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

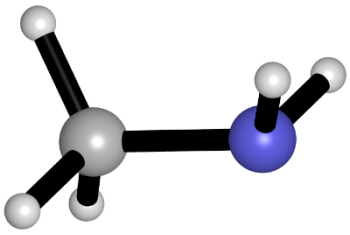
Supporting Information for "Important Features of the Potential Energy Surface of the Methylamine Plus O(^{1}O) Reaction"

Contains:
Geometries
NBO
Harmonic frequencies
Focal point tables for higher energy conformers

XYZ coordinates (BOHR)

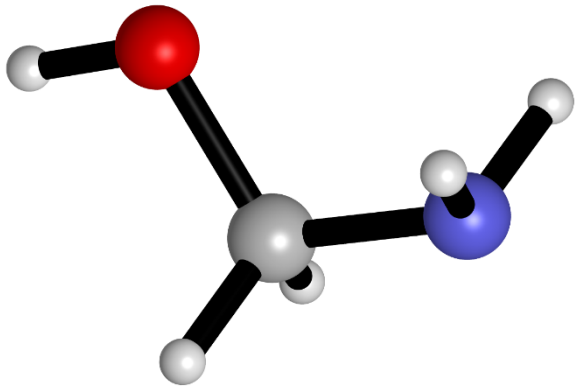
R: methylamine:

H	1.95663742	-2.16126380	0.00000000
C	0.02592780	-1.40492226	0.00000000
N	-0.13754535	1.36822098	0.00000000
H	0.77470865	2.07410673	-1.53096586
H	0.77470865	2.07410673	1.53096586
H	-0.95183463	-2.13466122	1.66328028
H	-0.95183463	-2.13466122	-1.66328028



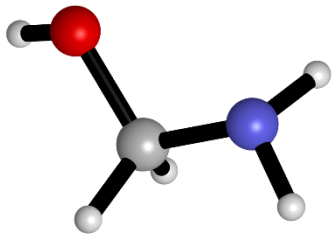
M1: aminomethanol Conformer 2

N	-2.32779582	0.36390948	0.00000000
C	-0.02484931	-1.05994478	0.00000000
O	2.12703404	0.59860585	0.00000000
H	-2.39027330	1.50027455	-1.54241381
H	-2.39027330	1.50027455	1.54241381
H	0.01233290	-2.25889499	1.68457033
H	0.01233290	-2.25889499	-1.68457033
H	3.63739397	-0.41877323	-0.00000000



M1:aminomethanol Conformer 4

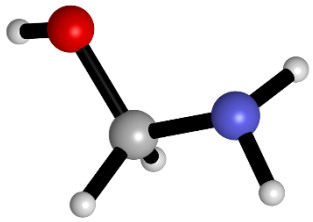
N	-2.22426944	0.53386688	-0.08454186
C	-0.00936162	-1.05722268	0.05434830
O	2.12393806	0.57567959	-0.08237431
H	-3.77218425	-0.50050708	-0.52776611
H	-2.54540409	1.40657033	1.58991940
H	-0.05583618	-2.34675296	-1.56533122
H	0.11506585	-2.18565644	1.79627441
H	3.56616616	-0.33967076	0.54178195



M1: aminomethanol Conformer 1

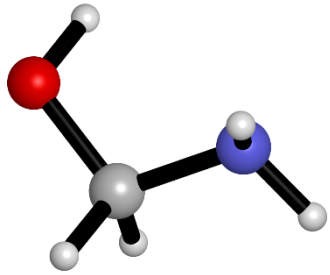
N	-2.36133924	0.36855432	0.02854674
C	-0.02004311	-1.02505816	-0.05336291
O	2.24002027	0.45012725	0.11526324
H	-2.56821517	1.47249316	-1.52412887
H	-2.39780232	1.51329283	1.56531789
H	0.05931365	-2.28295674	1.57466988

H	-0.00694851	-2.16250925	-1.77929735
H	2.41082943	1.40020289	-1.42712819



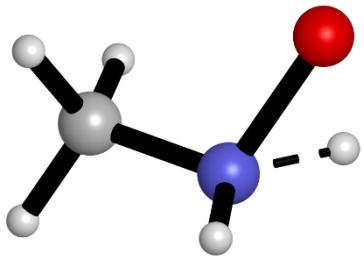
M1: aminomethanol Conformer 3

N	-2.22218900	0.54861320	0.06466385
C	0.00409473	-1.06245702	-0.01363832
O	2.21403838	0.44036850	-0.05550834
H	-2.60281614	1.27258764	-1.66834420
H	-3.76023142	-0.43390971	0.64562050
H	0.14113123	-2.25728038	-1.69583309
H	-0.04943944	-2.27889908	1.66221575
H	1.96007710	1.73640356	1.20122577



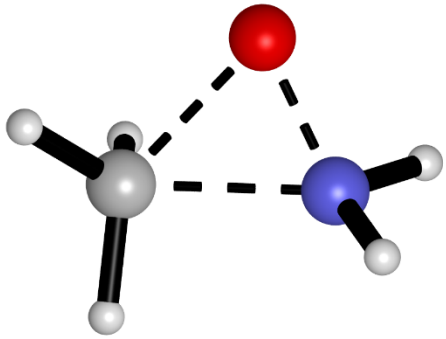
TS1

O	2.29122559	-0.55809315	-0.06243829
N	-0.10107785	1.06061525	0.06462863
H	1.39291976	1.02265338	1.56312747
H	0.01392332	2.34444799	-1.35022127
C	-2.33158654	-0.53925934	-0.00598514
H	-2.28630480	-1.78322901	1.63040309
H	-2.29044602	-1.68037127	-1.72610026
H	-4.02729253	0.63815096	0.04702328



