10.1071/CH14270_AC

Australian Journal of Chemistry 2014, 67(8 & 9), 1344-1352

SUPPLEMENTARY MATERIAL

Studies of the Structure, Amidicity and Reactivity of *N*-Chlorohydroxamic Esters and *N*-Chloro-β,β-dialkylhydrazides: Anomeric Amides with Low Resonance Energies

Stephen A. Glover[A, B], Adam A. Rosser[A] and Robert M. Spence[A]

[A] Chemistry, School of Science and Technology, University of New England, Armidale, NSW 2351, Australia.

[B] Corresponding author. Email: sglover@une.edu.au

A. Table S1. Full version of Table 2 incorporating B3LYP/6-31G(d) energies for *N*-chloro-*N*-methoxyacetamide **8a**, *N*-chloro-*N*-dimethylaminoacetamide **9a**, and *N*-chloro-*N*-methylaminoacetamide **10**, for relevant COSNAR and *trans*-amidation structures in Equations 1–3 and for complexes in Figure 5.

B Table S2. Full version of Table 4 incorporating DFT Energies and COSNAR data for *N*-chloro-*N*-methoxyacetamide **8a**, *N*-chloro-*N*-dimethylaminoacetamide **9a**, *N*-chloro-*N*-methylaminoacetamide **10** and *N*,*N*-dimethylacetamide **4** at B3LYP, M06 and ωB97X-D with the 6-311++G(d,p) basis set.

C B3LYP/6-31G(d) optimised Geometries of all structures in Table S1 and Figure 6 as *xyz* files.

D Full reference [59] for Gausian 03.

A. Table S1. Full version of Table 2 incorporating B3LYP/6-31G(d) energies for *N*-chloro-*N*-methoxyacetamide **8 a** , *N* -chloro-*N*-dimethylaminoacetamide **9a**, and *N*-chloro-*N*-methylaminoacetamide **10**, for relevant COSNAR and *trans*-amidation structures in Equations 1–3 and for complexes in Figure 5.

Structure	Energy/au[A]	Energy /kJmol^{-1} [A]
N-Chloro-*N*-methoxyacetamide **8a**	-783.232265(-783.128089)	
Complex (Figure 5) *anti* (*i*136 cm^{-1})	-783.166253(-783.064720)	173.3(166.3)[B]
Complex (Figure 5) *syn* (*i*178 cm^{-1})	-783.169415(-783.067757)	165.0(158.4)[B]
Twisted **8a**[C]	-783.222235	
1-Chloro-1-methoxypopanone **11**(Y=OMe)	-767.267346	
N-Chloro-*N*-methoxyethylamine **12** (Y=OMe)	-709.217348	
Twisted **12** (Y=OMe)[D]	-709.216035	
1-Chloro-1-methoxypropane **14** (Y=OMe)	-693.263705	
N,*N*-Dimethylacetamide **4**	-287.830189	
Twisted **3** (*i*128 cm^{-1})[E]	-287.803757	
N,*N*-Dimethylethylamine **15**	-213.788638	
ΔE_{COSNAR} for **8a** from Eq. 1	-0.011276	-29.60
ΔE_{React} for **8a** from Eq. 2	0.026634	69.91
$\Delta E_{Inductive}$ for **8a** from Eq. 3	0.008919	23.41
RE for **8a** from Eq. 4	-0.011228	-29.47
N-Chloro-*N*-dimethylaminoacetamide **9a**	-802.708083	
Twisted **9a** (*i*81 cm^{-1})[E]	-802.699531	
1-Chloro-1-dimethylaminopropanone **11** (Y=NMe$_2$)	-786.717533	
1-Chloro-1-ethyl-2,2-dimethylhydrazine **12** (Y=NMe$_2$)	-728.691118	
1-Choro-1-dimethylaminopropane **14** (Y=NMe$_2$)	-712.711513	
ΔE_{COSNAR} for **9a** from Eq. 1	-0.010945	-28.73
ΔE_{React} for **9a** from Eq. 2	0.024586	64.54
$\Delta E_{Inductive}$ for **9a** from Eq. 3	0.006706	17.60
RE for **9a** from Eq. 4	0.011063	-29.04
N-Chloro-*N*-methylaminoacetamide **10**	-763.396495	
Twisted **10**[C]	-763.385358	
1-Chloro-1-methylaminopropanone **11** (Y=NHMe)	-747.40786	
1-Chloro-1-ethyl-2-methylhydrazine **12** (Y=NHMe)	-689.380304	

