Supporting Information

The Element Effect Revisited: Factors Determining Leaving Group Ability in Activated Nucleophilic Aromatic Substitution Reactions

Nicholas A. Senger[†], Bo Bo[†], Qian Cheng[†], James R. Keeffe[†,*] Scott Gronert[‡] and Weiming Wu[†,*]

[†]Department of Chemistry and Biochemistry, San Francisco State University, San Francisco, CA 94132

[‡]Department of Chemistry, Virginia Commonwealth University, 1001 W. Main Street, Richmond, Virginia 23284.

***Corresponding Authors**: wuw@sfsu.edu, keeffe@sfsu.edu

Table of Contents

Reference 33: GAUSSIAN 03, Revision B.04, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.;. Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh PA, 2003.

* * *

Table S1. Rate constants for nucleophilic aromatic substitution reactions of 1-substituted-2,4-dinitrobenzenes with piperidine in methanol.

Substrates (L=)	Overall rate constant (0° C, $M^{-1}s^{-1}$)	Overall rate constant (10° C, $M^{-1}s^{-1}$)	Overall rate constant (20° C, $M^{-1}s^{-1}$)	Overall rate constant (30° C, $M^{-1}s^{-1}$)
Fluoro	1.10	2.46	3.50	4.93
Nitro	—	0.68	1.00	1.46
Chloro	—	0.00536	0.00970	0.0158
Bromo	—	0.00561	0.00928	0.0171
Iodo	—	0.00121	0.00217	0.00435

Table S2. MP2/6-31+G*//HF/6-31+G* energies (hartrees) and HF/6-31+G* zero point energies (kcal/mol) for substrates and transition states in reactions of 2,4-dinitrophenyl halides with dimethylamine (dma) and piperidine (pip).[a]

Compound	*E* (gas)	*E* (methanol)	ZPVE	iν (cm^{-1})
dimethylamine (dma)	-134.673944	-134.6795689	62.28	
piperidine (pip)	-251.0156561	-251.0219085	107.12	
2,4-DNP-F	-738.5129472	-738.5286788	66.54	
2,4-DNP-Cl	-1098.5229472	-1098.5376299	65.54	
2,4-DNP-Br	-3208.9357906	-3208.9508155	65.48	
2,4-DNP-F + dma, ts	-873.1876515	-873.2088138	130.68	424
2,4-DNP-Cl + dma, ts	-1233.1898624	-1233.2118589	129.70	445
2,4-DNP-Br + dma, ts	-3343.6084881	-3343.6304145	129.31	450
2,4-DNP-F + pip, ts	-989.5329467	-989.5549479	175.23	387
2,4-DNP-Cl + pip, ts	-1349.5360501	-1349.5597727	174.24	408
2,4-DNP-Br + pip, ts	-3459.9566101	-3459.9790140	173.86	411

[a]Energies in methanol were calculated as single-point energies using the optimized gas phase HF/6-31+G* geometries. ZPVE values (unscaled) and imaginary frequencies were calculated at HF/6-31+G*. The use of HF ZPVE values in place of MP2 ZPVE values has been found to cause insignificant differences in well over 100 ΔH calculations: see Gronert, S.; Keeffe, J. R.; *J. Org. Chem.* **2006**, *71*, 5959-5968 for example.

Table S3. MP2/6-31+G* energies (hartrees), ZPVE values (kcal/mol) and ΔH_{ADD} values (kcal/mol) for addition of fluoride ion to different positions of aryl fluorides.[a, b]

compound	*E*	ZPVE	ΔH_{ADD}
fluoride	-99.6238467	NA	
fluorobenzene	-330.5011021	62.12	
C-1 adduct	-430.130422	61.80	-3.7
4-nitrofluorobenzene	-534.5239818	64.42	
C-1 adduct	-634.1972231	65.15	-30.3
C-3 adduct	-634.1807831	65.31	-19.9
1,3-dinitrobenzene	-639.5159168	72.01	
C-6 adduct	-739.1968595	73.25	-34.7
2,4-dinitrofluorobenzene	-738.5324912	66.54	
C-1 adduct	-838.2354813	67.61	-48.7
C-3 adduct	-838.217464	67.74	-37.3
C-5 adduct	-838.219161	67.85	-38.2
C-6 adduct	-838.2017522	66.99	-28.1