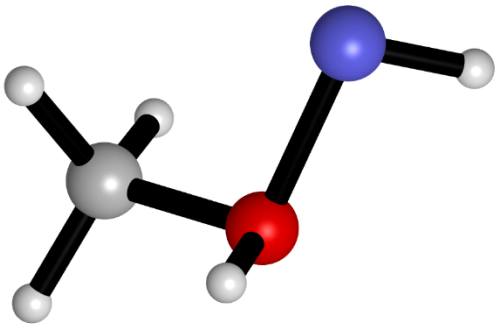
TS1 prime

O	2.29122559	-0.55809315	-0.06243829
N	-0.10107785	1.06061525	0.06462863
H	1.39291976	1.02265338	1.56312747
H	0.01392332	2.34444799	-1.35022127
C	-2.33158654	-0.53925934	-0.00598514
H	-2.28630480	-1.78322901	1.63040309
H	-2.29044602	-1.68037127	-1.72610026
H	-4.02729253	0.63815096	0.04702328



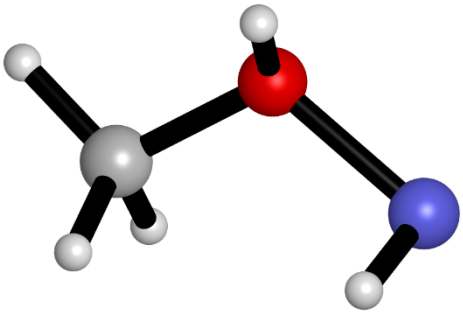
M4: Conformer 1

H	-3.25811870	-0.12251138	1.45144444
N	-2.40569930	0.62260065	-0.12541545
O	0.10721465	-1.07403069	0.10236218
H	-0.01227604	-1.97764610	-1.47878335
C	2.25199039	0.62453429	0.00836605
H	1.98617667	1.94837051	-1.54336363
H	3.96006631	-0.51124799	-0.21127164
H	2.23414238	1.62182709	1.80036514



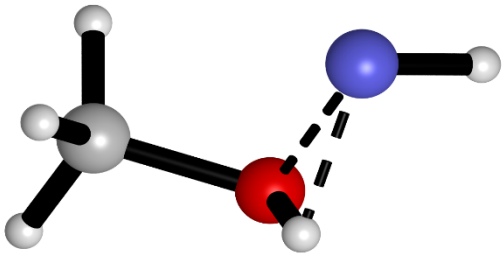
M4: Conformer 2

H	-2.2115378300	1.4831849900	1.5483810900
N	-2.505037830	0 0.4878465500	-0.1071983600
O	0.0913673300	-1.0260851200	-0.0831025900
H	0.0208077100	-2.1060670400	1.3877316900
C	2.2856185700	0.6018320200	-0.0064211300
H	3.9746790000	-0.5793219000	-0.0860576600
H	2.1117241600	1.7909027600	-1.6691031200
H	2.2456653700	1.7517951000	1.7038532100



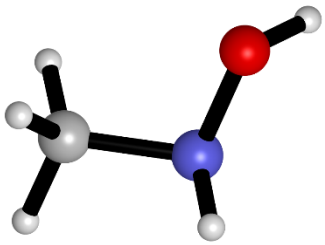
TS3

H	-3.50506759	0.58298530	-1.01357480
N	-2.44020681	-0.65508079	0.03961791
O	0.20623357	1.15327099	-0.04964878
H	-0.85993669	1.04644514	1.57538134
C	2.25115129	-0.64189986	-0.01965404
H	2.29476137	-1.53526631	-1.87131651
H	3.98507014	0.40926362	0.34825407
H	1.91311173	-2.06176169	1.43277011



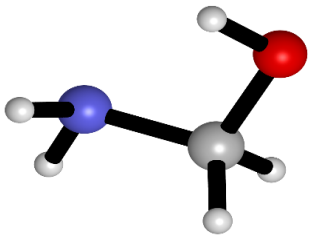
M3: n-methylhydroxylamine Conformer 1

N	0.05955799	1.10869485	-0.14899645
H	-0.00920931	2.15503806	1.46284627
C	2.28910316	-0.51916385	0.00048279
H	2.24131795	-1.78809690	1.63546425
H	3.94810893	0.70504395	0.12319581
H	2.41612895	-1.64325204	-1.72136621
O	-2.11661602	-0.53639649	0.12154741
H	-3.08759292	-0.13873112	-1.36472530



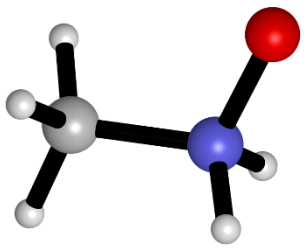
M3: n-methylhydroxylamine Conformer 2

H	-2.12571734	-1.40791579	1.47309551
O	-2.16635277	-0.45307073	-0.09097491
N	0.05512918	1.10336266	-0.11262215
C	2.28266348	-0.51791619	0.00288560
H	-0.04202461	2.17789325	1.47974057
H	2.28312156	-1.80292693	1.63855879
H	3.94920158	0.69680603	0.10641849
H	2.37174218	-1.63706325	-1.72352232



