

Diazo Chemistry Controlling the Selectivity of Olefin Ketonization by Nitrous Oxide

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SUPPORTING INFORMATION

GEOMETRIES AND VIBRATIONS OF RELEVANT STRUCTURES.

I. Cyclopentene system

Pre-reactive complex

E(RB+HF-LYP/6-311++G(d,p)) (Hartree): -380.100928178

Electronic state : 1-A

Cartesian coordinates (Angs):

C	-0.922471	-0.166220	1.206340
C	-0.946568	1.058129	0.678315
H	-0.469997	-0.424128	2.157614
H	-0.515193	1.941978	1.135312
O	2.273915	-1.174951	-0.372534
N	2.601090	-0.055056	-0.163900
N	2.914114	1.007514	0.033355
C	-1.613341	1.078936	-0.678794
H	-2.335249	1.894944	-0.783232
H	-0.867416	1.225956	-1.471549
C	-1.565555	-1.191338	0.300224
H	-2.257175	-1.852776	0.831287
H	-0.799320	-1.837426	-0.146879
C	-2.282609	-0.319053	-0.765193
H	-2.228966	-0.749752	-1.766917
H	-3.341168	-0.229120	-0.506896

Rotational constants (GHz): 3.3470800 0.9720400 0.8914900

Vibrational harmonic frequencies (cm-1):

-11.6922	13.8489	30.7003
33.0382	45.9786	137.9030
393.9608	577.9459	580.1713
617.6758	714.7938	783.0129
817.8573	889.9131	901.0690

915.6060	971.5482	973.5859
1034.4297	1068.0635	1128.1584
1154.6430	1223.6630	1230.4670
1307.6201	1316.9455	1325.7477
1327.6997	1377.1862	1484.2693
1490.3807	1509.2205	1669.4010
2345.5306	2995.0140	3006.9727
3035.5486	3045.2995	3055.2902
3090.2366	3165.0463	3189.7496

Zero-point correction (Hartree): 0.127521

TS^{add}

E(UB+HF-LYP/6-311++G(d,p)) (Hartree): -380.058016095

Electronic state : 1-A

Cartesian coordinates (Angs):

C	-0.180189	0.683690	0.928707
C	-0.185082	-0.711004	0.895673
C	-1.310194	-1.194537	-0.007257
C	-1.236606	1.243888	0.008589
C	-1.603432	0.039945	-0.888953
H	0.250554	1.264381	1.732940
H	0.159503	-1.303622	1.734091
H	-2.182133	-1.451448	0.607893
H	-1.045817	-2.083585	-0.583003
H	-0.908410	2.124470	-0.546520
H	-2.098335	1.551408	0.618411
H	-2.635139	0.074047	-1.242775
H	-0.953671	0.027560	-1.768755
O	1.615237	1.053785	-0.208001
N	1.913163	-0.118882	-0.452699
N	1.456060	-1.167600	-0.191420

Rotational constants (GHz): 3.4417300 1.9636200 1.6145900

Vibrational harmonic frequencies (cm-1):

-448.2327	110.5724	149.5595
224.8475	265.7118	310.0787
500.2777	567.3902	619.6552
709.2114	783.8796	834.0183
864.7152	877.7527	914.4600
926.0923	959.9603	1017.3795
1031.9363	1054.0848	1114.9423
1147.9467	1207.7318	1233.7309
1247.8503	1309.6247	1317.9996
1325.1792	1372.7845	1463.0296
1479.5750	1495.3280	1508.4930

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1893.0653	2990.8611	3008.5251
3047.4826	3083.1213	3085.6365
3098.1184	3182.5459	3212.7047

Zero-point correction (Hartree): 0.128826

OD

E(RB+HF-LYP/6-311++G(d,p)) (Hartree): -380.110040025

Electronic state : 1-A

Cartesian coordinates (Angs):

C	0.129924	0.783785	0.704861
C	-1.201806	1.200593	0.063619
O	1.253717	1.097459	-0.154538
N	1.837206	-0.121517	-0.604603
C	-1.635872	-0.023729	-0.762668
C	-1.202357	-1.216500	0.108173
C	0.135090	-0.763118	0.728505
N	1.280246	-1.108347	-0.151348
H	0.323081	1.256209	1.668380
H	-1.091836	2.115290	-0.520928
H	-1.930252	1.397446	0.858175
H	-2.705428	-0.029789	-0.981493
H	-1.105788	-0.040824	-1.719730
H	-1.092791	-2.152093	-0.442421
H	-1.927443	-1.384371	0.910763
H	0.328675	-1.218679	1.700268

Rotational constants (GHz): 3.6302400 2.3227700 1.7865100

Vibrational harmonic frequencies (cm-1):

99.3825	192.8504	331.1597
386.5797	533.0257	586.5951
632.1567	664.1602	786.5998
797.2327	857.8438	867.7768
890.2402	922.7935	940.5680
961.5306	988.3873	1030.3051
1047.9906	1106.0494	1162.2932
1189.8594	1223.3351	1276.2871
1299.0439	1302.2875	1323.7276
1337.2306	1356.5266	1362.9681
1476.5111	1487.6873	1504.0436
1657.9723	3029.8233	3038.8865
3046.2166	3085.2803	3091.6179
3098.9673	3101.5026	3105.4453

Zero-point correction (Hartree): 0.132545

TS^{diazo}

E(UB+HF-LYP/6-311++G(d,p)) (Hartree): -380.082151450

Electronic state : 1-A

Cartesian coordinates (Angs):

C	0.038123	1.084032	0.586713
C	0.230764	-0.819778	0.771807
O	0.993579	1.521914	-0.139579
N	1.365758	-0.953348	-0.020465
N	2.071571	-0.338520	-0.662351
H	0.077106	1.341243	1.662934
H	0.457010	-1.134290	1.788808
C	-1.056019	-1.363278	0.153608
H	-1.758559	-1.536110	0.973803
H	-0.908393	-2.321674	-0.349699
C	-1.393116	1.050459	-0.003744
H	-2.121966	1.110517	0.814042
H	-1.524071	1.927975	-0.639372
C	-1.586205	-0.259576	-0.775021
H	-2.628264	-0.437739	-1.052469
H	-1.004077	-0.233309	-1.701888