[a]ZPVE values (unscaled) and imaginary frequencies were calculated at HF/6-31+G*. The use of HF ZPVE values in place of MP2 ZPVE values has been found to cause insignificant differences in well over 100 ΔH calculations: see Gronert, S.; Keeffe, J. R.; *J. Org. Chem.* **2006**, *71*, 5959-5968 for example. [b]Reaction at sites not listed in the table resulted not in covalent complex formation, but in hydrogen bonding between substrate and fluoride.

Table S4. MP2/6-31+G*//HF/6-31+G* energies (hartrees) and HF/6-31+G* zero point energies (kcal/mol) for substrates and transition states in reactions of 2,4-dinitrophenyl halides with thiolate anion.[a]

Compound	*E* (gas)	ZPVE	iν (cm^{-1})
thiolate (SH^-)	-398.2295244	3.98	
2,4-DNP-F	-738.5129472	66.54	
2,4-DNP-F, ts	-1136.7836338	71.17	269
2,4-DNP-Cl	-1098.5226959	65.55	
2,4-DNP-Cl, ts	-1496.7890490	70.09	298
2,4-DNP-Br	-3208.9357906	65.48	
2,4-DNP-Br, ts	-3607.2039139	69.75	314

[a]ZPVE values (unscaled) and imaginary frequencies were calculated at HF/6-31+G*. The use of HF ZPVE values in place of MP2 ZPVE values has been found to cause insignificant differences in well over 100 ΔH calculations: see Gronert, S.; Keeffe, J. R.; *J. Org. Chem.* **2006**, *71*, 5959-5968 for example.

Table S5. Cartesian coordinates for compounds in this study.

HF/6-31+G* except where noted

dimethylamine, HF/6-31+G*

```
H 1.268644   -0.970560   -0.762219
C 1.210898   -0.221021    0.020110
H 1.272519   -0.736018    0.982396
H 2.074560    0.426447   -0.077794
N 0.000034    0.554581   -0.144817
H 0.000157    1.329963    0.487493
C -1.210912   -0.220983    0.020099
H -1.272211   -0.736514    0.982133
H -1.269338   -0.970091   -0.762609
H -2.074481    0.426735   -0.076937
```

piperidine, HF/6-31+G*

```
H -0.765655   -2.227696    0.000000
N -0.678315   -1.230897    0.000000
C -0.015759   -0.778275    1.211852
C -0.015759   -0.778275   -1.211852
C -0.015759    0.747397    1.260446
H 1.016896   -1.139857    1.271134
H -0.548327   -1.181733    2.066396
H -0.548327   -1.181733   -2.066396
H 1.016896   -1.139857   -1.271134
C -0.015759    0.747397   -1.260446
H -1.043123    1.093574    1.339108
H 0.511006    1.087542    2.148551
C 0.629439    1.330659    0.000000
H 0.511006    1.087542   -2.148551
H -1.043123    1.093574   -1.339108
H 0.548908    2.414390    0.000000
H 1.693627    1.097115    0.000000
```

thiolate (SH^-)

```
H 0.000000   0.000000  -1.267911
S 0.000000   0.000000   0.085771
```