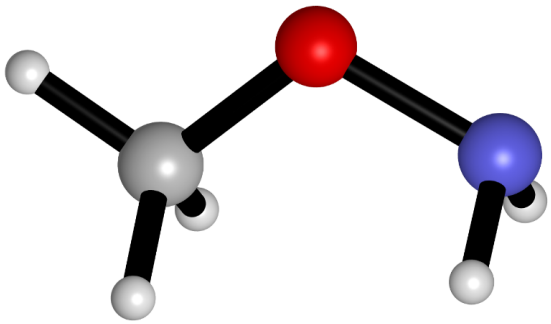
M2: methylamine oxide

O	8	-2.17510798	0.57620050	0.00000000
N	7	-0.09130243	-0.96247800	-0.00000000
C	6	2.30835639	0.49680992	0.00000000
H	1	3.93051554	-0.78474323	-0.00000000
H	1	2.28569777	1.67945458	-1.68037834
H	1	2.28569777	1.67945458	1.68037834
H	1	-0.09899258	-2.13065511	-1.55128625
H	1	-0.09899258	-2.13065511	1.55128625



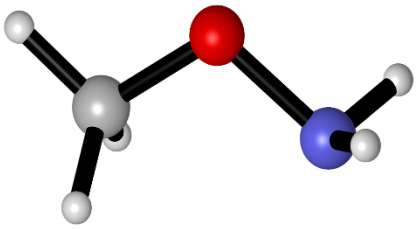
M5: methoxyamine Conformer 1

H	-3.84941213	0.71582756	-0.00000000
C	-2.20157862	-0.52210047	-0.00000000
O	-0.04734523	1.07588360	-0.00000000
N	2.23324034	-0.36530375	0.00000000
H	2.13007976	-1.52576637	-1.54169517
H	2.13007976	-1.52576637	1.54169517
H	-2.23747420	-1.72356464	-1.69052910
H	-2.23747420	-1.72356464	1.69052910



M5: methoxyamine Conformer 2

H	-3.84419373	0.78715062	-0.00000000
C	-2.23660230	-0.50401931	-0.00000000
O	-0.04996537	1.05641384	-0.00000000
N	2.12929878	-0.58718701	0.00000000
H	3.13513833	0.00274634	-1.53184236
H	3.13513833	0.00274634	1.53184236
H	-2.29373946	-1.69942197	-1.68551608
H	-2.29373946	-1.69942197	1.68551608



NBO Data:
The following shows the natural bond order between atoms for select structures.
M2

Natural Bond Order: (total/covalent/ionic)

	Atom		1	2	3	4	5	6	7	8
1.	O	t	2.9459	1.0468	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
		c	---	0.8528	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
		i	---	0.1939	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
2.	N	t	1.0468	0.0267	0.8998	1.0000	1.0000	0.0000	0.0000	0.0000
		c	0.8528	---	0.2953	0.5762	0.7334	0.0000	0.0000	0.0000
		i	0.1939	---	0.6045	0.4238	0.2666	0.0000	0.0000	0.0000
3.	H	t	0.0000	0.8998	0.0808	0.0000	0.0000	0.0000	0.0000	0.0000
		c	0.0000	0.2953	---	0.0000	0.0000	0.0000	0.0000	0.0000
		i	0.0000	0.6045	---	0.0000	0.0000	0.0000	0.0000	0.0000
4.	H	t	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
		c	0.0000	0.5762	0.0000	---	0.0000	0.0000	0.0000	0.0000
		i	0.0000	0.4238	0.0000	---	0.0000	0.0000	0.0000	0.0000
5.	C	t	0.0000	1.0000	0.0000	0.0000	0.0000	1.0000	1.0000	1.0000
		c	0.0000	0.7334	0.0000	0.0000	---	0.7634	0.7685	0.7829
		i	0.0000	0.2666	0.0000	0.0000	---	0.2366	0.2315	0.2171
6.	H	t	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000
		c	0.0000	0.0000	0.0000	0.0000	0.7634	---	0.0000	0.0000
		i	0.0000	0.0000	0.0000	0.0000	0.2366	---	0.0000	0.0000
7.	H	t	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000
		c	0.0000	0.0000	0.0000	0.0000	0.7685	0.0000	---	0.0000
		i	0.0000	0.0000	0.0000	0.0000	0.2315	0.0000	---	0.0000
8.	H	t	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000
		c	0.0000	0.0000	0.0000	0.0000	0.7829	0.0000	0.0000	---
		i	0.0000	0.0000	0.0000	0.0000	0.2171	0.0000	0.0000	---

