

# Diradical Ring Closure Reactions Displaying Woodward-Hoffmann Behaviour and Torquoselectivity

Roberto Villar López Olalla Nieto Faza and Carlos Silva López<sup>†</sup>

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1. Departamento de Química Orgánica, Universidade de Vigo, Lagoas Marcosende,  
36310, Vigo, Galicia, Spain

<sup>†</sup>*Correspondence: carlos.silva@uvigo.es*

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## 1 Gaussian reference

See References section at the end of this document (cite 1)

## 2 Cartesian Coordinates

Geometries: M06/6-31+G(d,p)

SCF energies: M06/6-31+G(d,p)

### 2.1 Disrotatory vs Conrotatory

#### A1

SCF Energy: -233.139763340

$S^2$  before (1.0447) and after higher multiplicity projection (0.4006)

Num. Imaginary Frequencies: 0

C	0.918273	-0.005994	-0.103220
C	2.003258	-0.600779	0.530968
C	-0.241697	-0.848811	-0.470613
C	-1.570283	-0.557166	-0.180071
C	-2.034259	0.514562	0.560401
C	0.926333	1.343170	-0.438228
H	2.887972	-0.018881	0.781748
H	0.104731	1.797581	-0.985523
H	1.782999	1.967232	-0.190113
H	-0.018061	-1.784515	-0.983759
H	-2.312033	-1.262061	-0.559449
H	-3.098235	0.657116	0.727708
H	-1.353000	1.228967	1.018027
H	1.995878	-1.655331	0.795946

#### A2<sub>Conrot</sub>

SCF Energy: -233.128315813

$S^2$  before (0.6607) and after higher multiplicity projection (0.1235)

Num. Imaginary Frequencies: 1

Imaginary Frequency: -461.2748

C	2.065017	-0.302916	0.450420
C	0.859791	-0.035924	-0.130635
C	0.460962	1.270186	-0.544139
C	-0.184407	-1.051705	-0.354153
H	2.823457	0.469815	0.551790
H	2.312533	-1.300840	0.803023
H	0.065985	-2.041886	-0.728618
C	-1.463048	-0.673267	-0.069107
C	-1.727190	0.570353	0.569572
H	1.067378	2.136246	-0.275896
H	-0.251129	1.396360	-1.353718
H	-2.301114	-1.304839	-0.368199
H	-2.697874	1.053337	0.471108
H	-1.085992	0.931445	1.368755

**A2**<sub>Disrot</sub>

SCF Energy: -233.118708378

 $S^2$  before (0.7005) and after higher multiplicity projection (0.1010)

Num. Imaginary Frequencies: 1

Imaginary Frequency: -427.6844

C	-2.143902	-0.339391	0.295924
C	-0.897607	0.028843	-0.110250
C	-0.512232	1.397349	-0.218552
C	0.117150	-1.014333	-0.309437
C	1.417362	-0.776755	-0.023045
C	1.973470	0.514172	0.295045
H	-2.895765	0.403658	0.554005
H	-2.425602	-1.387795	0.374213
H	-0.222302	-2.027634	-0.522178
H	2.078638	-1.643158	0.075777
H	2.683751	0.585874	1.119906
H	2.031223	1.318888	-0.427445
H	-1.106007	2.165125	0.274638
H	0.130621	1.725736	-1.027029

**A3**

SCF Energy: -233.233997477

Num. Imaginary Frequencies: 1

C	0.100449	-1.186373	0.036176
C	1.527683	-0.603320	-0.034314
C	1.311377	0.881998	0.001523
C	0.008666	1.203200	0.019366
C	-0.830683	0.010213	0.006786
C	-2.169766	-0.018561	-0.024310
H	-0.398118	2.211452	0.032868
H	2.130658	1.596568	0.000036
H	2.160958	-0.941583	0.797200
H	-2.720972	-0.956519	-0.038142
H	-2.752515	0.900061	-0.036615
H	-0.109571	-1.871412	-0.793603
H	-0.049916	-1.759149	0.959717
H	2.053116	-0.902368	-0.952818

**B1**

SCF Energy: -249.184161625

 $S^2$  before (0.9827) and after higher multiplicity projection (0.3069)

Num. Imaginary Frequencies: 0

N	1.971607	-0.641048	0.522195
C	0.941797	-0.062363	-0.045369
C	-0.222905	-0.911410	-0.371150
C	-1.554978	-0.560778	-0.170124
C	-2.012436	0.561166	0.492470
C	0.905237	1.296941	-0.451669
H	0.061893	1.706720	-1.001782
H	1.766061	1.941183	-0.276457
H	0.016457	-1.902471	-0.753368
H	-2.302987	-1.258977	-0.548633
H	-3.076104	0.768651	0.570683
H	-1.333480	1.250445	0.990690
H	2.726624	0.040442	0.638554