Twisted **12** (Y=NHMe)[D]	-689.379069	
1-Choro-1-methylaminopropane **14** (Y=NHMe)	-673.404072	
ΔE_{COSNAR} for **10** from Eq. 1	-0.012403	-32.56
ΔE_{React} for **10** from Eq. 2	0.02536	66.57
$\Delta E_{Inductive}$ for **10** from Eq. 3	0.00883	23.18
RE for **10** from Eq. 4	-0.012413	-32.58

[A] ZPE and enthalpy corrected values in parentheses.

[B] Relative to **8a**.

[C] Amide nitrogen lone pair and carbonyl oxygen *syn*

[D] N1 nitrogen lone pair and 2-methyl *anti*.

[E] Amide nitrogen lone pair and carbonyl oxygen *anti*

B. Table S2. Full version of Table 3 incorporating DFT Energies[A] and COSNAR data for *N*-chloro-*N*-methoxyacetamide **8a**, *N*-chloro-*N*-dimethylaminoacetamide **9a**, *N*-chloro-*N*-methylaminoacetamide **10** and *N,N*-dimethylacetamide **4** at B3LYP, M06 and ωB97X-D with the 6-311++G(d,p) basis set.

	B3LYP/au	M06/au	ωB97X-D/au
N-Chloro-*N*-methoxyacetamide **8a**	-783.36072	-783.125902	-783.23212
1-Chloro-1-methoxypropanone **11** (Y=OMe)	-767.392927	-767.161573	-767.272029
N-Chloro-*N*-methoxyethylamine **12** (Y=OMe)	-709.321758	-709.109039	-709.216337
1-Chloro-1-methoxypropane **14** (Y=OMe)	-693.36431	-693.157826	-693.269152
ΔE_{COSNAR} **8a**^{B}	-0.010345	-0.013116	-0.012906
ΔE_{COSNAR} **8a**^{B}/kJmol^{-1}	-27.2	-34.4	-33.9
N-Chloro-*N*-dimethylaminoacetamide **9a**	-802.839457	-802.573525	-802.707147
1-Chloro-1-dimethylaminopropanone **11** (Y=NMe_2)	-786.844485	-786.578837	-786.718143
1-Chloro-1-ethyl-2,2-dimethylhydrazine**12** (Y=NMe_2)	-728.798686	-728.551616	-728.686212
1-Chloro-1-dimethylaminopropane **14** (Y=NMe_2)	-712.814612	-712.575477	-712.715675
ΔE_{COSNAR} **9a**^{B}	-0.010898	-0.018549	-0.018467
ΔE_{COSNAR} **9a**^{B}/kJmol^{-1}	-28.6	-48.7	-48.5
N-Chloro-*N*-methylaminoacetamide **10**	-763.520598		-763.285879
1-Chloro-1-methylaminopropanone **11** (Y=NHMe)	-747.528765		-747.294415
1-Chloro-1-ethyl-2,2-dimethylhydrazine**12** (Y=NHMe)	-689.480304		-689.264293
1-Chloro-1-dimethylaminopropane **14** (Y=NHMe)	-673.499678		-673.290353
ΔE_{COSNAR} **10**^{B}	-0.011207		-0.017524
ΔE_{COSNAR} **10**^{B}/kJmol^{-1}	-29.4		-46.0
N,N-dimethylacetamide **4**	-287.91854	-287.714437	-287.821223
3-Methylbutanone **11** (Y,Cl=Me)	-271.866276	-271.662137	-271.775242
1,1-Dimethylethylamine **12** (Y,Cl=Me)	-213.852766	-213.67433	-213.780801
2-methylbutane **14** (Y,Cl=Me)	-197.829402	-197.650932	-197.764179
ΔE_{COSNAR} **4**^{B}	-0.0289	-0.028902	-0.029359
ΔE_{COSNAR} **4**^{B}/kJmol^{-1}	-75.9	-75.9	-77.1

Amidicity **8a**/%	35.8	45.4	44.0
Amidicity **9a**/%	37.7	64.2	62.9
Amidicity **10**/%	38.8	60.6	58.4

[A] Without ZPE and thermal corrections.