TS1 prime

```
Natural Bond Order:  (total/covalent/ionic)

    Atom       1      2      3      4      5      6      7      8
    ----   ------ ------ ------ ------ ------ ------ ------ ------
  1.  O  t 2.9313 1.0597 0.0037 0.0000 0.0039 0.0000 0.0000 0.0000
         c   ---  0.8816 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
         i   ---  0.1781 0.0037 0.0000 0.0038 0.0000 0.0000 0.0000

  2.  N  t 1.0597 0.0000 1.0014 0.0000 0.0000 0.0000 0.9694 0.9694
         c 0.8816   ---  0.7040 0.0000 0.0000 0.0000 0.5613 0.5613
         i 0.1781   ---  0.2975 0.0000 0.0000 0.0000 0.4081 0.4081

  3.  C  t 0.0037 1.0014 0.0218 0.9938 0.9855 0.9938 0.0000 0.0000
         c 0.0000 0.7040   ---  0.7541 0.7783 0.7541 0.0000 0.0000
         i 0.0037 0.2975   ---  0.2397 0.2072 0.2397 0.0000 0.0000

  4.  H  t 0.0000 0.0000 0.9938 0.0042 0.0000 0.0000 0.0000 0.0000
         c 0.0000 0.0000 0.7541   ---  0.0000 0.0000 0.0000 0.0000
         i 0.0000 0.0000 0.2397   ---  0.0000 0.0000 0.0000 0.0000

  5.  H  t 0.0039 0.0000 0.9855 0.0000 0.0052 0.0000 0.0000 0.0000
         c 0.0000 0.0000 0.7783 0.0000   ---  0.0000 0.0000 0.0000
         i 0.0038 0.0000 0.2072 0.0000   ---  0.0000 0.0000 0.0000

  6.  H  t 0.0000 0.0000 0.9938 0.0000 0.0000 0.0042 0.0000 0.0000
         c 0.0000 0.0000 0.7541 0.0000 0.0000   ---  0.0000 0.0000
         i 0.0000 0.0000 0.2397 0.0000 0.0000   ---  0.0000 0.0000

  7.  H  t 0.0000 0.9694 0.0000 0.0000 0.0000 0.0000 0.0264 0.0000
         c 0.0000 0.5613 0.0000 0.0000 0.0000 0.0000   ---  0.0000
         i 0.0000 0.4081 0.0000 0.0000 0.0000 0.0000   ---  0.0000

  8.  H  t 0.0000 0.9694 0.0000 0.0000 0.0000 0.0000 0.0000 0.0264
         c 0.0000 0.5613 0.0000 0.0000 0.0000 0.0000 0.0000   ---
         i 0.0000 0.4081 0.0000 0.0000 0.0000 0.0000 0.0000   ---
```

TS1

```
Natural Bond Order:  (total/covalent/ionic)

    Atom       1      2      3      4      5      6      7      8
    ----   ------ ------ ------ ------ ------ ------ ------ ------
  1.  O  t 2.5528 0.4270 1.0119 0.0000 0.0000 0.0000 0.0000 0.0000
         c   ---  0.1250 0.9394 0.0000 0.0000 0.0000 0.0000 0.0000
         i   ---  0.3021 0.0725 0.0000 0.0000 0.0000 0.0000 0.0000

  2.  C  t 0.4270 0.0257 0.5582 0.0000 0.0000 1.0000 1.0000 0.9890
         c 0.1250   ---  0.2088 0.0000 0.0000 0.7689 0.7618 0.7824
         i 0.3021   ---  0.3494 0.0000 0.0000 0.2311 0.2382 0.2066

  3.  N  t 1.0119 0.5582 0.4243 1.0000 1.0000 0.0000 0.0000 0.0000
         c 0.9394 0.2088   ---  0.5915 0.5947 0.0000 0.0000 0.0000
         i 0.0725 0.3494   ---  0.4085 0.4053 0.0000 0.0000 0.0000

  4.  H  t 0.0000 0.0000 1.0000 0.0000 0.0000 0.0000 0.0000 0.0000
         c 0.0000 0.0000 0.5915   ---  0.0000 0.0000 0.0000 0.0000
         i 0.0000 0.0000 0.4085   ---  0.0000 0.0000 0.0000 0.0000

  5.  H  t 0.0000 0.0000 1.0000 0.0000 0.0000 0.0000 0.0000 0.0000
         c 0.0000 0.0000 0.5947 0.0000   ---  0.0000 0.0000 0.0000
         i 0.0000 0.0000 0.4053 0.0000   ---  0.0000 0.0000 0.0000

  6.  H  t 0.0000 1.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
         c 0.0000 0.7689 0.0000 0.0000 0.0000   ---  0.0000 0.0000
         i 0.0000 0.2311 0.0000 0.0000 0.0000   ---  0.0000 0.0000

  7.  H  t 0.0000 1.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
         c 0.0000 0.7618 0.0000 0.0000 0.0000 0.0000   ---  0.0000
         i 0.0000 0.2382 0.0000 0.0000 0.0000 0.0000   ---  0.0000

  8.  H  t 0.0000 0.9890 0.0000 0.0000 0.0000 0.0000 0.0000 0.0110
         c 0.0000 0.7824 0.0000 0.0000 0.0000 0.0000 0.0000   ---
         i 0.0000 0.2066 0.0000 0.0000 0.0000 0.0000 0.0000   ---
```