**B2**<sub>Conrot</sub>

SCF Energy: -249.164464719

 $S^2$  before (0.7431) and after higher multiplicity projection (0.1406)

Num. Imaginary Frequencies: 1

Imaginary Frequency: -505.1392

C	2.091979	-0.238406	0.386341
C	0.837673	-0.009554	-0.115599
C	-0.181067	-1.070867	-0.250852
C	-1.465307	-0.692423	-0.032059
C	-1.759652	0.622881	0.435774
N	0.381781	1.189718	-0.572902
H	2.823891	0.563173	0.454352
H	2.411283	-1.240126	0.661624
H	0.098268	-2.084479	-0.528028
H	-2.287407	-1.367966	-0.271991
H	-2.684107	1.124015	0.156517
H	-1.186137	1.074028	1.241040
H	1.009989	1.933538	-0.244828

**B2***Disrot*

SCF Energy: -249.169673072

 $S^2$  before (0.5159) and after higher multiplicity projection (0.0569)

Num. Imaginary Frequencies: 1

Imaginary Frequency: -500.8056

C	-2.181983	-0.225772	0.164887
C	-0.846870	0.070087	-0.069912
C	0.089998	-1.046487	-0.185080
C	1.404783	-0.786677	0.042825
C	1.922764	0.538432	0.092558
N	-0.320724	1.293254	-0.159029
H	-2.894666	0.555242	0.423011
H	-2.565589	-1.231905	0.010682
H	-0.295018	-2.062367	-0.241707
H	2.066278	-1.611159	0.319355
H	2.703318	0.771096	0.820821
H	1.827152	1.222492	-0.738915
H	-0.928551	2.006325	0.248287

**B3**

SCF Energy: -249.273672860

Num. Imaginary Frequencies: 0

C	0.803225	0.004863	-0.026738
N	-0.067009	-1.080483	-0.117072
C	-1.451034	-0.666760	0.040569
C	-1.338959	0.826630	0.014342
C	-0.051084	1.191827	-0.021851
C	2.148246	-0.025800	0.037900
H	0.343924	2.202085	-0.038467
H	-2.201179	1.484752	0.026702
H	-2.089467	-1.052566	-0.770074
H	2.705635	-0.958423	0.031828
H	2.708235	0.901946	0.091126
H	-1.892201	-1.017263	0.990566
H	0.231752	-1.981711	0.222487

**C1**

SCF Energy: -269.068061385

 $S^2$  before (0.8037) and after higher multiplicity projection (0.1404)

Num. Imaginary Frequencies: 0

O	2.001441	-0.525209	0.491012
C	0.969768	-0.060474	-0.010374
C	0.869789	1.313232	-0.430505
C	-0.179589	-0.923906	-0.326170
C	-1.528121	-0.564323	-0.202305
C	-1.994815	0.532902	0.477789
H	-0.005292	1.701095	-0.944543
H	1.743977	1.949754	-0.312065
H	0.077788	-1.937800	-0.632081
H	-2.263174	-1.238204	-0.645074
H	-3.053774	0.777033	0.488667
H	-1.333248	1.165209	1.066384

**C2<sub>Conrot</sub>**

SCF Energy: -269.114851481

 $S^2$  before (0.9693) and after higher multiplicity projection (0.2798)

Num. Imaginary Frequencies: 0

C	-2.090103	0.149205	0.392379
C	-0.842232	-0.041758	-0.114430
C	0.149912	1.039457	-0.231199
C	1.433032	0.690261	-0.019436
C	1.761055	-0.616522	0.423582
O	-0.402253	-1.130271	-0.558585
H	-2.797367	-0.667516	0.452341
H	-2.428873	1.133671	0.684350
H	-0.153166	2.046445	-0.485688
H	2.234898	1.387763	-0.241707
H	2.697934	-1.082816	0.146397
H	1.194613	-1.099232	1.207616

**C2**<sub>Disrot</sub>

SCF Energy: -269.058314010

 $S^2$  before (0.1895) and after higher multiplicity projection (0.0035)

Num. Imaginary Frequencies: 1

Imaginary Frequency: -515.3312

C	-2.184586	0.131584	-0.093275
C	-0.821831	-0.101231	0.026732
O	-0.283244	-1.260753	0.005677
C	0.051903	1.052918	0.137162
C	1.384041	0.788216	-0.058498
C	1.856617	-0.529352	0.011878
H	-2.862905	-0.689021	-0.309028
H	-2.601148	1.104611	0.154258
H	-0.358857	2.059190	0.181489
H	2.041711	1.572867	-0.435343
H	2.688131	-0.833274	-0.627779
H	1.642149	-1.181157	0.846988