Rotational constants (GHz): 3.0931300 2.2442400 1.6101400

Vibrational harmonic frequencies (cm-1):

-415.6828	83.8232	184.5550
282.9839	288.8080	399.6542
478.6202	507.5276	586.0401
601.6356	714.9173	793.4974
808.0559	875.1593	918.7978
934.8821	962.8916	1020.2018
1056.1008	1086.2876	1105.4809
1169.4816	1207.2293	1264.6333
1306.7928	1328.3742	1338.9338
1346.1514	1361.4134	1443.1830
1476.2936	1485.5151	1500.9603
2122.9766	2880.1439	3015.1148
3037.3831	3046.4952	3079.0896
3090.7230	3098.2007	3135.0594

Zero-point correction (Hartree): 0.128543

TS^{H-shift}

E(UB+HF-LYP/6-311++G(d,p)) (Hartree): -380.078374076

Electronic state : 1-A

Cartesian coordinates (Angs):

C	0.128849	0.795988	0.492773
C	-0.909119	1.093972	-0.622654
O	1.335490	1.304355	0.460888
N	2.143852	-0.388271	-0.631145
C	-2.050974	0.105138	-0.345619
C	-1.357577	-1.166862	0.228596
C	-0.035532	-0.681457	0.747214
N	1.394639	-1.195089	-0.398344
H	-0.375709	1.043063	1.484457
H	-0.432278	0.906094	-1.589912
H	-1.222165	2.138187	-0.605109
H	-2.731588	0.515744	0.406445
H	-2.647262	-0.126267	-1.229106
H	-1.168287	-1.896458	-0.565492
H	-1.947605	-1.684511	0.988820
H	0.417651	-1.127844	1.627361

Rotational constants (GHz): 3.4566400 1.9294800 1.5229700

Vibrational harmonic frequencies (cm-1):

-411.3053	121.1333	196.1133
229.0841	263.4242	373.3941
426.3740	499.3442	576.5233
625.6234	639.7243	763.5233
810.8225	874.5906	893.7219
903.1172	959.3706	1024.2726
1040.0545	1073.7314	1097.5927
1157.7444	1186.2521	1198.9520
1232.7867	1267.8233	1294.2675
1312.9256	1341.5137	1366.9803
1467.3327	1491.6396	1506.8543
2143.2868	2635.0064	3038.3210
3042.3114	3046.4884	3076.1108
3097.3061	3110.6762	3170.1605

Zero-point correction (Hartree): 0.126612

5-diazopentanal

E(RB+HF-LYP/6-311++G(d,p)) (Hartree): -380.110389612

Electronic state : 1-A

Cartesian coordinates (Angs):

C	2.952343	-0.014133	-0.301591
C	-2.077087	0.636050	-0.355018
O	3.733818	-0.882619	-0.002234
N	-2.965834	-0.271421	-0.104416
N	-3.745137	-1.069250	0.136747
C	-0.801460	0.716670	0.441737

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C	1.732533	0.366479	0.499997
C	0.440534	0.220938	-0.324489
H	3.098242	0.570401	-1.237955
H	-2.299752	1.289394	-1.187509
H	-0.916286	0.141241	1.365446
H	-0.640431	1.757677	0.747214
H	1.701841	-0.243807	1.406024
H	1.851121	1.417577	0.798821
H	0.532740	0.784634	-1.260025
H	0.297598	-0.827497	-0.604273

Rotational constants (GHz): 7.1505400 0.6417400 0.6171100

Vibrational harmonic frequencies (cm-1):

27.7573	58.3593	88.1767
90.3309	179.3173	237.8087
322.8141	352.2936	482.5785
529.3906	539.1851	598.0414
744.1182	800.8427	896.9980
978.1013	978.8913	1030.1970
1084.9863	1133.7577	1190.7062
1216.7178	1252.0697	1289.0402
1323.3182	1340.1128	1378.8220
1415.5033	1436.0187	1466.7556
1475.9275	1499.9525	1801.4695
2160.2501	2858.8289	2999.7823
3009.2240	3020.9091	3052.2586
3070.3288	3088.6959	3203.1938

Zero-point correction (Hartree): 0.126903

II. Cyclohexene

TS^{add}(a)

E(RB+HF-LYP/6-311++G(d,p)) (Hartree): -419.384148102

Electronic state : 1-A

Cartesian coordinates (Angs):

C	-0.192197	-0.653569	0.943012
C	-0.173558	0.747544	0.889152
C	0.937514	-1.474635	0.344004
N	-1.672306	-1.158653	-0.265568
C	0.849164	1.517396	0.079915
O	-1.937130	1.045314	-0.311609
C	1.676619	-0.722875	-0.767739
C	2.082886	0.674703	-0.287695
N	-2.169791	-0.139364	-0.579787

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H	-0.684218	-1.094376	1.805051
H	-0.707713	1.295592	1.654715
H	0.545684	-2.426999	-0.021767
H	1.643866	-1.717917	1.148603
H	1.147842	2.406585	0.643891
H	0.375333	1.891076	-0.833491
H	2.557335	-1.293524	-1.076592
H	1.031038	-0.638485	-1.650029
H	2.665573	1.195710	-1.052808
H	2.734404	0.574564	0.588891

Rotational constants (GHz): 2.6646700 1.4498900 1.1569400

Vibrational harmonic frequencies (cm-1):

-455.9730	78.8378	102.3180
214.6376	243.7969	286.9285
343.9963	436.4000	470.1175
543.2039	586.9917	676.5857
726.2621	814.9424	824.9224
857.8817	888.9744	895.2186
941.9873	1010.9632	1049.3561
1053.8358	1069.1301	1111.9512
1151.3711	1177.8885	1214.6866
1256.1923	1274.2404	1299.9755
1356.0260	1361.3957	1374.0165
1384.6230	1415.1044	1469.9438
1486.0867	1495.9006	1503.6050
1511.2601	1869.2498	3003.1080
3010.4643	3021.0019	3029.8270
3055.2037	3062.9149	3066.5801
3069.7387	3141.0120	3187.9661