[B] From Eq. 1

C. B3LYP/6-31G(d) optimised Geometries of all structures in Table S1 and Figure 7 as XYZ files:

Structures:

N-Chloro-N-methoxyacetamide **8a**

H	-1.352912	-2.158192	0.613206
C	-1.786715	-1.471364	-0.118785
H	-1.521963	-1.841030	-1.114925
H	-2.871944	-1.442942	-0.011518
C	-1.267885	-0.059856	0.060513
O	-1.959497	0.925945	0.140271
O	0.838609	-0.966132	-0.461000
C	1.942319	-1.452286	0.317207
H	2.670286	-0.652330	0.487773
H	2.389469	-2.238998	-0.293929
H	1.594829	-1.855380	1.273649
N	0.149470	0.007469	0.249882
Cl	0.833608	1.630752	-0.052022

Complex Figure 5a *anti* (i136 cm^{-1})

H	0.287556	-1.083526	1.603534
C	1.223838	-1.237290	1.068681
H	2.057068	-0.956153	1.722667
H	1.334678	-2.286774	0.781450
N	-0.824087	-0.277625	-0.780691
O	-1.656811	-0.595661	0.105638
C	-3.005925	0.027556	-0.002780
H	-3.033403	0.821989	0.745370
H	-3.725592	-0.759126	0.228211
H	-3.104811	0.417277	-1.015481
C	1.306726	-0.402442	-0.175319
O	1.943000	-0.555188	-1.159024
Cl	0.736221	1.451149	0.263687

Complex Figure 5b *syn* (i178 cm^{-1})

H	-1.887022	-2.095311	0.808305
C	-1.965068	-1.004986	0.825066
H	-3.007845	-0.717051	0.646850
H	-1.648592	-0.609017	1.788764
N	0.873370	-0.318312	0.836828
O	1.667238	-0.528458	-0.101829
C	3.025392	0.082470	0.007059
H	3.077160	0.834436	-0.782293
H	3.737657	-0.724590	-0.172162
H	3.108127	0.516123	1.003623
C	-1.129295	-0.452541	-0.293339
O	-0.880709	-0.910986	-1.357849
Cl	-0.904205	1.458206	-0.041540

Twisted **8a**

H	1.043278	-0.503046	1.932164
C	1.753642	-0.135194	1.187239
H	1.856764	0.944909	1.332698
H	2.726803	-0.612878	1.312495
C	1.247774	-0.411890	-0.202620
O	1.883604	-0.853382	-1.117884
O	-0.866481	-0.958685	0.447394
C	-2.197252	-1.246648	-0.010498
H	-2.795513	-0.329857	-0.012065
H	-2.598081	-1.958116	0.713753
H	-2.164967	-1.680821	-1.012934
N	-0.211903	-0.184362	-0.489079
Cl	-0.522740	1.660332	-0.177857

1-Chloro-1-methoxypopanone **11**(Y=OMe)

H	-1.221728	-1.820423	-1.296733
C	-1.706639	-0.853242	-1.125221
H	-1.378177	-0.182461	-1.926625
H	-2.791729	-0.966686	-1.150016
C	-1.292160	-0.305631	0.218238

O	-2.056281	-0.081760	1.132233
O	0.944822	-1.061222	-0.082388
C	2.327312	-1.064504	0.280733
H	2.843689	-0.210292	-0.169753
H	2.742412	-1.996411	-0.105410
H	2.442360	-1.030553	1.372024
Cl	0.584942	1.599325	-0.420662
C	0.206963	-0.033801	0.431201
H	0.407440	0.175590	1.486147