M3

```
Natural Bond Order:  (total/covalent/ionic)

    Atom       1      2      3      4      5      6      7      8
    ----   ------ ------ ------ ------ ------ ------ ------ ------
  1.  N  t 0.9853 0.9861 1.0311 0.0000 0.0000 0.0000 0.9975 0.0000
         c   ---  0.6203 0.7782 0.0000 0.0000 0.0000 0.8315 0.0000
         i   ---  0.3657 0.2529 0.0000 0.0000 0.0000 0.1660 0.0000

  2.  H  t 0.9861 0.0093 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
         c 0.6203   ---  0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
         i 0.3657   ---  0.0000 0.0000 0.0000 0.0000 0.0000 0.0000

  3.  C  t 1.0311 0.0000 0.0056 0.9885 0.9852 0.9887 0.0009 0.0000
         c 0.7782 0.0000   ---  0.7771 0.7752 0.7710 0.0000 0.0000
         i 0.2529 0.0000   ---  0.2113 0.2100 0.2177 0.0009 0.0000

  4.  H  t 0.0000 0.0000 0.9885 0.0115 0.0000 0.0000 0.0000 0.0000
         c 0.0000 0.0000 0.7771   ---  0.0000 0.0000 0.0000 0.0000
         i 0.0000 0.0000 0.2113   ---  0.0000 0.0000 0.0000 0.0000

  5.  H  t 0.0000 0.0000 0.9852 0.0000 0.0039 0.0000 0.0009 0.0000
         c 0.0000 0.0000 0.7752 0.0000   ---  0.0000 0.0000 0.0000
         i 0.0000 0.0000 0.2100 0.0000   ---  0.0000 0.0009 0.0000

  6.  H  t 0.0000 0.0000 0.9887 0.0000 0.0000 0.0078 0.0000 0.0000
         c 0.0000 0.0000 0.7710 0.0000 0.0000   ---  0.0000 0.0000
         i 0.0000 0.0000 0.2177 0.0000 0.0000   ---  0.0000 0.0000

  7.  O  t 0.9975 0.0000 0.0009 0.0000 0.0009 0.0000 2.0000 0.9977
         c 0.8315 0.0000 0.0000 0.0000 0.0000 0.0000   ---  0.5078
         i 0.1660 0.0000 0.0009 0.0000 0.0009 0.0000   ---  0.4900

  8.  H  t 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.9977 0.0000
         c 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.5078   ---
         i 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.4900   ---
```

M5

```
Natural Bond Order:  (total/covalent/ionic)

    Atom       1      2      3      4      5      6      7      8
    ----   ------ ------ ------ ------ ------ ------ ------ ------
  1.  C  t 0.0051 1.0257 0.0015 0.0000 0.0000 0.9910 0.9857 0.9910
         c   ---  0.6271 0.0000 0.0000 0.0000 0.7923 0.7856 0.7923
         i   ---  0.3986 0.0015 0.0000 0.0000 0.1986 0.2000 0.1986

  2.  O  t 1.0257 1.9719 1.0024 0.0000 0.0000 0.0000 0.0000 0.0000
         c 0.6271   ---  0.8296 0.0000 0.0000 0.0000 0.0000 0.0000
         i 0.3986   ---  0.1728 0.0000 0.0000 0.0000 0.0000 0.0000

  3.  N  t 0.0015 1.0024 1.0036 0.9947 0.9947 0.0000 0.0015 0.0000
         c 0.0000 0.8296   ---  0.6228 0.6228 0.0000 0.0000 0.0000
         i 0.0015 0.1728   ---  0.3720 0.3720 0.0000 0.0015 0.0000

  4.  H  t 0.0000 0.0000 0.9947 0.0035 0.0000 0.0000 0.0000 0.0000
         c 0.0000 0.0000 0.6228   ---  0.0000 0.0000 0.0000 0.0000
         i 0.0000 0.0000 0.3720   ---  0.0000 0.0000 0.0000 0.0000

  5.  H  t 0.0000 0.0000 0.9947 0.0000 0.0035 0.0000 0.0000 0.0000
         c 0.0000 0.0000 0.6228 0.0000   ---  0.0000 0.0000 0.0000
         i 0.0000 0.0000 0.3720 0.0000   ---  0.0000 0.0000 0.0000

  6.  H  t 0.9910 0.0000 0.0000 0.0000 0.0000 0.0090 0.0000 0.0000
         c 0.7923 0.0000 0.0000 0.0000 0.0000   ---  0.0000 0.0000
         i 0.1986 0.0000 0.0000 0.0000 0.0000   ---  0.0000 0.0000

  7.  H  t 0.9857 0.0000 0.0015 0.0000 0.0000 0.0000 0.0061 0.0000
         c 0.7856 0.0000 0.0000 0.0000 0.0000 0.0000   ---  0.0000
         i 0.2000 0.0000 0.0015 0.0000 0.0000 0.0000   ---  0.0000

  8.  H  t 0.9910 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0090
         c 0.7923 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000   ---
         i 0.1986 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000   ---
```