Zero-point correction (Hartree): 0.158284

TS^{add}(b)

E(RB+HF-LYP/6-311++G(d,p)) (Hartree): -419.383758004

Electronic state : 1-A

Cartesian coordinates (Angs):

C	-0.193964	-0.598005	0.989681
C	0.828430	-1.501207	0.350527
C	1.604665	-0.806699	-0.772951
C	2.117518	0.555609	-0.292227
C	0.956195	1.494264	0.076259
C	-0.162764	0.796385	0.847093
O	-1.850608	-1.042442	-0.259643
N	-2.167595	0.108967	-0.584644
N	-1.743251	1.174250	-0.323617

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H	-0.750609	-1.012207	1.822468	
H	0.350914	-2.418660	-0.001827	
H	1.529883	-1.808746	1.140215	
H	2.435885	-1.440750	-1.094466	
H	0.953539	-0.674228	-1.644938	
H	2.741252	1.028044	-1.056369	
H	2.759256	0.400538	0.583934	
H	1.328470	2.327649	0.679480	
H	0.546412	1.944325	-0.833403	
H	-0.614692	1.368972	1.649571	
Rotational constants (GHz):				2.6524600 1.4612300 1.1648300
Vibrational harmonic frequencies (cm-1):				
-461.4395	69.9564	87.7521		
214.7590	247.1029	293.1003		
334.1321	440.6709	469.2964		
535.2339	587.9465	684.8092		
722.1441	810.8985	821.8168		
862.8552	885.4127	897.4990		
943.6845	1008.8409	1048.2994		
1052.4638	1068.4679	1108.8668		
1154.0049	1181.7561	1215.0354		
1251.8652	1276.8975	1298.6735		
1354.9008	1367.6190	1373.2222		
1384.4933	1413.2282	1462.7850		
1485.5131	1498.4253	1505.2860		
1510.9898	1872.6763	2984.3150		
3007.8109	3022.9229	3028.8541		
3056.1539	3064.5644	3067.4649		
3071.1242	3152.6024	3177.2086		
Zero-point correction (Hartree): 0.158188				

OD

E(RB+HF-LYP/6-311++G(d,p)) (Hartree): -419.434688747

Electronic state : 1-A

Cartesian coordinates (Angs):

C	-0.360315	-0.820228	0.605585
C	-0.493716	0.704319	0.679321
C	1.040290	-1.402526	0.410384
C	0.514628	1.482850	-0.178843
C	1.925797	-0.571368	-0.524886
C	1.932432	0.901954	-0.099274
H	-0.821326	-1.283309	1.487065
H	-0.504029	1.053711	1.712032

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H	0.940828	-2.431714	0.054986
H	1.517923	-1.457362	1.395369
H	0.496038	2.535604	0.114494
H	0.174073	1.441703	-1.218643
H	2.940445	-0.980302	-0.521043
H	1.559444	-0.650400	-1.555243
H	2.601554	1.484109	-0.739231
H	2.324923	0.989675	0.922353
N	-1.312166	-1.144020	-0.500148
O	-1.830599	0.900891	0.159103
N	-2.107802	-0.238672	-0.682521

Rotational constants (GHz): 2.9254500 1.6010200 1.2304300

Vibrational harmonic frequencies (cm⁻¹):

135.6372	136.6643	290.2314
332.3730	367.9315	418.6639
478.3429	525.1426	616.8100
620.8910	739.1093	782.1383
789.8608	858.5172	861.8992
915.6432	939.5913	941.3313
988.9929	1019.2941	1053.7013
1076.6159	1119.9353	1125.9234
1167.0833	1205.0171	1259.1988
1270.7749	1300.9260	1324.6062
1342.7488	1354.1181	1367.6965
1379.1435	1389.6367	1395.8435
1479.6164	1491.2955	1495.7842
1504.7043	1657.4603	3003.0348
3011.6431	3020.1590	3027.9952
3036.3157	3062.9893	3064.2763
3074.4373	3075.5331	3100.0150

Zero-point correction (Hartree): 0.161744

TS^{H-shift}

E(RB+HF-LYP/6-311++G(d,p)) (Hartree): -419.408592465

Electronic state : 1-A

Cartesian coordinates (Angs):

C	-0.482290	0.774505	0.597027
C	-0.260713	-0.695602	0.790970
O	-1.743877	1.151571	0.523909
N	-1.445561	-1.223453	-0.636176
N	-2.247896	-0.468988	-0.862004
H	-0.102252	0.959923	1.657335
C	0.502572	1.425430	-0.396368
H	0.094434	1.267046	-1.400385

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H	0.486140	2.504019	-0.223518
C	1.086521	-1.333050	0.620262
H	1.599598	-1.285731	1.591036
H	0.941330	-2.400619	0.426073
C	1.935823	-0.661055	-0.466854
H	1.534911	-0.926151	-1.451692
H	2.955555	-1.054017	-0.425947
C	1.929439	0.865180	-0.310110
H	2.555239	1.323779	-1.081366
H	2.382731	1.135475	0.652853
H	-0.910583	-1.141650	1.542040

Rotational constants (GHz): 2.5629800 1.4767200 1.1827700

Vibrational harmonic frequencies (cm-1):

-401.2039	115.1483	155.3213
237.1234	258.9053	297.7965
351.6466	404.6238	418.1566
475.8857	519.8585	602.3309
624.7542	710.9262	804.7301
829.0156	866.0874	908.5204
945.6753	985.5073	1032.1421
1044.8641	1062.7695	1082.3138
1127.4673	1159.4553	1195.6412
1221.5647	1264.2329	1284.2269
1296.0321	1332.6290	1366.6864
1374.1196	1380.7440	1388.7309
1452.2703	1485.1515	1493.7071
1502.4088	2153.2023	2625.8712
3000.7135	3001.3574	3025.2764
3036.1972	3056.6293	3060.7745
3069.5894	3085.6671	3138.0875