fluorobenzene

```
F  0.  0.  2.2928493848
C  0.  0.  0.9236174374
C  0.  0.  -1.8385931052
C  0.  1.2217247818  0.2609331681
C  0.  -1.2217247818  0.2609331681
C  0.  -1.2112332281  -1.1379456878
C  0.  1.2112332281  -1.1379456878
H  0.  2.146994419  0.8305650693
H  0.  -2.146994419  0.8305650693
H  0.  -2.154978488  -1.6784788847
```

```
H  0.  2.154978488  -1.6784788847
H  0.  0.  -2.9258125895

6,6-difluorocyclohexadienyl-
F  -1.7599988856  -0.0000000505  1.1030058258
C  -0.7462032102  -0.0000000577  -0.0000012857
F  -1.7600049448  -0.0000000885  -1.1030009134
C  0.0213254414  -1.2157881094  -0.0000035036
C  0.0213252911  1.2157882787  -0.0000035793
H  -0.5290404412  2.1554022606  -0.0000044372
C  1.4141604014  1.1992936705  0.000000206
H  -0.5290403737  -2.1554020538  -0.0000042333
C  1.4141604037  -1.1992936185  0.0000003322
C  2.1453456378  0.000000028  0.0000012198
H  1.9417246706  2.1559610951  -0.0000001328
H  1.9417245024  -2.1559611338  0.0000001126
H  3.2339823238  -0.00000003  0.0000041417

1,3-dinitrobenzene
H  -2.1671241609  0.  -2.0699118435
C  -1.2162205276  0.  -1.5474010116
C  1.1829058014  0.  -0.1542567672
C  -1.1829058014  0.  -0.1542567672
C  0.  0.  -2.2356947214
C  1.2162205276  0.  -1.5474010116
C  0.  0.  0.5788568669
N  -2.4626259463  0.  0.5872962431
H  0.  0.  -3.3226852202
H  2.1671241609  0.  -2.0699118435
H  0.  0.  1.6629076385
N  2.4626259463  0.  0.5872962431
O  -3.5101359632  0.  -0.0826922905
O  -2.4044738588  0.  1.8288406866
O  2.4044738588  0.  1.8288406866
O  3.5101359632  0.  -0.0826922905

6-fluoro-1,3-dinitrocyclohexadienide-
F  1.1470280336  0.3021958264  -2.3885631243
C  1.2819627611  0.7969500395  -0.9825204602
C  -0.0579540996  0.9725585491  -0.4070491045
H  1.8032531783  1.7425652418  -1.1353415733
C  2.0607396198  -0.2079067507  -0.2293190257
C  1.4532355009  -1.1713554294  0.5261861562
H  3.1387164154  -0.2335529957  -0.3777832332
C  -0.6912703465  -0.0135148367  0.3309540907
N  -0.7776644601  2.1585649645  -0.7516195225
C  0.0458990736  -1.1164177818  0.7559690068
H  2.0318747916  -1.9564623099  1.0042046159
H  -1.7323144297  0.0974011668  0.6162880964
N  -0.578156438  -2.1203765374  1.547721543
```

```
O  -1.9555234994  2.3082618731  -0.3390533357
O  -0.1912899446  3.0289724564  -1.4475314055
O  -1.8170272783  -2.0568081936  1.7618971376
O  0.1351268439  -3.0552905447  2.0061453647

4-nitrofluorobenzene
F  -0.0004734247  3.4202882906  0.
C  -0.0002525376  2.0578589447  0.
C  -0.0001369118  1.3925700858  1.2219215649
H  -0.00023786  1.9603793374  2.1480052336
C  0.0000841729  -0.0028522357  1.2238853406
C  0.0002342355  -0.672836658  0.
H  0.0001699045  -0.5631133207  2.1529400353
C  0.0000841729  -0.0028522357  -1.2238853406
N  0.0004577319  -2.1447261821  0.
C  -0.0001369118  1.3925700858  -1.2219215649
H  0.0001699045  -0.5631133207  -2.1529400353
H  -0.00023786  1.9603793374  -2.1480052336
O  0.0001209556  -2.721924456  -1.1027270675
O  0.0001209556  -2.721924456  1.1027270675

4-nitrophenylfluoride, C3 fluoride adduct
C  -1.9467899079  0.317288479  -0.6141750432
C  -1.4063543225  1.4123587722  0.0959282146
F  -3.2408759595  0.4689031763  -1.0977900445
C  0.6782871248  0.1851649362  0.1180320974
C  -0.0669110634  1.3312070611  0.4399371582
H  -2.017676507  2.2811394608  0.3210043525
N  2.0717765395  0.1741355638  0.3532934091
H  0.4385193723  2.167104999  0.9161137272
O  2.725659937  -0.8814222433  0.1167064027
O  2.6405861316  1.2253083197  0.7703505601
C  -1.2653338207  -0.8238316456  -0.9226300484
C  0.0397916851  -1.0613402652  -0.2943194206
F  -0.2046349878  -1.9422886043  0.9449802248
H  0.7014219656  -1.7179648159  -0.858396619
H  -1.7412088027  -1.6049323754  -1.5095803979

4-nitrofluorobenzene + F-, C1 fluoride adduct
F 1.098481   -2.788469    0.000000
C -0.000158   -1.847212    0.000000
C 0.000182   -1.065801    1.234004
H 0.000202   -1.622148    2.168885
C 0.000182    0.306360    1.222031
C 0.000180    1.021891    0.000000
H 0.000315    0.863386    2.155001
C 0.000182    0.306360   -1.222031
N 0.000206    2.426432    0.000000
C 0.000182   -1.065801   -1.234004
H 0.000315    0.863386   -2.155001
```

```
H 0.000202   -1.622148   -2.168885
O 0.000246    3.048848   -1.105344
O 0.000246    3.048848    1.105344
F -1.099696   -2.787515    0.000000
```