**C3**

SCF Energy: -269.139493631

Num. Imaginary Frequencies: 0

C	-0.782680	0.023048	-0.000015
O	0.011302	-1.093157	-0.000134
C	1.382764	-0.707428	0.000092
C	1.358105	0.785362	-0.000002
C	0.084695	1.193176	-0.000039
C	-2.120185	-0.041737	0.000061
H	-0.287058	2.211559	-0.000087
H	2.249312	1.402868	-0.000003
H	1.875193	-1.131559	0.888457
H	-2.638444	-0.994481	0.000034
H	-2.701134	0.874000	0.000146
H	1.875526	-1.131651	-0.888053

## 2.2 Torquoselectivity

### **A**lin<sub>CHO</sub>

SCF Energy: -346.411579196

 $S^2$  before (1.0283) and after higher multiplicity projection (0.4180)

Num. Imaginary Frequencies: 0

C	2.388723	-0.665218	-0.878066
C	1.521726	-0.186882	0.093449
C	1.167171	-0.941333	1.207099
C	1.014682	1.201194	-0.005115
C	-0.296340	1.615532	0.072688
C	-1.478398	0.854456	0.082577
H	2.817544	-1.661539	-0.795613
H	0.517473	-0.541471	1.981532
H	1.560479	-1.947394	1.339649
H	1.776748	1.975964	-0.102637
H	-0.440891	2.694794	0.146328
H	-2.414272	1.357443	0.329589
C	-1.643171	-0.530606	-0.318592
H	2.659119	-0.064803	-1.743082
O	-2.720534	-1.106111	-0.242150
H	-0.758291	-1.046973	-0.742799

### **A**lin<sub>Me</sub>

SCF Energy: -272.424181363

 $S^2$  before (1.0535) and after higher multiplicity projection (0.4294)

Num. Imaginary Frequencies: 0

C	2.194223	0.004685	-0.886116
C	1.227915	0.056354	0.109959
C	1.149224	-0.921417	1.096427
C	0.306693	1.216652	0.163464
C	-1.081555	1.194686	0.183183
C	-1.968514	0.146104	-0.043017
H	2.914519	-0.810761	-0.920881
H	0.422496	-0.852376	1.902332
H	1.830386	-1.770868	1.090607
H	0.788956	2.192710	0.238169
H	-1.551460	2.159942	0.383547
H	-3.025627	0.375740	0.098343
C	-1.648651	-1.234846	-0.502371
H	2.255466	0.771219	-1.654974
H	-2.462617	-1.628715	-1.122119
H	-0.721955	-1.275889	-1.083814
H	-1.526177	-1.934311	0.339615

**A1in<sub>NH2</sub>**

SCF Energy: -288.476544885

 $S^2$  before (0.9826) and after higher multiplicity projection (0.2622)

Num. Imaginary Frequencies: 0

C	2.373315	0.132511	-0.672339
C	1.234320	0.001757	0.125525
C	0.995694	-1.172327	0.831645
C	0.328486	1.163643	0.206851
C	-1.058523	1.177132	0.227364
C	-1.983154	0.172416	-0.059214
H	3.075486	-0.691961	-0.783096
H	0.195125	-1.239180	1.564562
H	1.675643	-2.017076	0.740687
H	0.826601	2.129699	0.298785
H	-1.518318	2.140627	0.447724
H	-3.042336	0.395689	0.048292
N	-1.705935	-1.063374	-0.574054
H	2.581064	1.054845	-1.210034
H	-2.435544	-1.759415	-0.550827
H	-0.757006	-1.420402	-0.496708

**A1in<sub>NO2</sub>**

SCF Energy: -437.554243738

 $S^2$  before (1.0229) and after higher multiplicity projection (0.3425)

Num. Imaginary Frequencies: 0

C	2.825383	-0.470201	-0.553938
C	1.707874	-0.154927	0.195646
C	1.169368	1.205249	0.030749
C	-0.132559	1.671646	0.100262
C	-1.374240	1.048714	0.115572
N	-1.643995	-0.306783	-0.231890
O	-0.813285	-0.934120	-0.883443
C	1.141510	-1.060102	1.095559
O	-2.726937	-0.758479	0.149532
H	3.253664	-1.469109	-0.519892
H	0.299032	-0.795301	1.728756
H	1.550206	-2.062517	1.192116
H	1.926936	1.976719	-0.119722
H	-0.222244	2.757017	0.172797
H	-2.282392	1.587239	0.364866
H	3.280534	0.251942	-1.227503

**A1in<sub>OMe</sub>**

SCF Energy: -347.603697258

$S^2$  before (1.0446) and after higher multiplicity projection (0.3580)