Zero-point correction (Hartree): 0.155627

TS^{diazo}

E(RB+HF-LYP/6-311++G(d,p)) (Hartree): -419.404995900

Electronic state : 1-A

Cartesian coordinates (Angs):

C	-0.371800	-0.879511	0.686007
C	-0.567098	1.014951	0.614563
C	1.049956	-1.403122	0.554291
C	0.521616	1.499499	-0.356296
C	1.890519	-0.646632	-0.480094
C	1.907403	0.862017	-0.205631
H	-0.866917	-1.181325	1.611182

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H	-0.272149	1.104953	1.683318
H	1.049444	-2.480377	0.357019
H	1.503730	-1.278678	1.543019
H	0.588020	2.584837	-0.219057
H	0.141650	1.348040	-1.373026
H	2.907945	-1.049598	-0.463746
H	1.501576	-0.831781	-1.489352
H	2.605081	1.351309	-0.892250
H	2.298382	1.042269	0.804668
N	-1.278173	-1.175549	-0.338245
O	-1.775004	1.264954	0.318682
N	-2.127584	-0.740523	-0.945793

Rotational constants (GHz): 2.3974600 1.5800000 1.1630600

Vibrational harmonic frequencies (cm-1):

-404.5561	91.1213	145.3608
206.5661	263.9862	329.0703
351.7020	367.4633	450.6983
490.1083	556.4278	603.2463
609.5790	753.3085	812.2989
854.6202	867.0537	902.5969
941.1957	994.4167	1011.4598
1077.1383	1099.6894	1114.8623
1139.8956	1197.0720	1201.9374
1269.2730	1287.2231	1304.9661
1340.8789	1352.5962	1372.5665
1382.7841	1388.9003	1465.9735
1473.5899	1477.4637	1495.8768
1501.2375	2136.1397	2829.1874
3000.3196	3012.1028	3019.9433
3025.8848	3051.7291	3056.0451
3057.8774	3065.0983	3096.3575

Zero-point correction (Hartree): 0.156959

diazo

E(RB+HF-LYP/6-311++G(d,p)) (Hartree): -419.435051682

Electronic state : 1-A

Cartesian coordinates (Angs):

C	2.715116	0.723791	0.202419
C	-3.567828	-0.448328	-0.226465
C	1.397095	0.598848	-0.518409
C	-2.283344	-0.295668	0.549333
C	0.226343	0.175962	0.389024
C	-1.108450	0.105453	-0.361395
H	2.942507	1.527334	0.889545

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H	-3.529591	-1.191788	-1.054596
H	1.504223	-0.118103	-1.338936
H	1.160494	1.562813	-0.984517
H	-2.062402	-1.267131	1.012919
H	-2.438136	0.434704	1.347213
H	0.452173	-0.798675	0.836179
H	0.142234	0.884921	1.220614
H	-1.024102	-0.611846	-1.187243
H	-1.324272	1.078667	-0.817403
N	3.636822	-0.174572	0.069180
O	-4.582168	0.169485	-0.015324
N	4.443267	-0.970732	-0.070355

Rotational constants (GHz): 8.0334900 0.4206000 0.4149700

Vibrational harmonic frequencies (cm-1):

29.2739	41.5819	55.5023
116.4578	123.1117	133.0256
237.4880	264.4371	330.3782
400.4792	507.2920	524.5005
537.9696	598.9283	735.6843
778.2484	830.7088	935.0857
968.7381	998.3908	1022.4459
1047.1624	1096.1555	1141.5916
1184.2604	1216.0548	1245.5446
1271.3383	1307.3087	1328.4654
1335.0397	1368.6664	1392.8256
1417.0934	1436.4535	1467.2804
1477.7201	1490.1237	1507.0226
1801.7984	2157.8350	2857.6510
3001.9498	3007.5150	3009.4855
3021.3048	3033.0986	3049.2303
3069.2749	3089.1310	3203.1928

Zero-point correction (Hartree): 0.155374

III. Methylcyclohexene

TS^{Me-Shift}

E(RB+HF-LYP/6-311++G(d,p)) (Hartree): -458.729702301

Electronic state : 1-A

Cartesian coordinates (Angs):

C	-0.231316	-0.328775	0.962008
C	-0.492900	0.767745	-0.019403
C	1.119496	-0.927755	1.163910
N	-1.400607	-1.671621	0.015899

C	0.448498	0.689252	-1.252073
O	-1.768292	0.975442	-0.302839
C	1.920800	-1.053488	-0.139952
C	1.889527	0.251111	-0.946387
N	-2.209594	-1.189416	-0.590313
H	-0.909726	-0.346068	1.812112
H	1.010305	-1.889621	1.674442
H	1.652931	-0.282475	1.880776
H	0.426448	1.662780	-1.748195
H	-0.013792	-0.018664	-1.946997
H	2.949565	-1.344405	0.090552
H	1.490725	-1.863396	-0.739659
H	2.438111	0.118278	-1.884069
H	2.419763	1.036307	-0.394141
C	-0.023460	1.985955	0.948268
H	-0.691845	2.063303	1.804802
H	1.015574	1.916769	1.274144
H	-0.154175	2.866645	0.321609

Rotational constants (GHz): 1.7487900 1.3205100 1.0718700

Vibrational harmonic frequencies (cm-1):

-318.7948	122.4425	149.4708
207.4013	224.7202	246.3030
252.7164	316.0298	345.6255
372.4015	422.4714	455.9612
477.5508	489.5579	533.9919
615.2573	701.2413	754.2579
812.2183	846.3911	892.1104
909.4066	974.3755	979.9925
1011.4727	1016.9264	1039.1287
1078.2936	1108.0167	1155.2319
1161.1681	1206.0549	1257.4224
1265.0094	1290.7835	1330.0887
1356.7044	1365.2356	1369.1530
1385.3061	1390.8949	1446.2100
1473.5688	1483.9146	1490.7060
1498.0563	1506.8203	2185.7400
2969.7184	3016.2033	3025.7367
3039.8737	3045.8315	3056.7187
3059.1695	3069.3942	3084.1435
3133.2738	3145.3147	3151.3650