1-fluoro-2,4-dinitrobenzene

```
C  0.9696723272  0.  -1.3886845063
C  0.4259664659  0.  1.3136725507
C  -0.3595115292  0.  -0.9443288646
C  2.0183278118  0.  -0.468716175
C  1.7569737632  0.  0.8978455967
C  -0.6382903703  0.  0.4225278856
N  -1.5081824989  0.  -1.8716733205
H  3.0362669859  0.  -0.8488744743
H  2.5611271677  0.  1.6262751915
H  -1.6657564309  0.  0.7694516599
N  0.1301317864  0.  2.7594295034
O  -1.2687110592  0.  -3.0906943936
O  -2.6402250985  0.  -1.3593037763
O  -1.0648498229  0.  3.100284758
O  1.1003131512  0.  3.5371857702
F  1.295963232  0.  -2.6949803829
```

2,4-dinitrophenyl fluoride, C1 fluoride adduct

```
C -0.028910   -1.949257   -0.000105
C -1.194208   -1.044986    0.000004
F -2.027050   -1.376702   -1.101977
C -0.812607    0.381443   -0.000092
F -2.026808   -1.376680    1.102188
H -0.268078   -3.010321   -0.000095
C 1.261649   -1.512770   -0.000159
N -1.851410    1.371989   -0.000065
C 0.504605    0.806205   -0.000140
H 2.084396   -2.221389   -0.000215
H 0.714897    1.870688   -0.000173
C 1.546051   -0.115962   -0.000199
N 2.893637    0.331708   -0.000247
O -3.042654    0.982933    0.000253
O -1.530954    2.586538   -0.000133
O 3.813048   -0.533114    0.000248
O 3.135365    1.567086    0.000245
```

