928626	-0.01144503
H	1	-3.28970065	-0.06923884	-1.73167481

Cyano RDX

C	6	-0.94665877	-0.62352910	-1.06271504
C	6	-0.40170405	0.71073171	1.01075595
C	6	1.36624244	-0.03973730	-0.58383408
H	1	-1.64141121	-1.46559065	-0.94082588
H	1	-0.67630727	1.67803350	1.45115297
H	1	1.30805046	0.55650829	-1.51192656

N	7	0.96859531	0.82688733	0.55405994
N	7	-1.27930755	0.48059355	-0.13838441
N	7	0.38289121	-1.08899145	-0.74031398
N	7	1.44349513	2.16809723	0.42773176
N	7	0.45214871	-2.26929655	0.10368833
N	7	-2.65320071	0.69730094	0.06651220
O	8	1.46647889	-2.39168727	0.73425906
O	8	-0.50001967	-3.00262662	0.03228399
O	8	-3.37645623	0.21584494	-0.77717276
O	8	-2.95068759	1.35587722	1.03630187
O	8	2.36161919	2.30356259	-0.34705649
O	8	0.91818220	3.00143407	1.12575509
C	6	2.75067994	-0.50419978	-0.48968556
N	7	3.87341799	-0.78987106	-0.49168709
C	6	-0.55104812	-0.33052261	2.03848327
N	7	-0.72026236	-1.16516934	2.82570319
C	6	-0.98109259	-0.14171811	-2.44961042
N	7	-0.96419019	0.25334056	-3.53935378

Cyano RDX Triple Whammy TS

C	6	1.50775091	0.58899287	1.18437006
N	7	-0.17415538	1.56329393	0.68913644
C	6	-1.26236074	1.00835640	1.18471430
N	7	-1.26579234	-0.93112757	0.68938860
C	6	-0.24304057	-1.59759303	1.18594092
N	7	1.44245016	-0.63053985	0.68919932
N	7	-0.25575156	2.06929878	-0.64971795
N	7	-1.66401052	-1.25499117	-0.64955961
N	7	1.91954881	-0.81377155	-0.65042249
O	8	0.66838870	1.73764313	-1.36140562
O	8	-1.17823577	2.80243505	-0.91325851
O	8	-1.83832033	-0.28888353	-1.36121011
O	8	-1.83858885	-2.42041813	-0.91228334
O	8	1.16859606	-1.44797806	-1.36058143
O	8	3.01564563	-0.38253210	-0.91569229
H	1	1.23139262	0.65279877	2.23504652
H	1	-1.17829242	0.73794945	2.23556502
H	1	-0.04946954	-1.38841655	2.23624298
C	6	0.14533343	-2.94173861	0.81737435
N	7	0.50154155	-4.03211740	0.69131615
C	6	2.47600624	1.59823227	0.81352223
N	7	3.24136077	2.45234863	0.68536308
C	6	-2.62106962	1.34356678	0.81633675
N	7	-3.74362693	1.57950149	0.69032007

4.) Reference SCF Wavefunctions used in MBPT(2) Geometry Optimizations

By default, a UHF wavefunction was used in all cases for MBPT(2) wavefunctions. However, in some cases, difficulty in convergence of either the geometry optimization or the reference SCF itself was observed. In these cases, we switched to an ROHF reference wavefunction. The following compounds used an ROHF rather than UHF wavefunction:

-AE form of RDR
-RDR-o compound, the product in Figure S2
-Transition state of NN homolysis into a second NN homolysis, (TS of the reaction in Figure S1)

5.) RDR Energetics

Table 2: Electronic Energies, Enthalpies, and Gibbs Energies of RDR Isomers (kcal/mol). Here, AA refers to axial-axial, AE refers to axial-equatorial, etc. The enthalpy and Gibbs energies use the MBPT(2)/cc-pVTZ partition functions and CCSD(T)/cc-pVTZ electronic energies. We list energies to 0.1 kcal/mol for the sake of comparison of internal predictions to the method; we emphasize that the accuracy of the method is no better than what is discussed in the Computational Methodology section.