Num. Imaginary Frequencies: 0

C	2.676643	-0.537522	-0.797550
C	1.643530	-0.235020	0.080979
C	1.149536	-1.190326	0.962476
C	1.136918	1.154457	0.108854
C	-0.175459	1.599298	0.163270
C	-1.379943	0.919720	0.063524
H	3.105547	-1.537199	-0.828862
H	0.373483	-0.952347	1.683767
H	1.536658	-2.207486	0.943396
H	1.906102	1.927573	0.085042
H	-0.309259	2.676731	0.264425
H	-2.328279	1.456513	0.133581
O	-1.463607	-0.409340	-0.139584
H	3.075173	0.207824	-1.481967
C	-2.772095	-0.903679	-0.335035
H	-2.691399	-1.985756	-0.454108
H	-3.410764	-0.680811	0.531513
H	-3.223186	-0.471889	-1.239217

**A1out**<sub>CHO</sub>

SCF Energy: -346.418238384

$S^2$  before (1.0491) and after higher multiplicity projection (0.4185)

Num. Imaginary Frequencies: 0

C	2.975828	-0.043183	0.809123
C	1.893609	0.130469	-0.047727
C	1.636996	1.347191	-0.666197
C	1.035434	-1.039918	-0.333590
C	-0.343582	-1.057280	-0.304788
C	-1.181275	-0.008842	0.079698
H	3.641318	0.786612	1.036502
H	0.831078	1.464660	-1.385428
H	2.277422	2.205699	-0.474766
H	1.553731	-1.971916	-0.562776
H	-0.832508	-1.993639	-0.585643
C	-2.618470	-0.158771	0.049479
H	-0.785664	0.941719	0.437226
H	3.177504	-1.001164	1.282102
O	-3.408787	0.712608	0.380586
H	-2.983822	-1.150835	-0.307895

**A1out<sub>Me</sub>**

SCF Energy: -272.428343339

 $S^2$  before (1.0435) and after higher multiplicity projection (0.3971)

Num. Imaginary Frequencies: 0

C	2.574187	-0.345871	0.732201
C	1.507461	0.050910	-0.065977
C	1.394099	1.361490	-0.517657
C	0.508268	-0.960038	-0.479378
C	-0.868463	-0.825815	-0.355633
C	-1.554799	0.223238	0.237595
H	3.349091	0.362951	1.017806
H	0.596216	1.662348	-1.191605
H	2.132758	2.108945	-0.233345
H	0.901786	-1.893059	-0.883247
H	-1.473399	-1.648382	-0.747237
C	-3.037838	0.292933	0.319059
H	-0.983195	1.036217	0.689522
H	2.661953	-1.368285	1.091933
H	-3.430575	1.189575	-0.181666
H	-3.508467	-0.582140	-0.144321
H	-3.383661	0.350750	1.360900

**A1out<sub>NH2</sub>**

SCF Energy: -288.474781751

 $S^2$  before (1.0374) and after higher multiplicity projection (0.3132)

Num. Imaginary Frequencies: 0

C	2.694760	-0.344126	0.528831
C	1.499661	0.060536	-0.064520
C	1.307091	1.396699	-0.399324
C	0.486149	-0.971565	-0.348150
C	-0.891354	-0.837080	-0.258458
C	-1.622779	0.261573	0.173506
H	3.482516	0.375548	0.742505
H	0.434352	1.730031	-0.953983
H	2.070178	2.135835	-0.164272
H	0.874419	-1.954073	-0.615008
H	-1.476454	-1.722015	-0.526276
N	-2.996805	0.234811	0.318413
H	-1.134881	1.166507	0.528287
H	2.869149	-1.383585	0.797324
H	-3.484904	1.117640	0.324250
H	-3.497905	-0.505787	-0.153031

**A1out<sub>NO2</sub>**

SCF Energy: -437.564474717

 $S^2$  before (1.0428) and after higher multiplicity projection (0.3795)

Num. Imaginary Frequencies: 0

C	-3.305788	-0.098595	-0.804406
C	-2.233689	0.068126	0.067013
C	-2.055569	1.232372	0.802440
C	-1.295113	-1.061012	0.241197
C	0.082913	-0.981545	0.203430
C	0.793896	0.165618	-0.108601
H	-4.027560	0.701290	-0.952849
H	-1.257294	1.331925	1.533034
H	-2.757063	2.057667	0.700896
H	-1.741164	-2.044738	0.390264
H	0.670412	-1.876882	0.400441
N	2.223496	0.156214	-0.113841
H	0.372673	1.120143	-0.404947
H	-3.443410	-1.018999	-1.366312
O	2.770834	1.208910	-0.440882
O	2.816545	-0.873122	0.202123