2,4-dinitrophenyl fluoride, C3 adduct

```
C 0.118655    2.154056    0.158847
C 1.202644    1.279838    0.075336
F 2.443007    1.852136    0.085432
C 1.038574   -0.095557   -0.055875
H 0.300733    3.217330    0.279540
C -1.168106    1.629141    0.018089
N 2.118048   -0.991584   -0.316630
```

```
H -2.030494    2.286061   -0.058647
C -1.351866    0.259401   -0.078670
N -2.657175   -0.266365   -0.315427
O 3.224822   -0.532880   -0.692398
O 1.901110   -2.223208   -0.185176
O -3.613161    0.530178   -0.505323
O -2.804204   -1.515000   -0.340308
C -0.275576   -0.688726    0.243506
H -0.402120   -1.665029   -0.218898
F -0.348421   -1.000398    1.696863

2,4-dinitrophenyl fluoride, C5 adduct
C -0.044298   -1.882076   -0.451007
C -1.183379   -1.147534   -0.324884
F -2.372051   -1.749114   -0.638621
C -1.161569    0.255693   -0.054315
H -0.118411   -2.923407   -0.752137
N -2.342183    1.017696    0.183488
C 1.241612    0.150395   -0.149919
N 2.499523    0.827926   -0.190157
O -3.391994    0.414986    0.519437
O -2.284691    2.268137    0.060544
O 3.544782    0.131396   -0.266643
O 2.524874    2.083890   -0.172034
C 0.080247    0.889189   -0.014708
H 0.127038    1.968183    0.091768
C 1.256915   -1.316589   -0.058133
H 2.102042   -1.766030   -0.579646
F 1.539497   -1.704201    1.357961

2,4-dinitrophenyl fluoride, C6 adduct
C 1.140984    0.948767   -0.317525
F 2.395243    1.457932   -0.485449
C 0.964321   -0.402561   -0.028634
N 2.100250   -1.306003    0.047682
C -1.382734   -0.090403   -0.093986
N -2.726844   -0.660685   -0.101467
O 2.059060   -2.209366    0.910920
O 3.039042   -1.151809   -0.761042
O -3.682655    0.071973   -0.436538
O -2.867539   -1.858002    0.232282
C -0.312121   -0.959469    0.117006
H -0.446796   -2.006049    0.359673
C -1.223621    1.262421   -0.405943
H -2.094646    1.875963   -0.607353
C 0.058117    1.868284   -0.264357
F 0.143416    2.595685    1.347842
H 0.226723    2.829740   -0.741712
```

1-fluoro-2,4-dinitrobenzene + dimethylamine, ts, HF/6-31+G*

N	3.234992	-0.218913	0.170351
C	1.836825	-0.243124	-0.145530
C	1.254326	-1.414796	-0.681007
C	1.077681	0.886540	0.020976
C	-0.277174	0.861249	-0.268181
H	1.521291	1.796128	0.371437
H	1.878377	-2.262053	-0.886889
C	-0.065099	-1.457300	-0.974663
N	-1.038961	2.052076	-0.050011
H	-0.501142	-2.315594	-1.448752
O	3.862360	-1.225649	-0.009186
O	3.701288	0.797200	0.601025
C	-0.932799	-0.337692	-0.706522
N	-2.135189	-0.871780	0.663495
F	-1.927256	-0.202597	-1.591182
C	-1.470411	-1.010652	1.958701
C	-2.915254	-2.060300	0.307373
H	-2.738691	-0.068671	0.678767
O	-2.237715	1.941849	0.039127
O	-0.459477	3.089774	0.062064
H	-0.977893	-0.085127	2.217845
H	-0.732533	-1.799674	1.896444
H	-2.252628	-2.911122	0.219209
H	-3.418264	-1.896926	-0.633556
H	-2.186176	-1.255834	2.735568
H	-3.653144	-2.276366	1.072593