Zero-point correction (Hartree): 0.184009

TS^{alkyl-shift}

E(RB+HF-LYP/6-311++G(d,p)) (Hartree): -458.730539212

Electronic state : 1-A

Cartesian coordinates (Angs):

C	-0.425080	0.754411	0.027039
C	1.118381	1.344563	-0.072551
C	2.163243	0.417557	0.528586
C	2.188697	-0.918353	-0.214611
C	0.761375	-1.525202	-0.222176
C	-0.177797	-0.495720	-0.768991
O	-0.743079	0.530963	1.287581
N	-2.275467	-1.025580	0.664902
N	-1.866719	-1.317410	-0.339116
H	1.029473	2.277497	0.484491
H	1.353561	1.591806	-1.112135
H	3.145202	0.900553	0.472493
H	1.933907	0.256533	1.584835
H	2.872422	-1.632111	0.253189
H	2.537334	-0.769150	-1.243816
H	0.732780	-2.433716	-0.827785
H	0.477215	-1.766751	0.803658
H	-0.192332	-0.402008	-1.855546
C	-1.335168	1.766592	-0.702496
H	-2.364784	1.403338	-0.700545
H	-1.317513	2.708829	-0.151820
H	-1.029242	1.955311	-1.736970

Rotational constants (GHz): 2.0039100 1.2748100 0.9777300

Vibrational harmonic frequencies (cm-1):

-369.3305	134.4793	153.7632
187.5031	197.8931	244.8691
267.0244	296.1374	326.6531
345.1290	423.6817	437.8616
480.8456	518.7467	565.3947
577.1166	698.9131	761.4496
856.3757	862.9731	884.4557
931.9486	939.5572	983.5299
1010.5177	1029.5548	1050.9761
1071.0056	1097.3871	1126.4122
1167.4102	1192.5010	1241.1457
1262.5056	1290.8279	1310.4386
1342.4879	1359.4250	1380.7810
1391.2973	1403.7616	1473.6220
1477.2915	1485.5988	1488.6872
1492.4264	1501.7350	2161.6361
3013.3232	3021.7237	3029.3355
3041.0506	3054.5426	3068.5524
3084.9143	3095.1036	3104.3392

3109.2953 3115.4927 3122.6481
Zero-point correction (Hartree): 0.183953

TS^{diazo}

E(UB+HF-LYP/6-311++G(d,p)) (Hartree): -458.731259327

Electronic state : 1-A

Cartesian coordinates (Angs):

C	-0.261575	-0.787203	0.822437
C	-0.680588	0.883766	-0.017369
C	1.216525	-1.120780	0.959552
C	0.455122	1.077805	-1.053260
C	2.046081	-0.755082	-0.275048
C	1.890510	0.724492	-0.643525
H	-0.787426	-0.771442	1.779906
H	1.350045	-2.173118	1.231933
H	1.574662	-0.542354	1.817309
H	0.403263	2.128243	-1.363377
H	0.169200	0.492297	-1.933493
H	3.095865	-0.990744	-0.074121
H	1.747012	-1.379287	-1.126595
H	2.563703	0.965003	-1.472763
H	2.216057	1.345598	0.200341
N	-1.033035	-1.603361	-0.014902
O	-1.846469	0.752304	-0.525186
N	-1.867524	-1.552339	-0.777906
C	-0.585431	1.791609	1.228180
H	-0.698879	2.827029	0.893619
H	-1.407517	1.569931	1.910807
H	0.365814	1.712665	1.761785

Rotational constants (GHz): 1.6891800 1.3734200 1.0542600

Vibrational harmonic frequencies (cm-1):

-414.0095	89.2641	142.8398
199.8357	230.5062	243.2818
298.2629	310.7128	345.0264
369.2760	440.6695	470.9268
513.0836	533.0781	579.9346
608.5826	722.0467	809.8114
819.1915	865.8705	884.5312
913.0417	969.7116	974.1110
1016.2584	1049.2731	1059.8905
1104.8006	1132.2948	1152.7868
1201.9794	1210.9906	1275.6481

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1289.2529	1340.8118	1351.3870
1372.4563	1382.0269	1387.1226
1392.3771	1417.3860	1473.8632
1478.3008	1482.9460	1494.2910
1499.6433	1501.1633	2131.8572
3006.0422	3011.9052	3017.9329
3025.4089	3027.2453	3047.7725
3054.4726	3059.7179	3065.5014
3087.2249	3088.6610	3112.7547

Zero-point correction (Hartree): 0.184844

diazo

E(UB+HF-LYP/6-311++G(d,p)) (Hartree): -458.771968955

Electronic state : 1-A

Cartesian coordinates (Angs):

C	3.200610	-0.002294	0.705293
C	-3.182514	0.088969	-0.162241
C	1.877961	0.656947	0.406252
N	4.084721	-0.181320	-0.221867
C	-1.834808	-0.571677	0.099259
O	-3.284867	1.275597	-0.385930
C	0.684597	-0.316515	0.380607
C	-0.650222	0.392564	0.127990
N	4.857333	-0.321182	-1.051419
H	3.462927	-0.391059	1.679928
H	1.946342	1.178367	-0.553787
H	1.693258	1.431532	1.160323
H	-1.691831	-1.340342	-0.672663
H	-1.911208	-1.129767	1.042148
H	0.860210	-1.073722	-0.392544
H	0.643988	-0.856649	1.334580
H	-0.610373	0.938521	-0.819904
H	-0.822133	1.150487	0.899388
C	-4.396610	-0.820644	-0.120595
H	-5.281986	-0.274180	-0.443037
H	-4.248812	-1.700027	-0.754321
H	-4.549905	-1.184521	0.900936

Rotational constants (GHz): 4.8981300 0.3507700 0.3452300

Vibrational harmonic frequencies (cm-1):