**A1out<sub>OMe</sub>**

SCF Energy: -347.607288813

 $S^2$  before (1.0153) and after higher multiplicity projection (0.3619)

Num. Imaginary Frequencies: 0

C	-2.829911	-0.208177	1.016671
C	-1.929529	-0.140342	-0.037302
C	-1.749623	-1.208527	-0.912685
C	-1.174128	1.111967	-0.278981
C	0.206642	1.188661	-0.275441
C	1.066078	0.143657	0.024095
H	-3.448079	-1.091941	1.165056
H	-1.077412	-1.132143	-1.763994
H	-2.315394	-2.130635	-0.787000
H	-1.751965	2.020876	-0.439034
H	0.680868	2.143896	-0.504003
O	2.400859	0.342821	-0.047618
H	0.726162	-0.848377	0.328180
H	-2.950106	0.620386	1.710347
C	3.192909	-0.756430	0.350087
H	4.236779	-0.460794	0.229123
H	3.007732	-1.013859	1.402274
H	2.989928	-1.634835	-0.278669

**A2in<sub>CHO</sub>**

SCF Energy: -346.406499263

 $S^2$  before (0.7321) and after higher multiplicity projection (0.1430)

Num. Imaginary Frequencies: 1

Imaginary Frequency: -282.9612

C	2.304681	-1.000848	-0.598138
C	1.427279	-0.238591	0.125628
C	1.155112	1.175173	-0.193127
C	-0.102547	1.653495	-0.056752
C	-1.237277	0.816979	0.254349
C	0.687024	-0.752384	1.217888
H	2.504334	-2.034442	-0.326784
H	2.840367	-0.589849	-1.450082
H	1.968888	1.818411	-0.523852
H	0.652647	-1.825051	1.405908
H	0.325209	-0.098370	2.005138
H	-0.279397	2.725665	-0.159208
H	-2.017177	1.191482	0.921230
C	-1.587733	-0.389862	-0.472588
O	-2.626549	-1.007715	-0.285467
H	-0.861717	-0.709891	-1.252181

**A2in<sub>Me</sub>**

SCF Energy: -272.411868097

 $S^2$  before (0.7530) and after higher multiplicity projection (0.1487)

Num. Imaginary Frequencies: 1

Imaginary Frequency: -325.3105

C	2.162264	-0.412327	-0.696326
C	1.166571	0.058882	0.117539
C	0.401513	1.286347	-0.183554
C	-0.940639	1.254362	-0.018314
C	-1.651739	0.027116	0.262240
C	0.751193	-0.602045	1.297991
H	2.738464	-1.294084	-0.424672
H	2.424006	0.096237	-1.621045
H	0.921462	2.192129	-0.491393
H	1.140601	-1.591294	1.539869
H	0.224668	-0.064928	2.080456
H	-1.507831	2.188432	-0.055559
H	-2.500049	0.090330	0.949127
C	-1.637911	-1.151196	-0.654760
H	-1.836644	-2.086869	-0.118887
H	-2.426689	-1.048202	-1.418084
H	-0.685504	-1.248578	-1.188719

**A2in<sub>NH2</sub>**

SCF Energy: -288.460651798

 $S^2$  before (0.5037) and after higher multiplicity projection (0.0512)

Num. Imaginary Frequencies: 1

Imaginary Frequency: -306.4597

C	1.920689	-0.594653	-0.722309
C	1.111121	0.163766	0.087300
C	0.266341	1.260746	-0.440526
C	-1.060819	1.130776	-0.230284
C	-1.580692	-0.128270	0.267661
C	0.879415	-0.081775	1.455299
H	2.582918	-1.349614	-0.303065
H	1.998184	-0.392528	-1.788442
H	0.707337	2.137076	-0.911708
H	1.387287	-0.904461	1.960043
H	0.387616	0.661911	2.074115
H	-1.753271	1.957191	-0.401549
H	-2.402103	-0.144296	0.983199
N	-1.418648	-1.282472	-0.452661
H	-1.647807	-2.140449	0.032915
H	-0.545956	-1.351063	-0.979737

**A2in<sub>NO2</sub>**

SCF Energy: -437.549986083

 $S^2$  before (0.6871) and after higher multiplicity projection (0.1195)

Num. Imaginary Frequencies: 1

Imaginary Frequency: -227.3349

C	2.044060	-1.262106	-0.451522
C	1.493219	-0.198551	0.230024
C	1.315279	1.132304	-0.383873
C	0.104002	1.718418	-0.275967
C	-1.017098	1.011097	0.279033
C	0.984798	-0.323222	1.525744
H	2.175783	-2.225264	0.035148
H	2.357254	-1.167867	-1.487682
H	2.148241	1.627098	-0.879437
H	0.954684	-1.296730	2.013775
H	0.754017	0.548345	2.130229
H	-0.042340	2.760258	-0.562827
H	-1.762354	1.464761	0.925735
N	-1.442897	-0.259662	-0.207253
O	-2.381275	-0.790738	0.397288
O	-0.872545	-0.754338	-1.180389