M4

```
Natural Bond Order:  (total/covalent/ionic)

    Atom       1      2      3      4      5      6      7      8
    ----   ------ ------ ------ ------ ------ ------ ------ ------
  1.  H  t 0.0000 1.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
         c   ---  0.6824 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
         i   ---  0.3176 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000

  2.  N  t 1.0000 1.9957 0.9940 0.0000 0.0043 0.0000 0.0044 0.0000
         c 0.6824   ---  0.4550 0.0000 0.0000 0.0000 0.0000 0.0000
         i 0.3176   ---  0.5390 0.0000 0.0043 0.0000 0.0044 0.0000

  3.  O  t 0.0000 0.9940 0.9925 0.9928 1.0207 0.0000 0.0000 0.0000
         c 0.0000 0.4550   ---  0.4565 0.5753 0.0000 0.0000 0.0000
         i 0.0000 0.5390   ---  0.5363 0.4454 0.0000 0.0000 0.0000

  4.  H  t 0.0000 0.0000 0.9928 0.0038 0.0000 0.0000 0.0000 0.0000
         c 0.0000 0.0000 0.4565   ---  0.0000 0.0000 0.0000 0.0000
         i 0.0000 0.0000 0.5363   ---  0.0000 0.0000 0.0000 0.0000

  5.  C  t 0.0000 0.0043 1.0207 0.0000 0.0044 0.9937 0.9853 0.9915
         c 0.0000 0.0000 0.5753 0.0000   ---  0.7662 0.7846 0.7615
         i 0.0000 0.0043 0.4454 0.0000   ---  0.2275 0.2007 0.2300

  6.  H  t 0.0000 0.0000 0.0000 0.0000 0.9937 0.0063 0.0000 0.0000
         c 0.0000 0.0000 0.0000 0.0000 0.7662   ---  0.0000 0.0000
         i 0.0000 0.0000 0.0000 0.0000 0.2275   ---  0.0000 0.0000

  7.  H  t 0.0000 0.0044 0.0000 0.0000 0.9853 0.0000 0.0059 0.0000
         c 0.0000 0.0000 0.0000 0.0000 0.7846 0.0000   ---  0.0000
         i 0.0000 0.0044 0.0000 0.0000 0.2007 0.0000   ---  0.0000

  8.  H  t 0.0000 0.0000 0.0000 0.0000 0.9915 0.0000 0.0000 0.0047
         c 0.0000 0.0000 0.0000 0.0000 0.7615 0.0000 0.0000   ---
         i 0.0000 0.0000 0.0000 0.0000 0.2300 0.0000 0.0000   ---
```

TS2

```
Natural Bond Order:  (total/covalent/ionic)

    Atom       1      2      3      4      5      6      7      8
    ----   ------ ------ ------ ------ ------ ------ ------ ------
  1.  H  t 0.0000 1.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
         c   ---  0.7613 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
         i   ---  0.2387 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000

  2.  C  t 1.0000 0.0275 0.4465 0.0000 0.5379 0.0000 0.9882 1.0000
         c 0.7613   ---  0.1500 0.0000 0.1798 0.0000 0.7845 0.7642
         i 0.2387   ---  0.2965 0.0000 0.3581 0.0000 0.2037 0.2358

  3.  N  t 0.0000 0.4465 1.5314 1.0000 1.0013 0.0000 0.0000 0.0000
         c 0.0000 0.1500   ---  0.6681 0.5924 0.0000 0.0000 0.0000
         i 0.0000 0.2965   ---  0.3319 0.4089 0.0000 0.0000 0.0000

  4.  H  t 0.0000 0.0000 1.0000 0.0000 0.0000 0.0000 0.0000 0.0000
         c 0.0000 0.0000 0.6681   ---  0.0000 0.0000 0.0000 0.0000
         i 0.0000 0.0000 0.3319   ---  0.0000 0.0000 0.0000 0.0000

  5.  O  t 0.0000 0.5379 1.0013 0.0000 1.4555 1.0000 0.0000 0.0000
         c 0.0000 0.1798 0.5924 0.0000   ---  0.4925 0.0000 0.0000
         i 0.0000 0.3581 0.4089 0.0000   ---  0.5075 0.0000 0.0000

  6.  H  t 0.0000 0.0000 0.0000 0.0000 1.0000 0.0000 0.0000 0.0000
         c 0.0000 0.0000 0.0000 0.0000 0.4925   ---  0.0000 0.0000
         i 0.0000 0.0000 0.0000 0.0000 0.5075   ---  0.0000 0.0000

  7.  H  t 0.0000 0.9882 0.0000 0.0000 0.0000 0.0000 0.0118 0.0000
         c 0.0000 0.7845 0.0000 0.0000 0.0000 0.0000   ---  0.0000
         i 0.0000 0.2037 0.0000 0.0000 0.0000 0.0000   ---  0.0000

  8.  H  t 0.0000 1.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
         c 0.0000 0.7642 0.0000 0.0000 0.0000 0.0000 0.0000   ---
         i 0.0000 0.2358 0.0000 0.0000 0.0000 0.0000 0.0000   ---
```

TS3

Natural Bond Order: (total/covalent/ionic)