N-Chloro-N-methoxyethylamine **12** (Y=OMe)

H	-2.619464	0.071320	1.209741
C	-2.510588	0.246439	0.134322
H	-2.633860	-0.704980	-0.389833
H	-3.309550	0.924150	-0.186321
O	-0.026936	-1.070558	-0.469916
C	0.688437	-2.136764	0.162238
H	1.743978	-1.866195	0.274333
H	0.590372	-2.987364	-0.515133
H	0.254005	-2.365588	1.139726
Cl	1.528102	1.012217	0.101678
C	-1.156179	0.881388	-0.179465
H	-1.018197	1.023529	-1.257958
H	-1.053023	1.847112	0.319820
N	-0.078468	0.027064	0.371006

Twisted **12** (Y=OMe)

H	1.411606	-1.559966	1.252870
C	1.953145	-0.870305	0.601007
H	2.061676	0.087973	1.116005
H	2.952690	-1.279894	0.417770
O	-0.821764	-0.915498	0.241353
C	-2.234883	-0.747939	0.086874
H	-2.524267	0.268299	0.375050
H	-2.685085	-1.474372	0.766250

H	-2.532910	-0.944001	-0.947330
Cl	-0.030254	1.634657	-0.041390
C	1.232828	-0.690294	-0.732533
H	1.776077	-0.016767	-1.399775
H	1.120840	-1.654898	-1.245132
N	-0.153090	-0.166176	-0.703677

1-Chloro-1-methoxypropane **14** (Y=OMe)

H	-2.678069	-0.301078	1.179999
C	-2.576614	-0.109909	0.104577
H	-2.520352	-1.074177	-0.407491
H	-3.484368	0.404942	-0.227278
O	0.122403	-1.101697	-0.416506
C	1.146034	-1.956138	0.084266
H	2.133670	-1.504145	-0.060600
H	1.076952	-2.885426	-0.484097
H	0.995632	-2.166947	1.152600
Cl	1.382403	1.252820	-0.021283
C	-0.058662	0.072714	0.266848
H	-0.024845	-0.074411	1.353571
C	-1.339507	0.745550	-0.197370
H	-1.252875	0.931610	-1.273359
H	-1.414185	1.718907	0.297302

N,N-Dimethylacetamide **4**

H	2.755227	0.326788	0.017950
C	1.779169	0.812361	0.000022
H	1.689989	1.462000	0.877883
H	1.714508	1.443186	-0.893634
C	0.728813	-0.294522	-0.003354
O	1.066182	-1.474091	0.007794
N	-0.595866	0.083523	-0.025435
C	-1.080819	1.450823	0.008583
H	-1.595637	1.666656	0.956798
H	-1.798447	1.617618	-0.806393

H	-0.266420	2.164119	-0.108385
C	-1.625977	-0.944101	0.002226
H	-2.228956	-0.865459	0.917414
H	-1.139711	-1.917898	-0.029898
H	-2.296064	-0.836300	-0.860902

Twisted **4** (i128 cm^{-1})

H	-2.828674	-0.003022	-0.277505
C	-1.871757	-0.017359	-0.803230
H	-1.799381	-0.909925	-1.436064
H	-1.794767	0.844009	-1.477247
C	-0.721718	0.001569	0.173276
O	-0.859972	0.025886	1.376243
N	0.585884	-0.013454	-0.470797
C	1.333436	-1.215918	-0.078155
H	0.761760	-2.110600	-0.348237
H	1.554359	-1.255035	1.000638
H	2.276391	-1.236883	-0.634443
C	1.332165	1.206587	-0.134555
H	2.276379	1.201837	-0.688949
H	1.550424	1.296868	0.941727
H	0.760890	2.087226	-0.448140

N,N-Dimethylethylamine **15**

H	2.181017	-1.009620	-0.184008
C	2.044653	0.020543	0.161201
H	2.103541	0.026307	1.254891
H	2.880267	0.609093	-0.234035
C	0.717340	0.621358	-0.303382
H	0.656361	0.579054	-1.411396
H	0.702860	1.684800	-0.034289
N	-0.455399	0.006345	0.320425
C	-1.655834	0.791660	0.069782
H	-2.504142	0.351752	0.605982