1-fluoro-2,4-dinitrobenzene + piperidine, ts, HF/6-31+G*

N	-3.548757	-1.190241	-0.351809
C	-2.333482	-0.614424	0.145711
C	-1.589284	-1.288355	1.141177
C	-1.923445	0.613415	-0.305581
C	-0.741200	1.165194	0.162341
H	-2.509856	1.157797	-1.017319
H	-1.967631	-2.206328	1.545881
C	-0.435670	-0.763211	1.612475
N	-0.334118	2.434245	-0.358467
H	0.100635	-1.230822	2.415626
O	-3.877428	-2.257894	0.085891
O	-4.167039	-0.582953	-1.179133
C	0.101736	0.464683	1.085642
N	1.725850	0.020510	0.159140
F	0.767983	1.193259	1.985581
C	1.480882	-0.702462	-1.096535
C	2.714402	-0.662374	1.010610
H	2.051006	0.949354	-0.047269
O	0.822801	2.749840	-0.227145
O	-1.144525	3.107787	-0.920689
H	0.773151	-0.131902	-1.682182

H 1.011985 -1.646016 -0.838239
C 2.767100 -0.940556 -1.886066
C 4.036702 -0.895216 0.279911
H 2.284406 -1.612198 1.309972
H 2.862301 -0.065506 1.899369
H 2.532713 -1.522247 -2.772348
C 3.817045 -1.651409 -1.030997
H 3.157370 0.014629 -2.231496
H 4.707667 -1.443626 0.934518
H 4.509270 0.064109 0.078723
H 4.751030 -1.739195 -1.576688
H 3.484087 -2.664922 -0.814354

2,4-dinitrophenyl fluoride + SH^-, transition state, HF/6-31+G*
S -2.032759 -1.678186 1.408809
C -1.027625 -0.633875 -0.672602
F -2.153433 -0.784010 -1.332271
C -0.021650 -1.599682 -0.969211
C 1.279285 -1.362245 -0.689319
H -0.354230 -2.538815 -1.364188
C 1.660299 -0.116182 -0.139797
H 2.024833 -2.107070 -0.882338
N 3.034562 0.134833 0.167528
C 0.730639 0.878230 0.050182
H 1.023485 1.833007 0.431001
C -0.596733 0.656901 -0.276369
N -1.522912 1.736424 -0.068416
O -1.083550 2.774905 0.363187
O -2.669032 1.571553 -0.348822
O 3.341592 1.207051 0.615039
O 3.828909 -0.745288 -0.039718
H -0.859236 -1.783513 2.036458

1-chloro-2,4-dinitrobenzene
C 0.8611778853 0. -1.1484829572
C 0.3015746862 0. 1.5826048948
C -0.4677581167 0. -0.6845572168
C 1.8923883836 0. -0.1935377561
C 1.6324927076 0. 1.1717952387
C -0.7528009642 0. 0.6826396343
N -1.6525136019 0. -1.5787106684
H 2.9192168105 0. -0.5491985727
H 2.4374437187 0. 1.8994881615
H -1.7813315061 0. 1.0245486588
N -0.0043235047 0. 3.0260087143
O -1.4590514905 0. -2.8047992838
O -2.76862261 0. -1.0322947066
O -1.2016193847 0. 3.3591475106
O 0.9612010458 0. 3.8098632867
Cl 1.3508719264 0. -2.8014135323

1-chloro-2,4-dinitrobenzene + dimethylamine, ts, HF/6-31+G*

N	3.388071	-0.225751	0.035246
C	1.970114	-0.253784	-0.163103
C	1.338450	-1.439259	-0.602030
C	1.227096	0.881975	0.025498
C	-0.147249	0.856297	-0.149290
H	1.697869	1.800042	0.312474
H	1.936336	-2.301553	-0.823150
C	0.000872	-1.481522	-0.792574
N	-0.866524	2.062583	0.128750
H	-0.458822	-2.357678	-1.206038
O	3.995928	-1.242426	-0.157205
O	3.891661	0.803063	0.387622
C	-0.854251	-0.345116	-0.510599
N	-1.921220	-0.838213	0.985184
Cl	-2.188415	-0.190943	-1.681742
C	-1.136650	-0.766387	2.220642
C	-2.582882	-2.139479	0.845537
H	-2.604612	-0.102014	0.985319
O	-2.040765	1.965104	0.390012
O	-0.273109	3.099041	0.129428
H	-0.774190	0.238152	2.369938
H	-0.297039	-1.444711	2.146143
H	-1.832790	-2.917507	0.807182
H	-3.172423	-2.161318	-0.057504
H	-1.745613	-1.047896	3.072373
H	-3.230671	-2.324435	1.695284