15.1188	29.4038	42.5312
84.7819	91.2674	116.1929
129.5365	212.7194	231.0010
288.8785	368.8706	442.0626
476.2665	500.4428	536.9893

591.7443	607.4511	723.2293
760.4630	825.7388	860.5659
934.9645	962.5861	1000.0316
1020.1212	1051.8350	1085.8661
1129.1687	1173.3981	1175.2607
1215.9692	1258.4277	1272.9805
1322.6796	1328.3218	1334.5228
1378.8951	1387.8584	1400.2448
1436.3344	1452.8220	1467.3360
1477.0647	1478.5635	1488.6569
1505.8639	1781.7236	2156.2197
3000.7260	3005.4141	3012.3566
3023.2250	3029.2119	3031.4718
3035.6401	3060.7977	3074.6901
3085.2540	3138.3987	3201.1092

Zero-point correction (Hartree): 0.182963

IV. 1-Hexene

TS^{addNterm}

E(RB+HF-LYP/6-311++G(d,p)) (Hartree): -420.593297174

Electronic state : 1-A

Cartesian coordinates (Angs):

C	-2.167010	1.267740	0.082975
C	-0.941137	0.836250	0.580426
C	0.342244	0.949715	-0.195845
N	-3.103436	-0.373040	-0.553481
N	-2.384077	-1.237006	-0.214707
O	-1.297184	-1.299345	0.367453
H	-2.953939	1.540931	0.775247
H	-0.845626	0.685812	1.651097
H	0.662744	2.000984	-0.134355
H	0.146654	0.760285	-1.257418
H	-2.201928	1.761498	-0.882046
C	1.485731	0.059219	0.303376
H	1.651875	0.252308	1.371082
H	1.184286	-0.989347	0.222550
C	2.795773	0.282610	-0.459742
H	3.090687	1.336154	-0.377625
H	2.627685	0.096061	-1.527487
C	3.938842	-0.606689	0.037691
H	4.858423	-0.426105	-0.525570
H	4.154346	-0.419685	1.094422

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H 3.688200 -1.666885 -0.065500
Rotational constants (GHz): 3.6767000 0.6903800 0.6197100

Vibrational harmonic frequencies (cm-1):

-449.9298	52.8122	65.4185
95.6879	125.3464	146.7921
197.8443	246.6782	266.6912
331.0920	392.0054	472.3046
497.5921	575.3781	719.5253
730.7537	764.3789	830.9252
898.8541	911.2773	942.3453
1004.7228	1023.2475	1036.4359
1066.4618	1072.5382	1122.8249
1189.5867	1221.2382	1244.1126
1277.9661	1284.2639	1314.1465
1334.3348	1352.7851	1399.3574
1414.4425	1445.8419	1466.6293
1489.4539	1498.6192	1500.3670
1511.8619	1544.4442	1889.8459
2977.0374	3001.2148	3006.8412
3019.8725	3028.1337	3038.6404
3069.4339	3081.8637	3085.9083
3133.0928	3160.3302	3220.2177

Zero-point correction (Hartree): 0.177223

OD^{Nterm}

E(RB+HF-LYP/6-311++G(d,p)) (Hartree): -420.643470370

Electronic state : 1-A

Cartesian coordinates (Angs):

C	-2.253795	1.042129	0.131249
C	-0.981334	0.332057	0.613003
C	0.288330	0.717933	-0.140653
C	1.534182	-0.046511	0.316772
C	2.797173	0.338584	-0.461624
C	4.043265	-0.421011	0.002022
H	-2.881079	1.433511	0.935772
H	-2.069354	1.848742	-0.581072
H	-0.839878	0.432531	1.691426
H	0.444552	1.796472	-0.006527
H	0.119378	0.555425	-1.212254
H	1.697691	0.137701	1.386815
H	1.351846	-1.121102	0.213532
H	2.969725	1.417725	-0.364858
H	2.632211	0.151357	-1.529544
H	4.925357	-0.129077	-0.574282

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H	4.256521	-0.225171	1.057638
H	3.912786	-1.501331	-0.113671
N	-3.018990	-0.027138	-0.549250
N	-2.501237	-1.122342	-0.398351
O	-1.305637	-1.066189	0.370703

Rotational constants (GHz): 4.8901000 0.6705700 0.6323000

Vibrational harmonic frequencies (cm-1):

50.0101	65.6593	89.0256
119.3188	146.3515	241.7283
276.1147	297.7268	433.5343
457.0795	541.8146	672.8838
733.9292	756.3851	810.0085
844.2540	886.5133	905.2463
913.1899	964.0941	975.8230
1016.9475	1042.6766	1066.2282
1077.0220	1130.2930	1150.9992
1209.2470	1244.5042	1272.2403
1305.5457	1310.3358	1322.0843
1337.0020	1355.7629	1396.2749
1407.0638	1415.2918	1475.1965
1482.7501	1490.1223	1499.2025
1499.5495	1512.0466	1662.2459
2999.6007	3000.6742	3007.4240
3019.4476	3028.3939	3034.9822
3057.9669	3062.2249	3071.6028
3081.0051	3085.8372	3101.8043

Zero-point correction (Hartree): 0.180915

TSaddOterm

E(RB+HF-LYP/6-311++G(d,p)) (Hartree): -420.589774252

Electronic state : 1-A

Cartesian coordinates (Angs):

C	-1.541610	0.045980	0.315373
C	-0.365691	0.860509	-0.236246
C	0.914628	0.745815	0.571775
C	2.108685	1.306962	0.126750
N	1.315556	-1.242687	0.384697
N	2.361329	-1.249723	-0.146785
O	3.159037	-0.381256	-0.517081
H	-1.721280	0.338462	1.358270
H	-1.274091	-1.014502	0.335483
H	-0.166804	0.575394	-1.275782
H	-0.654989	1.919571	-0.262265