**A2in<sub>OMe</sub>**

SCF Energy: -347.589609194

 $S^2$  before (0.6722) and after higher multiplicity projection (0.1081)

Num. Imaginary Frequencies: 1

Imaginary Frequency: -327.7736

C	1.953069	-1.230319	-0.716784
C	1.372272	-0.305068	0.103789
C	1.256185	1.126541	-0.253366
C	0.058906	1.727994	-0.074201
C	-1.095680	0.921012	0.232561
C	0.813261	-0.616556	1.369516
H	2.076707	-2.262620	-0.396454
H	2.317028	-0.961647	-1.704995
H	2.133310	1.677419	-0.589286
H	0.791505	-1.651549	1.713508
H	0.657537	0.159171	2.112846
H	-0.041087	2.813629	-0.121362
H	-1.888392	1.249283	0.913527
O	-1.442028	-0.034363	-0.653947
C	-2.228994	-1.074749	-0.118462
H	-2.567721	-1.692031	-0.952766
H	-1.617018	-1.673978	0.574705
H	-3.099760	-0.675911	0.423531

**A2out<sub>CHO</sub>**

SCF Energy: -346.406105730

 $S^2$  before (0.6678) and after higher multiplicity projection (0.1237)

Num. Imaginary Frequencies: 1

Imaginary Frequency: -361.1041

C	2.866720	-0.536381	-0.528042
C	1.708439	-0.196442	0.113904
C	1.196546	1.182628	0.193692
C	-0.137557	1.338651	0.029042
C	-0.967776	0.221497	-0.350691
C	0.851073	-1.153997	0.721127
H	3.217594	-1.565259	-0.544845
H	3.482782	0.214648	-1.015731
H	1.867217	2.020537	0.371402
H	0.997550	-2.218460	0.537834
H	0.228722	-0.881265	1.567655
H	-0.611062	2.306699	0.203985
C	-2.345837	0.118548	0.069595
H	-0.650982	-0.460951	-1.139433
O	-3.108470	-0.772944	-0.279462
H	-2.693715	0.920574	0.763069

**A2out<sub>Me</sub>**

SCF Energy: -272.416916048

 $S^2$  before (0.6437) and after higher multiplicity projection (0.1096)

Num. Imaginary Frequencies: 1

Imaginary Frequency: -378.0004

C	-2.584581	-0.152278	0.538850
C	-1.387442	-0.087368	-0.110251
C	-0.637280	1.163338	-0.317797
C	0.709848	1.098405	-0.124935
C	1.322442	-0.070262	0.417230
C	-0.701142	-1.232471	-0.620288
H	-3.127587	-1.090590	0.624599
H	-3.042812	0.735502	0.967143
H	-1.144715	2.080799	-0.608321
H	-1.059233	-2.234319	-0.379195
H	-0.039305	-1.136900	-1.476277
H	1.352294	1.930705	-0.424229
C	2.750881	-0.411604	0.173126
H	0.812640	-0.592756	1.225318
H	2.864582	-1.459516	-0.135667
H	3.189730	0.214671	-0.612000
H	3.358047	-0.294150	1.083010

**A2out<sub>NH2</sub>**

SCF Energy: -288.468599980

 $S^2$  before (0.5372) and after higher multiplicity projection (0.0560)

Num. Imaginary Frequencies: 1

Imaginary Frequency: -288.9606

C	2.537163	-0.095079	-0.592037
C	1.370550	-0.079785	0.115413
C	0.586278	1.145475	0.339439
C	-0.758998	1.067874	0.142147
C	-1.345649	-0.106655	-0.410381
C	0.747953	-1.235673	0.677411
H	3.128688	-1.003473	-0.680080
H	2.921272	0.804383	-1.066267
H	1.074237	2.078210	0.614728
H	1.172106	-2.224027	0.494179
H	0.078645	-1.135082	1.527096
H	-1.420413	1.893744	0.413988
N	-2.678075	-0.377589	-0.243300
H	-0.840231	-0.662995	-1.193336
H	-3.054838	-1.225100	-0.637557
H	-3.136729	-0.059479	0.598395

**A2out<sub>NO2</sub>**

SCF Energy: -437.554850866

 $S^2$  before (0.6916) and after higher multiplicity projection (0.1232)