Atom		1	2	3	4	5	6	7	8
1. H	t	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	c	---	0.6659	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	i	---	0.3341	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
2. N	t	1.0000	1.9541	1.0381	0.0000	0.0000	0.0000	0.0000	0.0000
	c	0.6659	---	0.4722	0.0000	0.0000	0.0000	0.0000	0.0000
	i	0.3341	---	0.5660	0.0000	0.0000	0.0000	0.0000	0.0000
3. O	t	0.0000	1.0381	1.0194	0.9230	1.0000	0.0000	0.0000	0.0000
	c	0.0000	0.4722	---	0.3193	0.5936	0.0000	0.0000	0.0000
	i	0.0000	0.5660	---	0.6037	0.4064	0.0000	0.0000	0.0000
4. H	t	0.0000	0.0000	0.9230	0.0654	0.0000	0.0000	0.0000	0.0000
	c	0.0000	0.0000	0.3193	---	0.0000	0.0000	0.0000	0.0000
	i	0.0000	0.0000	0.6037	---	0.0000	0.0000	0.0000	0.0000
5. C	t	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000	1.0000	1.0000
	c	0.0000	0.0000	0.5936	0.0000	---	0.7771	0.7924	0.7793
	i	0.0000	0.0000	0.4064	0.0000	---	0.2229	0.2076	0.2207
6. H	t	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000
	c	0.0000	0.0000	0.0000	0.0000	0.7771	---	0.0000	0.0000
	i	0.0000	0.0000	0.0000	0.0000	0.2229	---	0.0000	0.0000
7. H	t	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000
	c	0.0000	0.0000	0.0000	0.0000	0.7924	0.0000	---	0.0000
	i	0.0000	0.0000	0.0000	0.0000	0.2076	0.0000	---	0.0000
8. H	t	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000
	c	0.0000	0.0000	0.0000	0.0000	0.7793	0.0000	0.0000	---
	i	0.0000	0.0000	0.0000	0.0000	0.2207	0.0000	0.0000	---

Table 1: Harmonic vibrational frequencies in cm $^{-1}$ for C_S symmetry minimum geometry structures. Conformers are ordered from lowest in energy (1) counting up to the higher energy geometries.

Symmetry	Number	**M1**-Conformer 1	**M2**	**M5**-Conformer 1	**M5**-Conformer 2	Symmetry	number	Methylamine
a′	1	465	432	455	456	a′	1	854
	2	864	889	875	882		2	1060
	3	1009	1023	1028	1067		3	1178
	4	1097	1172	1195	1161		4	1460
	5	1271	1402	1252	1249		5	1510
	6	1441	1432	1465	1464		6	1662
	7	1538	1509	1519	1507		7	2997
	8	1675	1667	1649	1647		8	3077
a″	9	3027	3041	3016	2984		9	2494
	10	3502	3148	3124	3123	a″	10	293
	11	3812	3301	3133	3371		11	972
	12	217	256	148	256		12	1353
	13	358	881	233	314		13	1529
	14	942	1179	1176	1172		14	3113
	15	1249	1357	1314	1337		15	3575
	16	1395	1480	1489	1493			
	17	3069	3181	3084	3042			
	18	3585	3356	3519	3466			

Table 2: Harmonic vibrational frequencies in cm $^{-1}$ for C_1 symmetry minimum geometry structures. Conformers are ordered from lowest in energy (1) counting up to the higher energy geometries.

Number	**M1**-Conformer 1	**M1**-Conformer 3	**M1**-Conformer 4	**M3**-Conformer 1	**M3**-Conformer 2	**M4**-Conformer 1	**M4**-Conformer 2
1	266	240	192	265	279	214	211
2	382	356	226	315	373	238	301
3	477	531	505	436	447	361	332
4	828	830	799	851	839	574	569
5	909	964	972	976	963	785	778
6	1015	1011	1029	1060	1084	1001	1000
7	1108	1121	1130	1154	1152	1079	1070
8	1162	1217	1244	1228	1224	1177	1178
9	1374	1311	1269	1366	1374	1350	1330
10	1392	1389	1361	1443	1444	1362	1396
11	1423	1455	1472	1483	1477	1461	1456
12	1519	1544	1547	1487	1490	1483	1493
13	1668	1651	1654	1524	1522	1510	1509
14	3047	3014	2961	3015	2969	3054	3047
15	3122	3057	3031	3093	3082	3153	3135
16	3500	3504	3512	3125	3132	3193	3190
17	3587	3595	3605	3469	3461	3386	3289
18	3819	3800	3832	3820	3685	3792	3774

Table 3: Harmonic vibrational frequencies in cm $^{-1}$ for transition state structures. The first harmonic frequency listed for each strcuture is the single imaginary mode.

Number	**TS1**	**TS1'**	**TS2**	**TS3**
1	1659i	1114i	1048i	1054i
2	234	158	171	196
3	370	468	501	333
4	740	591	559	430
5	790	901	693	573
6	1050	1029	755	1015
7	1119	1075	978	1110
8	1177	1106	1006	1168
9	1212	1143	1052	1262
10	1406	1368	1330	1331
11	1449	1447	1354	1465
12	1486	1540	1466	1492
13	1511	1582	1505	1508
14	2738	3008	2999	2931
15	3037	3090	3162	3054
16	3116	3212	3249	3146
17	3155	3387	3376	3161
18	3538	3516	3754	3392

Table 4: Incremental focal point table for the higher energy conformers of the minima on the potential energy surface relative to the reactants in kcal mol^{-1}. Bracketed terms are either extrapolated values or additive corrections. The CCSDT(Q)/CBS estimates were further improved by a series of additive corrections: $\delta E_{O(^1D)-O(^3P)} + \delta E_{ZPVE} + \delta E_{FC} + \delta E_{jul} + \delta E_{Rel} + E_{DBOC}$.