1-chloro-2,4-dinitrobenzene + piperidine, ts, HF/6-31+G*

N	-3.609641	-1.264426	-0.110417
C	-2.375602	-0.617811	0.222082
C	-1.620484	-1.059143	1.332415
C	-1.948738	0.462051	-0.504555
C	-0.747189	1.081274	-0.196894
H	-2.534541	0.837851	-1.318371
H	-2.000848	-1.853858	1.943634
C	-0.454064	-0.458959	1.657329
N	-0.333340	2.162556	-1.040025
H	0.072455	-0.745133	2.546507
O	-3.949300	-2.195113	0.566893
O	-4.233357	-0.850818	-1.046508
C	0.104763	0.617510	0.864915
N	1.692485	-0.089285	0.041145
Cl	0.920500	1.844814	1.862693
C	1.353114	-0.954927	-1.100474
C	2.613061	-0.762677	0.974254
H	2.111501	0.757074	-0.303678
O	0.841454	2.435033	-1.064869
O	-1.154888	2.718139	-1.706403

```
H 0.700107   -0.405378   -1.761496
H 0.797426   -1.799489   -0.707855
C 2.596422   -1.427640   -1.853065
C 3.895876   -1.222452    0.281225
H 2.086403   -1.616391    1.385301
H 2.837115   -0.083848    1.783622
H 2.286552   -2.095348   -2.651059
C 3.585056   -2.120690   -0.915745
H 3.072987   -0.572247   -2.327359
H 4.514882   -1.743179    1.005785
H 4.460466   -0.351329   -0.045075
H 4.497396   -2.370986   -1.447443
H 3.158512   -3.058630   -0.565025
```

6-mercapto-6-chloro-1,3-dinitrocyclohexadienide-, ts, HF

```
S -1.764362   -1.390690    1.822913
C -0.942068   -0.550704   -0.449096
Cl -2.471719   -0.741334   -1.265151
C -0.008824   -1.598705   -0.736810
C 1.322839   -1.436333   -0.573834
H -0.413064   -2.543834   -1.037379
C 1.825841   -0.184141   -0.156861
H 1.997462   -2.246892   -0.762900
N 3.233796   -0.005368    0.027561
C 0.978173    0.880247    0.019348
H 1.359950    1.838056    0.299380
C -0.385793    0.728547   -0.182377
N -1.192446    1.902273    0.038803
O -0.617413    2.957231    0.172291
O -2.376756    1.792861    0.075490
O 3.641285    1.072307    0.368776
O 3.952012   -0.950183   -0.171380
H -0.518825   -1.483123    2.293655
```