Num. Imaginary Frequencies: 1

Imaginary Frequency: -310.5169

C	3.231054	-0.431132	-0.424244
C	2.027201	-0.111596	0.149986
C	1.387477	1.208405	0.011336
C	0.049536	1.224713	-0.196474
C	-0.629455	-0.007756	-0.454480
C	1.266929	-1.040902	0.898624
H	3.679797	-1.409856	-0.274109
H	3.782342	0.291448	-1.020140
H	1.973224	2.122223	0.080291
H	1.549305	-2.093492	0.917160
H	0.553246	-0.706234	1.645525
H	-0.535319	2.142024	-0.155187
N	-1.997398	-0.154486	-0.100456
H	-0.280063	-0.774672	-1.137425
O	-2.576687	-1.165587	-0.502150
O	-2.515464	0.723033	0.594473

**A2out<sub>OMe</sub>**

SCF Energy: -347.600256863

 $S^2$  before (0.5925) and after higher multiplicity projection (0.0817)

Num. Imaginary Frequencies: 1

Imaginary Frequency: -297.0267

C	2.819658	-0.601931	-0.706707
C	1.782961	-0.211172	0.089633
C	1.299121	1.180082	0.161501
C	-0.048073	1.366425	0.087906
C	-0.892464	0.269608	-0.223088
C	1.021374	-1.100431	0.904991
H	3.189840	-1.624347	-0.684450
H	3.324474	0.102704	-1.362461
H	1.995220	2.011026	0.250669
H	1.215377	-2.173323	0.865695
H	0.481314	-0.724469	1.769058
H	-0.515255	2.331643	0.284869
O	-2.189979	0.345731	0.117258
H	-0.612395	-0.500877	-0.941158
C	-2.979763	-0.751863	-0.300087
H	-3.999668	-0.562261	0.038390
H	-2.968030	-0.847661	-1.394376
H	-2.607936	-1.682581	0.150815

**A3<sub>CHO</sub>**

SCF Energy: -346.496779211

Num. Imaginary Frequencies: 0

C	1.590737	-0.078254	-0.085347
C	0.473753	-1.068782	0.173251
C	-0.735181	-0.199829	0.592120
C	-0.293557	1.208678	0.311101
C	0.996436	1.254151	-0.051516
C	2.878645	-0.372297	-0.301798
H	1.557045	2.155115	-0.287491
H	-0.965374	2.055937	0.405716
C	-2.019082	-0.598774	-0.089920
H	3.239700	-1.398396	-0.299057
H	3.609458	0.411294	-0.488790
H	0.747909	-1.815275	0.926386
H	0.246137	-1.620579	-0.751001
H	-0.940842	-0.330855	1.671023
O	-2.831896	0.172003	-0.540094
H	-2.189381	-1.702625	-0.143377

**A3<sub>Me</sub>**

SCF Energy: -272.518517436

Num. Imaginary Frequencies: 0

C	1.260566	-0.119751	-0.039058
C	0.061972	-1.029187	0.124224
C	-1.130578	-0.099014	0.437159
C	-0.577631	1.267728	0.131656
C	0.739838	1.241747	-0.120868
C	2.548027	-0.484955	-0.095749
H	1.366757	2.103789	-0.336340
H	-1.198493	2.161690	0.147284
C	-2.391295	-0.432035	-0.349663
H	2.850531	-1.526444	-0.009458
H	3.337098	0.252172	-0.229597
H	0.221942	-1.800746	0.886297
H	-0.125742	-1.554160	-0.824912
H	-1.372380	-0.148059	1.512772
H	-3.206693	0.264125	-0.117750
H	-2.195635	-0.372815	-1.428801
H	-2.742778	-1.446747	-0.125703

**A3<sub>NH2</sub>**

SCF Energy: -288.555853189

Num. Imaginary Frequencies: 0

C	1.244514	-0.110392	-0.038043
C	0.058191	-1.035079	0.105589
C	-1.145809	-0.125917	0.421099
C	-0.610708	1.255287	0.124832
C	0.708236	1.245562	-0.122132
C	2.537944	-0.455089	-0.075304
H	1.327759	2.113456	-0.337354
H	-1.248050	2.137608	0.140900
N	-2.333962	-0.535506	-0.321084
H	2.855172	-1.492329	0.007853
H	3.317493	0.295892	-0.186694
H	0.214134	-1.820118	0.853164
H	-0.134002	-1.544379	-0.850123
H	-1.407101	-0.195681	1.489214
H	-3.149109	0.003875	-0.046679
H	-2.192766	-0.396016	-1.318932