M1: Conformer 2

	HF	+δ MP2	+δ CCSD	+δ (T)	+δ T	+δ (Q)	NET
aug–cc–pVDZ	–54.76	–49.57	+11.47	–2.90	+0.15	–0.33	[–95.94]
aug–cc–pVTZ	–55.59	–53.84	+12.29	–3.97	[+0.15]	[–0.33]	[–101.30]
aug–cc–pVQZ	–55.77	–55.89	+12.41	–4.19	[+0.15]	[–0.33]	[–103.62]
aug–cc–pV5Z	–55.74	–56.58	+12.56	–4.26	[+0.15]	[–0.33]	[–104.20]
CBS LIMIT	[-55.70]	[–57.29]	[+12.71]	[–4.33]	[+0.15]	[–0.33]	[–104.79]

$E_{CCSDT(Q)/CBS+\Delta}$ =–104.79–45.37+3.42–0.72+0.17+0.20 –0.06 = **−147.14**

M1: Conformer 3

	HF	+δ MP2	+δ CCSD	+δ (T)	+δ T	+δ (Q)	NET
aug–cc–pVDZ	–54.31	–49.45	+11.39	–2.88	+0.15	–0.33	[–95.43]
aug–cc–pVTZ	–55.14	–53.80	+12.21	–3.97	[+0.15]	[–0.33]	[–100.88]
aug–cc–pVQZ	–55.33	–55.86	+12.34	–4.18	[+0.15]	[–0.33]	[–103.21]
aug–cc–pV5Z	–55.31	–56.54	+12.49	–4.25	[+0.15]	[–0.33]	[–103.79]
CBS LIMIT	[-55.27]	[–57.25]	[+12.64]	[–4.33]	[+0.15]	[–0.33]	[–104.39]

$E_{CCSDT(Q)/CBS+\Delta}$ =–104.39–45.37+3.52–0.70+0.17+0.21+0.17–0.06 = **−146.63**

M1: Conformer 4

	HF	+δ MP2	+δ CCSD	+δ (T)	+δ T	+δ (Q)	NET
aug–cc–pVDZ	–50.68	–49.48	+11.37	–2.86	+0.14	–0.32	[–91.83]
aug–cc–pVTZ	–51.59	–53.77	+12.21	–3.94	[+0.14]	[–0.32]	[–97.28]
aug–cc–pVQZ	–51.79	–55.80	+12.34	–4.16	[+0.14]	[–0.32]	[–99.59]
aug–cc–pV5Z	–51.76	–56.47	+12.48	–4.23	[+0.14]	[–0.32]	[–100.16]
CBS LIMIT	[-51.72]	[–57.17]	[+12.63]	[–4.30]	[+0.14]	[–0.32]	[–100.75]

$E_{CCSDT(Q)/CBS+\Delta}$ =–100.75–45.37+3.17–0.70+0.18+0.20–0.05 = **−143.32**

M3: Conformer 2

	HF	+δ MP2	+δ CCSD	+δ (T)	+δ T	+δ (Q)	NET
aug–cc–pVDZ	–12.24	–50.53	+9.67	–3.45	+0.12	–0.45	[–56.88]
aug–cc–pVTZ	–12.82	–54.85	+10.81	–4.62	[+0.12]	[–0.45]	[–61.81]
aug–cc–pVQZ	–12.97	–56.63	+11.04	–4.85	[+0.12]	[–0.45]	[–63.74]
aug–cc–pV5Z	–12.93	–57.25	+11.20	–4.93	[+0.12]	[–0.45]	[–64.24]
CBS LIMIT	[–12.89]	[–57.89]	[+11.36]	[–5.02]	[+0.12]	[–0.45]	[–64.76]

$E_{CCSDT(Q)/CBS+\Delta}$ =–64.76–45.37+2.68–0.58+0.19+0.13–0.02 = **−107.73**

M4: Conformer 2

	HF	+δ MP2	+δ CCSD	+δ (T)	+δ T	+δ (Q)	NET
aug–cc–pVDZ	+51.07	–45.41	+6.41	–4.16	–0.05	–0.45	[+7.42]
aug–cc–pVTZ	+49.97	–49.14	+7.58	–5.18	[–0.05]	[–0.45]	[+2.73]
aug–cc–pVQZ	+50.05	–50.56	+7.90	–5.40	[–0.05]	[–0.45]	[+1.50]
aug–cc–pV5Z	+50.11	–51.08	+8.10	–5.47	[–0.05]	[–0.45]	[+1.16]
CBS LIMIT	[+50.14]	[–51.64]	[+8.32]	[–5.55]	[–0.05]	[–0.45]	[+0.77]

$E_{CCSDT(Q)/CBS+\Delta}$ = 0.77–45.37+1.33–0.26+0.17+0.05–0.01 = **−43.32**

M5: Conformer 2

	HF	+δ MP2	+δ CCSD	+δ (T)	+δ T	+δ (Q)	NET
aug–cc–pVDZ	–7.85	–49.77	+9.24	–3.54	+0.11	–0.45	[–52.26]
aug–cc–pVTZ	–9.39	–53.95	+10.42	–4.68	[+0.11]	[–0.45]	[–57.93]
aug–cc–pVQZ	–9.45	–55.62	+10.65	–4.91	[+0.11]	[–0.45]	[–59.67]
aug–cc–pV5Z	–9.42	–56.22	+10.80	–5.00	[+0.11]	[–0.45]	[–60.18]
CBS LIMIT	[–9.39]	[–56.85]	[+10.95]	[–5.08]	[+0.11]	[–0.45]	[–60.71]

$E_{CCSDT(Q)/CBS+\Delta}$ =–60.71–45.37+2.67–0.51+0.19+0.12–.01 = **−103.61**