H	-1.927538	0.851555	-1.003805
H	-1.514121	1.813332	0.439310
C	-0.651490	-1.378270	-0.088139
H	0.213243	-1.986853	0.190467
H	-0.814063	-1.490209	-1.179720
H	-1.526548	-1.789465	0.426823

N-Chloro-N-dimethylaminoacetamide **9a**

H	1.170158	2.246574	-0.882090
C	1.628738	1.789500	0.000000
H	1.170158	2.246574	0.882090
H	2.702679	1.981619	0.000000
C	1.438065	0.279081	0.000000
O	2.353208	-0.515265	0.000000
N	0.099836	-0.117947	0.000000
N	-0.962314	0.716782	0.000000
C	-1.754685	0.681737	-1.232317
H	-1.084439	0.791137	-2.087644
H	-2.311967	-0.261134	-1.333764
H	-2.462478	1.515781	-1.219474
C	-1.754685	0.681737	1.232317
H	-2.462478	1.515781	1.219474
H	-2.311967	-0.261134	1.333764
H	-1.084439	0.791137	2.087644
Cl	-0.193761	-1.914524	0.000000

Twisted **9a** (i81 cm^{-1})

N	-0.042467	0.111104	0.555487
N	0.949136	-0.701129	0.226551
C	1.349865	-0.895230	-1.176505
H	1.821282	0.024766	-1.547202
H	0.482364	-1.117926	-1.795746
H	2.060135	-1.723919	-1.218326
C	2.060628	-0.654732	1.177036

H	2.682312	0.231324	0.990771
H	2.666898	-1.557298	1.063204
H	1.651772	-0.601171	2.186043
C	-1.306048	-0.184853	-0.161868
O	-1.510530	0.022786	-1.327092
C	-2.301170	-0.763078	0.813094
H	-2.570865	0.009756	1.541927
H	-1.852149	-1.590086	1.372830
H	-3.190424	-1.098896	0.276835
Cl	0.357684	2.079854	0.048593

1-Chloro-1-dimethylaminopropanone **11** (Y=NMe_2)

H	2.613019	-0.996179	-0.629672
C	2.558343	0.090826	-0.732914
H	2.557690	0.326053	-1.805906
H	3.427723	0.560005	-0.268923
C	1.297653	0.641740	-0.097798
O	1.309589	1.613677	0.629061
C	0.002528	-0.078468	-0.500127
H	0.096941	-0.526624	-1.487399
Cl	0.160811	-1.789072	0.607847
N	-1.202811	0.552719	-0.353508
C	-1.576511	1.112375	0.949379
H	-0.734668	1.655465	1.370156
H	-1.880200	0.309592	1.636554
H	-2.417267	1.796836	0.804142
C	-2.327792	-0.058155	-1.058857
H	-2.700391	-0.948333	-0.531150
H	-2.023366	-0.350252	-2.067969
H	-3.138224	0.672305	-1.137550

1-Chloro-1-ethyl-2,2-dimethylhydrazine **12** (Y=NMe_2)

N	0.267682	0.093241	-0.582824
N	-0.345148	-0.969785	-0.137303
C	-0.606735	-1.187178	1.292267

H	0.324091	-1.203103	1.860699
H	-1.252792	-0.379470	1.661394
H	-1.106176	-2.149612	1.413107
C	-1.374227	-1.463016	-1.051520
H	-1.580117	-2.514600	-0.836440
H	-2.288156	-0.866086	-0.932615
H	-1.005450	-1.349640	-2.070549
Cl	-1.082745	1.812237	-0.290069
C	1.419853	0.558543	0.210227
H	1.183753	0.698107	1.270592
H	1.663121	1.538618	-0.199604
C	2.590847	-0.412794	0.015393
H	3.487110	0.004621	0.486648
H	2.797115	-0.558635	-1.049472
H	2.394118	-1.393106	0.462160