**A3<sub>NO2</sub>**

SCF Energy: -437.654331536

Num. Imaginary Frequencies: 0

C	1.741366	-0.089037	0.020086
C	0.653884	-0.660501	0.904622
C	-0.528872	0.289689	0.741449
C	0.016536	1.456985	-0.029812
C	1.269897	1.210672	-0.441036
C	2.918299	-0.652319	-0.273041
H	1.876124	1.879946	-1.045841
H	-0.581905	2.338319	-0.238394
N	-1.663971	-0.305456	-0.111260
H	3.189948	-1.636155	0.102049
H	3.641805	-0.144125	-0.906263
H	0.975404	-0.659194	1.953307
H	0.392654	-1.688534	0.636048
H	-1.042082	0.567414	1.667144
O	-2.744701	0.248429	-0.006310
O	-1.409151	-1.229981	-0.859045

**A3<sub>OMe</sub>**

SCF Energy: -347.694443369

Num. Imaginary Frequencies: 0

C	1.717469	-0.094490	-0.039493
C	0.552872	-1.047744	0.089087
C	-0.663260	-0.167498	0.398071
C	-0.173030	1.229348	0.110700
C	1.149749	1.248480	-0.110359
C	3.018555	-0.407298	-0.071417
H	1.752061	2.133661	-0.302314
H	-0.821881	2.101250	0.128461
O	-1.753435	-0.581537	-0.404142
H	3.360292	-1.437678	-0.002641
H	3.779975	0.364113	-0.165958
H	0.722750	-1.832053	0.833973
H	0.358856	-1.541497	-0.872607
H	-0.967804	-0.250725	1.461083
C	-2.972195	0.010846	-0.041849
H	-3.752563	-0.437139	-0.662768
H	-3.209728	-0.177021	1.019044
H	-2.975438	1.099528	-0.211576

### 3 Electronic Energies + ZPE

#### 3.1 Disrotatory vs Conrotatory

**Table 1:** Electronic and zero-point Energies (kcal/mol) computed at the M06/6-31+G(d,p) level of theory for the conrotatory and disrotatory ring closure of A1, B1 and C1.

	Conrotatory	Disrotatory
X	$\Delta E^\ddagger$	$\Delta E^\ddagger$
<b>CH<sub>2</sub></b>	7.6	13.1
<b>NH</b>	12.1	9.3
<b>O</b>		6.8

### 3.2 Torquoselectivity

**Table 2:** Electronic and zero-point Energies (kcal/mol) for the two conrotatory ring closure alternatives of  $A1_{CHO}$ ,  $A1_{NO_2}$ ,  $A1_{Me}$ ,  $A1_{NH_2}$  and  $A1_{OMe}$

X	Conrotatory in    Disrotatory out		$\Delta\Delta E_{TSin-TSout}^\ddagger$
	$\Delta E^\ddagger$	$\Delta E^\ddagger$	
$A1_{CHO}$	3.4	7.9	-0.3
$A1_{NO_2}$	2.9	6.3	2.9
$A1_{Me}$	7.8	7.4	3.1
$A1_{NH_2}$	10.1	4.3	5.2
$A1_{OMe}$	9.0	5.0	6.4

## 4 Computing diradical wavefunctions

Diradical species feature high multireference character (also known as *non-dynamical correlation*) which often times requires MRSCF-time wavefunctions to correctly describe their chemistry. MRSCF methods are however prohibitively expensive for most molecular systems. Fortunately, some density functionals are able to mimic this non-dynamical correlation through the inclusion of the so-called self interaction error (SIE).<sup>2</sup> This effect has also been tested for popular density functionals on very simple models (homologous to the diradicals studied in this work). Results obtained with DFT for these simple systems correlate very well with those obtained with MRSCF methods.<sup>3</sup>

One referee was also interested in the effect of electron correlation to the correct description of this chemistry. Hartree-Fock (HF) calculations were therefore performed on the unsubstituted systems to explore this effect. We found that at the HF level (employing the same basis set used for the DFT calculations, i.e. 6-31+G(d,p)) the conrotatory transition state cannot be located on the potential energy surface. Additionally, the activation energies for the disrotatory alternative are extremely high (between 22 and 30 kcal/mol, approximately). These values are not reasonable for the intramolecular diradical collapse of an almost strain-free system. Additionally, HF describes the cyclic products as open shell systems with a near-degeneracy problem, which further emphasizes the ill-behaviour of HF when describing diradical species.

**Table 3:** Electronic and thermal Free Energies (kcal/mol) computed at the HF/6-31+G(d,p) level of theory for the disrotatory ring closure of A1, B1 and C1.

	Conrotatory	Disrotatory
X	$\Delta G^\ddagger$	$\Delta G^\ddagger$
<b>CH<sub>2</sub></b>	–	21.8
<b>NH</b>	–	24.7
<b>O</b>		29.5

## References

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