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H	0.786882	0.657409	1.647256
H	2.891514	1.567131	0.826646
H	2.172335	1.765765	-0.852667
C	-2.831350	0.236868	-0.490016
H	-2.651513	-0.052170	-1.532731
H	-3.093883	1.301899	-0.510690
C	-4.010443	-0.567967	0.064130
H	-4.237628	-0.278217	1.094954
H	-4.914374	-0.412520	-0.531130
H	-3.791978	-1.640301	0.063327

Rotational constants (GHz): 3.9042000 0.6624800 0.6035800

Vibrational harmonic frequencies (cm-1):

-467.3796	43.1039	58.8934
93.8248	123.2588	141.8818
214.2454	242.2404	269.8220
328.6837	388.2469	470.3259
505.3532	584.6053	719.4725
730.8448	759.9595	814.6499
896.0440	908.6158	938.9047
999.7563	1025.3688	1037.0767
1064.6993	1071.6186	1126.3108
1178.3913	1220.6221	1245.2434
1277.3331	1282.5483	1316.6771
1334.4668	1354.4394	1399.0100
1413.5372	1438.7703	1479.9036
1489.4569	1499.3475	1499.7637
1512.6874	1541.6769	1895.2974
2996.8277	2999.8080	3005.9054
3019.2157	3027.6824	3037.1367
3069.2239	3081.0590	3085.1663
3139.6020	3149.7326	3240.5387

Zero-point correction (Hartree): 0.177216

OD^{Oterm}

E(RB+HF-LYP/6-311++G(d,p)) (Hartree): -420.641516554

Electronic state : 1-A

Cartesian coordinates (Angs):

C	-1.581356	-0.090881	0.287484
C	-0.350171	0.699756	-0.166628
C	0.954415	0.264733	0.504816
C	2.204596	1.063127	0.106494
N	1.326519	-1.123562	0.111065
N	2.478503	-1.208985	-0.275194

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O	3.162759	0.048304	-0.253695
C	-2.873006	0.364694	-0.400844
C	-4.105679	-0.420005	0.057014
H	-1.695209	0.011492	1.374515
H	-1.417718	-1.155982	0.094951
H	-0.226881	0.616269	-1.252811
H	-0.496563	1.765227	0.048986
H	0.814134	0.235792	1.590912
H	2.621178	1.652344	0.923279
H	2.029826	1.703841	-0.763067
H	-2.758031	0.261876	-1.486592
H	-3.029098	1.433889	-0.210989
H	-4.268857	-0.308635	1.133578
H	-5.009112	-0.074871	-0.452872
H	-3.993692	-1.488386	-0.151449

Rotational constants (GHz): 5.2072900 0.6444700 0.6007800

Vibrational harmonic frequencies (cm-1):

45.7228	61.3458	77.0399
118.2144	146.1027	239.0884
272.9903	291.0550	378.0410
455.0479	607.4015	636.3024
729.8530	741.7851	780.2299
831.0431	898.8560	924.0307
931.5361	977.4433	988.9812
1018.9435	1056.3373	1067.6654
1088.1543	1139.2519	1164.5233
1204.5587	1239.2086	1275.2612
1301.6227	1322.2951	1333.6382
1337.7078	1356.2313	1384.9040
1403.1661	1415.3868	1483.1416
1489.8913	1499.7972	1500.1305
1512.6354	1518.5937	1669.9694
3001.3109	3005.2370	3012.5837
3020.4800	3029.0507	3030.4382
3037.8056	3047.2210	3066.7197
3081.9708	3086.9029	3108.9816

Zero-point correction (Hartree): 0.180986

TS^{Nterm_Hshift}

E(RB+HF-LYP/6-311++G(d,p)) (Hartree): -420.607721452

Electronic state : 1-A

Cartesian coordinates (Angs):

C	-2.182405	1.164474	-0.007404
C	-0.967412	0.489868	0.521787
C	0.246020	0.473269	-0.427959
C	1.549966	0.143357	0.302442
C	2.749718	-0.011828	-0.638066
C	4.051878	-0.336367	0.099871
H	-3.000192	1.296679	0.695073
H	-2.090484	1.942114	-0.763354
H	-0.867152	1.418279	1.209996
H	0.334559	1.437602	-0.944704
H	0.051469	-0.288349	-1.192496
H	1.764189	0.932140	1.036148
H	1.400172	-0.776875	0.875038
H	2.880746	0.908484	-1.221165
H	2.535698	-0.804535	-1.365310
H	4.888402	-0.447042	-0.595691
H	4.312243	0.455372	0.809501
H	3.962318	-1.269242	0.664808
N	-2.954626	-0.343187	-0.811241
N	-2.651117	-1.321935	-0.350880
O	-1.202294	-0.585676	1.227872

Rotational constants (GHz): 3.9628900 0.6488900 0.6397300

Vibrational harmonic frequencies (cm⁻¹):

-549.7523	51.1169	72.6114
98.8089	137.0496	177.7359
236.6516	247.2961	267.4128
305.3537	344.3132	442.8858
507.4846	512.6910	627.4737
725.0930	742.6696	802.3785
870.3189	884.3909	909.2020
954.6982	1000.3615	1026.9697
1058.2334	1067.6504	1112.0219
1135.0235	1162.1359	1194.0097
1245.0015	1285.8860	1314.8632
1331.9688	1358.8155	1367.8060
1399.6761	1413.6936	1453.6835
1474.1243	1489.1643	1499.7093
1500.2900	1512.3503	2159.6158
2485.2497	2995.7695	2999.7950
3004.7003	3019.2266	3027.3892
3042.8453	3069.6065	3081.1005
3084.7834	3111.7960	3215.2481

Zero-point correction (Hartree): 0.174549

TS^{Nterm_diazo}

E(RB+HF-LYP/6-311++G(d,p)) (Hartree): -420.611799691

Electronic state : 1-A

Cartesian coordinates (Angs):