1-Choro-1-dimethylaminopropane **14** (Y=NMe_2)

H	2.926602	-0.342764	-0.139764
C	2.646876	0.686873	-0.380129
H	2.685000	0.806089	-1.469859
H	3.397691	1.356005	0.053406
N	-1.154482	0.612714	-0.250381
C	-2.175933	-0.106512	-1.005546
H	-1.842391	-0.239473	-2.039116
H	-2.384679	-1.098523	-0.577732
H	-3.099576	0.480605	-1.012493
C	-1.578772	0.964301	1.102034
H	-2.550726	1.463388	1.046716
H	-1.671912	0.078736	1.749431
H	-0.868392	1.657463	1.556801
C	1.257256	1.023817	0.165808
H	1.006111	2.065315	-0.080481
H	1.254874	0.937425	1.256900
C	0.147954	0.160623	-0.426549
H	0.323140	-0.063828	-1.478667

Cl	0.406946	-1.664865	0.332159

N-Chloro-N-methylaminoacetamide **10**

H	-1.580624	-2.049628	-0.598563
C	-1.970405	-1.337077	0.132000
H	-1.784457	-1.754164	1.127573
H	-3.043336	-1.194728	-0.006626
C	-1.308620	0.025040	0.000751
O	-1.917355	1.068987	-0.040286
N	0.095755	-0.038347	-0.149637
N	0.796550	-1.095844	0.337769
C	1.946475	-1.489637	-0.473735
H	1.598167	-1.737268	-1.478994
H	2.704423	-0.697369	-0.543312
H	2.393357	-2.378295	-0.018498
Cl	0.912811	1.592981	-0.043773
H	1.043438	-0.975095	1.321990

Twisted N-chloro-N-methylaminoacetamide **10**

N	-0.330157	-0.390966	0.342617
N	-1.258318	0.228140	-0.672682
C	-2.477905	0.325762	0.140499
H	-2.675999	-0.610133	0.677211
H	-3.352424	0.663465	-0.448129
H	-2.232739	1.113774	0.901078
C	0.744463	0.937613	0.191833
O	0.911232	1.577754	1.245607
C	1.255984	1.195477	-1.117717
H	0.763383	0.593884	-1.881920
H	2.336952	1.006196	-1.065588
H	1.099294	2.265994	-1.333843
Cl	0.707533	-1.806881	0.095962
H	-1.367635	-0.560258	-1.463879

1-Chloro-1-methylaminopropanone **11** (Y=NHMe)

H	1.498264	-1.757708	-1.389827
C	1.759277	-0.716839	-1.157811
H	1.286746	-0.067925	-1.901577
H	2.844657	-0.615679	-1.210166
C	1.297594	-0.379097	0.244701
O	2.048686	-0.324091	1.194621
C	-0.197964	-0.127463	0.465585
H	-0.400739	0.002259	1.526635
Cl	-0.462811	1.696970	-0.207768
N	-1.034562	-1.067301	-0.117577
C	-2.462983	-0.992798	0.181352
H	-2.922108	-0.066012	-0.189954
H	-2.604771	-1.042979	1.265350
H	-2.966357	-1.851757	-0.270134
H	-0.853539	-1.202390	-1.107484

1-Chloro-1-ethyl-2-methylhydrazine **12** (Y=NHMe)

N	0.160977	-0.090995	-0.391453
N	-0.162104	-1.135872	0.334738
C	-1.235018	-1.977501	-0.170990
H	-1.259356	-2.903976	0.408654
H	-2.197384	-1.454679	-0.091239
H	-1.035222	-2.200109	-1.220412
Cl	-1.391482	1.362856	-0.237189
C	1.300267	0.643270	0.189949
H	1.178000	0.770895	1.277166
H	1.291669	1.632159	-0.266084
C	2.601688	-0.095504	-0.138681
H	3.451838	0.502121	0.208329
H	2.699807	-0.239088	-1.219189
H	2.646776	-1.075955	0.345379
H	-0.143224	-1.018442	1.353776