1-bromo-2,4-dinitrobenzene

```
C  0.6388133795  0.  -0.6846488895
C  0.0804263585  0.  2.0457298648
C  -0.688282513  0.  -0.2208376027
C  1.6711847624  0.  0.2698015195
C  1.4112291122  0.  1.6357548294
C  -0.9746693978  0.  1.1463878075
N  -1.8767056202  0.  -1.1141763653
H  2.6996038414  0.  -0.0807679375
H  2.2161110172  0.  2.3636031522
H  -2.0027212959  0.  1.4896662486
N  -0.2255836328  0.  3.4892706906
O  -1.6881769991  0.  -2.340660587
O  -2.9908567717  0.  -0.5637226676
O  -1.4227987509  0.  3.8226623862
O  0.7399376418  0.  4.2730364465
```

```
Br  1.1961708582  0.  -2.4880517583

1-bromo-2,4-dinitrobenzene + dimethylamine, ts, HF/6-31+G*
N 3.687129   -0.277853   -0.210365
C 2.254275   -0.282913   -0.218152
C 1.551434   -1.476564   -0.495482
C 1.562768    0.878115    0.005266
C 0.176140    0.874645    0.014401
H 2.082602    1.798546    0.176559
H 2.099730   -2.365328   -0.739039
C 0.199113   -1.494580   -0.506244
C -0.586807   -0.325043   -0.180330
N -0.479437    2.109465    0.327008
H -0.324664   -2.384305   -0.795057
Br -2.192806   -0.191448   -1.282932
N -1.482786   -0.718769    1.464710
C -0.568996   -0.549019    2.597418
C -2.127197   -2.035691    1.494715
H -2.177155    0.005952    1.490541
O 4.246924   -1.317276   -0.424537
O 4.249749    0.755828    0.015047
O 0.130078    3.130224    0.210236
O -1.614145    2.050785    0.732275
H -0.215789    0.468900    2.638693
H 0.272851   -1.217867    2.475672
H -1.367545   -2.804686    1.462549
H -2.789961   -2.147299    0.651215
H -1.073245   -0.781276    3.528950
H -2.698183   -2.152056    2.409363

1-bromo-2,4-dinitrobenzene + piperidine, ts, HF/6-31+G*
N -3.854889    1.120851   -0.345607
C -2.552638    0.522943   -0.383108
C -1.766732    0.611711   -1.553941
C -2.082474   -0.164270    0.704010
C -0.814289   -0.726476    0.679535
H -2.684411   -0.273657    1.582834
H -2.170878    1.090213   -2.424238
C -0.536131    0.053479   -1.600198
C 0.054547   -0.596163   -0.452785
N -0.361725   -1.373867    1.874943
H 0.021783    0.055592   -2.515499
Br 1.109541   -2.154801   -0.965678
N 1.547227    0.511075    0.094435
C 1.082746    1.681646    0.856057
C 2.445827    0.907034   -1.002806
H 2.023451   -0.116698    0.718295
O -4.227069    1.702006   -1.327186
O -4.498874    1.017021    0.659570
O -1.170627   -1.708847    2.688399
```

O 0.827185 -1.515581 2.017311
C 2.246066 2.499280 1.417008
H 0.445238 1.337297 1.656425
H 0.480028 2.283041 0.184089
C 3.654391 1.693679 -0.496100
H 1.868266 1.516132 -1.689096
H 2.761501 0.017756 -1.526666
H 2.767404 1.908224 2.167068
H 1.845565 3.369659 1.927655
C 3.218390 2.914968 0.313034
H 4.274299 1.042948 0.117442
H 4.259211 1.989917 -1.348012
H 4.082422 3.414220 0.739584
H 2.734767 3.633187 -0.346514

2,4-dinitrophenyl bromide + SH^-, transition state, HF/6-31+G*
S -1.299411 -0.928339 2.256148
C -0.634979 -0.413555 -0.166755
Br -2.407634 -0.573113 -0.844768
C 0.171786 -1.568882 -0.413762
C 1.522935 -1.513048 -0.398696
H -0.331914 -2.504100 -0.549057
C 2.165489 -0.275415 -0.179450
H 2.106171 -2.399117 -0.549093
N 3.595461 -0.209755 -0.142617
C 1.431087 0.876043 -0.052709
H 1.915558 1.818972 0.081098
C 0.045779 0.827227 -0.115104
N -0.634335 2.085265 0.075112
O 0.025016 3.094391 -0.015698
O -1.799878 2.081015 0.311116
O 4.121570 0.855303 0.037198
O 4.210258 -1.232432 -0.295625
H -0.028244 -1.112392 2.621009

^{1}H NMR of 1,2,4-trinitrobenzene in $CDCl_3$ with 0.05% v/v TMS