Many-Body Method	AA	AE	EE	Twist
ΔE MBPT(2)	1.4	0	3.2	0.0
ΔE CCSD	1.7	0	2.4	0.5
ΔE CCSD(T)	2.2	0	3.3	0.6
ΔH	3.0	0.4	0	1.3
ΔG	6.0	3.3	0	2.5

We can see that upon consideration of the free energy, the AA form is much less stable, and EE dominates in RDR.

6.) Testing CCSD(T) in Overcoming Transition State Static Correlation

We now take an aside from the chemistry to examine, critically, whether we believe we have overcome the static correlation inherent to the transition states. The only reason not to trust CCSD(T)/CBS results, quantitatively, is if the static correlation (reflecting too many degeneracies in the single-particle SCF energy levels) is too high to be overcome with only up to perturbative triples excitations. We therefore examine the CCSDT/cc-pVDZ for a smaller model system. If the CCSD(T) and CCSDT numbers agree, it is much harder to argue that the perturbative triples calculation are diverging considering the much higher static correlation captured by full triples excitations. We now examine the HONO elimination vs. NN homolysis of 2-nitramine propane, shown in Figure 3. The "arrow-pushing" mechanisms of 2-nitramine propane are analogous to that of the aforementioned RDX HONO elimination and NN homolysis.

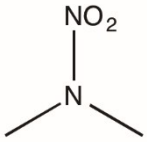

Fig. 3: 2-Nitramine Propane

Obviously, the chemistry of 2-nitramine propane is **not** going to be the same as that of RDX; the latter has a ring structure with several electron withdrawing groups, whereas this one nitramine of 2-nitramine propane has electron donating methyl groups. The relevant feature is the convergence of MBPT(2), CCSD, and CCSD(T) to CCSDT. As the point of this aside is calibration orientated (testing convergence) rather than quantitative, we cheaply calculate the stationary state geometries of the potential energy surface for these reactions with M06[96]/cc-pVTZ. Table 7 gives the values of CCSDT/cc-pVDZ calculations with varying references for the two reaction pathways (dropped core, spherical d functions, and same convergence criteria as before).

Table 7: Electronic Energies of NN Homolysis and HONO Elimination of 2-Nitramine Propane, kcal/mol.

Many-Body Method	HONO	NN Homolysis
RHF-Instability		
$\Delta E^{\ddagger}$ MBPT(2)	53.4	26.9
$\Delta E^{\ddagger}$ CCSD	54.6	26.7
$\Delta E^{\ddagger}$ CCSD(T)	48.9	20.3
$\Delta E^{\ddagger}$ CCSDT	49.0	20.6
UHF-No Instability		
$\Delta E^{\ddagger}$ MBPT(2)	56.3	42.2
$\Delta E^{\ddagger}$ CCSD	54.7	28.9
$\Delta E^{\ddagger}$ CCSD(T)	49.1	24.0

In Table 7, we demonstrate that the CCSD(T) calculation is well-converged to the CCSDT value; they are trivially different. As in RDX, we do see that the CCSD estimate is a bit off from the CCSD(T) value. Given the presence of an SCF instability, we present both the restricted and un-restricted calculation through CCSD(T) to show the lack of reference dependence as soon as one uses an infinite-order method like CCSD. This is in contrast to MBPT(2), which may diverge as a perturbation and exhibit greater reference dependence as in the NN homolysis barrier being very far away from the CCSD and CCSD(T) values. This gives us greater confidence in our RDX barriers for HONO-style mechanisms and NN homolysis-style mechanisms ("triple whammy" and NONO isomerization being so high in energy that they do not seem worthy of consideration).

There is also an interesting chemical insight to be had. 2-nitramine propane, which may be an acceptable small model for RDX, has chemistry that is very clearly different from RDX. The HONO mechanism is highly unfeasible compared to NN homolysis, whereas the situation is reversed in RDX. The biggest difference seems to be that 2-nitramine propane is not nearly as saturated with electron withdrawing groups, whose effect seems to be to make NN homolysis more favourable. It would seem that the electron deficient nitrogen radical is supported in 2-nitramine propane by the electron donating methyl groups, making the mechanism more favourable than HONO elimination. By contrast, in RDX, the electron deficient nitrogen radical does not have electron-donating groups around it (it has electron-withdrawing groups).