C	-2.286959	1.125812	0.256763
C	-0.840736	-0.049864	0.703338
C	0.341914	0.563814	-0.059920
C	1.654970	-0.150023	0.287587
C	2.869861	0.414787	-0.456924
C	4.176210	-0.304313	-0.107154
H	-2.814704	1.470891	1.144747
H	-1.962157	1.944474	-0.383571
H	-0.840997	0.221638	1.779567
H	0.428690	1.632688	0.177282
H	0.149658	0.474622	-1.135979
H	1.828356	-0.081052	1.369642
H	1.540053	-1.214955	0.061581
H	2.971041	1.484166	-0.232751
H	2.693398	0.345676	-1.537290
H	5.023746	0.117364	-0.654836
H	4.397813	-0.223742	0.961771
H	4.117865	-1.369232	-0.352254
N	-3.069839	0.223385	-0.442493
N	-3.131005	-0.866421	-0.738535
O	-1.202302	-1.237820	0.415893

Rotational constants (GHz): 4.6811500 0.6046100 0.5787400

Vibrational harmonic frequencies (cm-1):

-416.0424	42.9014	67.2823
91.9024	111.2643	144.9160
233.0621	242.6697	260.3534
299.0909	377.1172	427.4057
514.0181	559.9382	654.5103
690.2980	739.9703	806.2963
893.9165	916.9226	959.5052
982.8821	1016.6858	1058.9829
1070.7680	1103.4701	1130.3898
1155.0076	1175.6065	1238.4288
1272.5222	1313.0210	1323.3368
1335.5676	1356.7186	1391.3497
1413.3633	1456.8636	1461.6898
1470.7714	1487.7652	1497.7492
1499.6227	1510.8490	2159.6812
2852.5970	2991.9613	2998.4379
3004.6334	3018.6116	3026.3558
3037.3954	3064.1813	3080.3223
3083.3113	3096.2722	3175.1153

Zero-point correction (Hartree): 0.176206

TS^{Oterm_Hshift}

E(RB+HF-LYP/6-311++G(d,p)) (Hartree): -420.610867434

Electronic state : 1-A

Cartesian coordinates (Angs):

C	1.585918	0.047415	0.265689
C	0.415194	-0.803902	-0.250193
C	-0.910743	-0.450814	0.348023
C	-2.202545	-1.018262	-0.131647
N	-1.387776	1.394463	-0.157638
N	-2.494121	1.573847	-0.210399
O	-3.311106	-0.423099	0.251506
C	2.933016	-0.374102	-0.331474
C	4.101258	0.477560	0.172566
H	1.632046	-0.026805	1.358982
H	1.394671	1.099752	0.033548
H	0.351265	-0.754872	-1.342020
H	0.612463	-1.856923	-0.003135
H	-0.907714	-0.189833	1.406121
H	-2.029884	-1.962481	0.479517
H	-2.131836	-1.325537	-1.195151
H	2.879043	-0.309839	-1.424710
H	3.120261	-1.428958	-0.096399
H	4.203523	0.406818	1.259808
H	5.046626	0.155035	-0.271163
H	3.959067	1.532894	-0.078976

Rotational constants (GHz): 4.0360800 0.6296600 0.5665800

Vibrational harmonic frequencies (cm-1):

-379.2150	29.1025	63.2790
95.2497	119.4042	194.8568
221.1794	242.0270	280.4233
306.9576	314.8832	397.2207
457.8727	503.4743	580.4278
658.5219	732.8374	783.6879
898.7740	913.5304	1005.2144
1007.3693	1024.7338	1040.4751
1060.2484	1117.9718	1131.7635
1165.8228	1229.1267	1238.2041
1272.8718	1301.8587	1319.1288
1333.9531	1338.9856	1385.4395
1400.2514	1416.1768	1431.6717
1462.9742	1489.6966	1498.3021

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1500.0509	1511.6842	2171.2500
2665.4794	2876.9647	2996.4496
3006.2352	3014.9627	3022.5129
3032.4229	3050.0113	3068.9913
3084.4264	3090.3117	3130.3400

Zero-point correction (Hartree): 0.174708

TS^{Oterm_diazo}

E(RB+HF-LYP/6-311++G(d,p)) (Hartree): -420.610468955

Electronic state : 1-A

Cartesian coordinates (Angs):

C	1.656832	0.135826	0.290230
C	0.365576	-0.595610	-0.106203
C	-0.897519	-0.115318	0.583707
C	-2.460329	-1.151027	0.079023
N	-1.381574	1.111725	0.155143
N	-2.269748	1.637406	-0.308392
O	-3.373052	-0.381898	-0.346257
C	2.902889	-0.443317	-0.389943
C	4.190701	0.290747	-0.006225
H	1.780581	0.089883	1.379328
H	1.562457	1.198319	0.036160
H	0.216845	-0.548363	-1.190177
H	0.454076	-1.658515	0.146037
H	-0.833993	-0.099091	1.672901
H	-2.587329	-1.629592	1.069255
H	-1.934368	-1.802442	-0.646089
H	2.770406	-0.405456	-1.477699
H	2.995403	-1.504843	-0.130684
H	4.368995	0.241012	1.072404
H	5.059376	-0.145092	-0.506437
H	4.142330	1.347642	-0.285741

Rotational constants (GHz): 4.2892900 0.6121300 0.5621000

Vibrational harmonic frequencies (cm-1):

-369.2314	42.6231	71.1417
82.6679	108.4344	148.0499
197.0679	236.6567	252.5000
279.4381	371.9404	451.7749
531.8023	559.0604	597.2242
737.2430	789.1829	818.4464

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895.2897	917.2439	958.3277
1005.8107	1009.3265	1057.2724
1107.1664	1120.9064	1164.4136
1190.6979	1235.3234	1243.9148
1282.5955	1311.7414	1335.0223
1352.7266	1380.6164	1392.6613
1396.7037	1416.4986	1476.4192
1488.1705	1497.6378	1501.2460
1510.9715	1548.8147	2149.4759
2864.2257	2897.3375	3003.5926
3011.0433	3021.7330	3024.4386
3027.6121	3045.3606	3068.7350
3083.1180	3089.4826	3104.8853

Zero-point correction (Hartree): 0.176476