Twisted **12** (Y=NHMe)

N	-0.137726	-0.280693	-0.749820

N	-0.843593	-0.976321	0.105896
C	-2.280220	-0.746519	0.099312
H	-2.762113	-1.511996	0.713041
H	-2.502865	0.252958	0.494886
H	-2.638252	-0.812657	-0.929550
Cl	-0.078268	1.773502	-0.101746
C	1.297646	-0.631880	-0.746307
H	1.781438	0.138347	-1.346306
H	1.335838	-1.574969	-1.310372
C	2.000166	-0.786553	0.603437
H	3.064906	-0.974146	0.430649
H	1.622149	-1.634597	1.187310
H	1.904034	0.130717	1.192119
H	-0.438285	-1.156554	1.027735

1-Choro-1-methylaminopropane **14** (Y=NHMe)

H	-2.735649	0.325774	1.218257
C	-2.639680	0.174734	0.136404
H	-2.597553	1.160369	-0.335841
H	-3.544667	-0.336985	-0.208851
N	0.178092	1.204685	-0.341849
C	1.340039	1.959296	0.114601
H	1.247013	2.146516	1.189438
H	2.286319	1.429109	-0.063809
H	1.363927	2.925316	-0.397740
C	-1.396567	-0.661767	-0.198302
H	-1.322960	-0.825632	-1.281283
H	-1.470682	-1.651566	0.260587
C	-0.110077	-0.004690	0.284238
H	-0.076044	0.110711	1.368462
Cl	1.309157	-1.339223	0.036310
H	0.140345	1.129800	-1.354916

Contracted transition state for **8a** in Fig. 7a Energy -783.21114 au

H	-2.474489	-1.580877	0.858145
C	-2.134490	-0.576012	0.585233
H	-2.949793	-0.075650	0.054693
H	-1.886627	-0.000167	1.476692
N	0.265869	-0.049540	0.178667
O	1.208930	-0.143680	-0.715814
C	2.444210	0.439116	-0.239056
H	2.337004	1.525482	-0.311126
H	3.216064	0.067419	-0.912351
H	2.618449	0.136454	0.795070
C	-0.960383	-0.710844	-0.346261
O	-0.910705	-1.387565	-1.340082
Cl	-0.591397	2.173331	0.006439

Transition state for **9a** in Fig. 7b Energy -802.690236 au

N	0.000331	-0.168631	0.660088
N	0.978510	-0.744479	-0.012119
C	1.291652	-0.439927	-1.420683
H	1.398756	0.646787	-1.531407
H	0.521103	-0.803298	-2.096751
H	2.232782	-0.929899	-1.673990
C	2.170919	-0.920645	0.828614
H	2.730909	0.022025	0.897102
H	2.807263	-1.694489	0.390977
H	1.845358	-1.219349	1.824396
C	-1.409998	-0.288950	0.237701
O	-2.222058	-0.198629	1.119837
C	-1.798973	-0.574361	-1.196165
H	-1.407263	-1.541954	-1.527709
H	-1.425417	0.205544	-1.865726
H	-2.888773	-0.600536	-1.240809
Cl	0.157247	1.927809	0.591693

Acetly chloride. Energy -613.445909

H	2.368967	0.723956	0.000000
C	1.313050	1.002636	0.000000
H	1.078484	1.605512	0.882777
H	1.078484	1.605512	-0.882777
C	0.475626	-0.245892	0.000000
O	0.843716	-1.374348	0.000000
Cl	-1.318257	0.142129	0.000000

Methoxy nitrene Energy -169.718110 au

H	-1.191690	-0.755604	0.901643
C	-1.123956	-0.148430	-0.000000
H	-1.191690	-0.755604	-0.901643
O	0.283625	0.480617	0.000000
H	-1.826885	0.685174	0.000000
N	1.240714	-0.304047	-0.000000

D. Full Reference [59] for *Gaussian 03*:

[59] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ocherski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenburg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. C. Ortiz, Q., A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople *Gaussian 03*, 2005. Revision E.01 (Gaussian, Inc.: Wallingford, CT)