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Supplementary Information

A Theoretical Study of the Inversion and Rotation Barriers in Methyl-Substituted Amines

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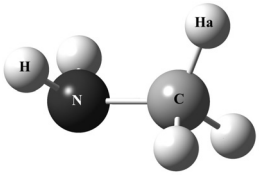
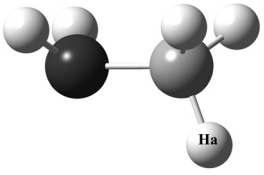
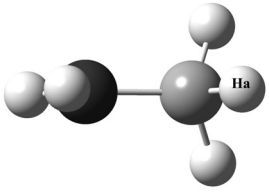
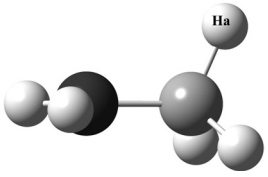
Table S1. Optimized geometries of methylamine. Bond distances (in Å) and angle (in degrees)

Ground state	Rotation transition state
	
First order inversion transition state	Second order inversion transition state
	

Ground State							
Method/Basis	CN	NH	CHa	CH	NCHa	NCH	CNH
B3LYP/cc-pVQZ	1.463	1.011	1.097	1.090	115.2	109.2	110.7
CCSD(T)/cc-pVTZ (valence)	1.469	1.014	1.097	1.091	115.1	109.1	109.2
CCSD(T)/cc-pVQZ (valence)	1.465	1.012	1.096	1.090	115.0	109.1	109.8
CCSD(T)-CBS (valence)	1.462	1.011	1.095	1.089	114.9	109.1	110.2
CCSD(T)/cc-pCVTZ (valence)	1.468	1.013	1.097	1.091	115.1	109.1	109.2
CCSD(T) /cc-pCVTZ (full)	1.466	1.012	1.096	1.090	115.1	109.1	109.4
CCSD(T)/(equation 2)	1.460	1.010	1.094	1.088	114.9	109.1	110.4
Rotation transition state							
B3LYP/cc-pVQZ	1.468	1.009	1.092	1.091	110.9	112.0	111.6
CCSD(T)/cc-pVTZ (valence)	1.473	1.010	1.092	1.093	110.9	111.7	110.6
CCSD(T)/cc-pVQZ (valence)	1.469	1.008	1.091	1.091	110.8	111.7	111.1
CCSD(T)-CBS (valence)	1.466	1.008	1.090	1.090	110.7	111.7	111.4
CCSD(T)/cc-pCVTZ (valence)	1.473	1.009	1.091	1.092	110.9	111.7	110.6
CCSD(T) /cc-pCVTZ (full)	1.470	1.008	1.090	1.091	111.0	111.7	110.7
CCSD(T)/(equation 2)	1.464	1.006	1.089	1.089	110.7	111.7	111.4

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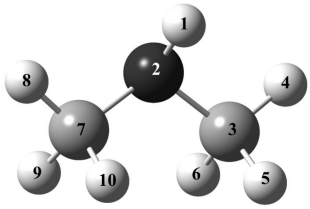
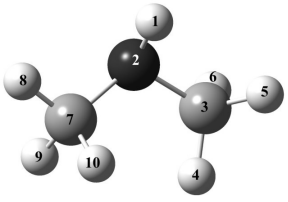
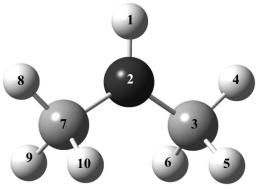
Table S1. Optimized geometries of methylamine. Bond distances (in Å) and angle (degree) (cont.)

First order inversion transition state							
B3LYP/cc-pVQZ	1.437	0.997	1.089	1.096	109.1	113.2	121.2
CCSD(T)/cc-pVTZ (valence)	1.439	0.997	1.091	1.096	108.9	113.1	121.0
CCSD(T)/cc-pVQZ (valence)	1.438	0.996	1.089	1.095	109.0	112.9	121.1
CCSD(T)-CBS (valence)	1.437	0.995	1.088	1.094	109.1	112.8	121.2
CCSD(T)/cc-pCVTZ (valence)	1.438	0.997	1.091	1.096	108.9	113.1	121.0
CCSD(T) /cc-pCVTZ (full)	1.437	0.996	1.089	1.095	109.0	113.1	121.2
CCSD(T)/(Eq.2)	1.436	0.994	1.086	1.093	109.2	112.8	121.2
Second order inversion transition state							
B3LYP/cc-pVQZ	1.438	0.998	1.098	1.091	114.4	110.5	121.2
CCSD(T)/cc-pVTZ (valence)	1.439	0.997	1.098	1.093	114.0	110.6	121.0
CCSD(T)/cc-pVQZ (valence)	1.438	0.997	1.097	1.091	113.9	110.5	121.0
CCSD(T)-CBS (valence)	1.437	0.996	1.095	1.091	113.7	110.4	121.0
CCSD(T)/cc-pCVTZ (valence)	1.439	0.997	1.098	1.092	114.0	110.5	121.0
CCSD(T) /cc-pCVTZ (full)	1.437	0.996	1.097	1.091	114.0	110.5	121.0
CCSD(T)/(equation 2)	1.435	0.995	1.094	1.089	113.8	110.4	121.0

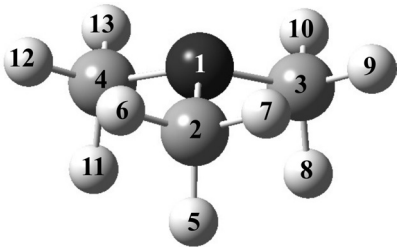
Table S2. Optimized geometries of dimethylamine. Bond distances (in Å) and angle (degree)

Ground State (C_s)	Rotation transition state (C_1)	Inversion transition state (C_{2v})
		

Geometric parameters	Ground State (C_s)	Rotation transition state (C1)	Inversion transition state (C_{2v})
	B3LYP cc-pVQZ	B3LYP cc-pVQZ	B3LYP cc-pVQZ
R (1-2)	1.011	1.008	0.997
R (2-3)	1.454	1.464	1.432
R (2-7)	1.454	1.454	1.432
R (3-6)	1.091	1.092	1.099
R (7-9)	1.091	1.091	1.099
R (3-5)	1.101	1.093	1.099
R (7-10)	1.101	1.101	1.099
R (3-4)	1.089	1.092	1.089
R (7-8)	1.089	1.090	1.089
A(3,2,7)	113.3	115.1	120.6
A(2,7,8)	109.8	109.5	109.9
A(2,3,4)	109.8	110.9	109.9
A(1,2,7)	109.9	110.1	119.7
A(1,2,3)	109.9	110.5	119.7
A(2,3,6)	109.5	111.4	112.5
A(2,7,9)	109.5	109.8	112.5
A(2,7,10)	114.0	114.4	112.5
A(2,3,5)	114.0	112.3	112.5
|D(1,2,7,8)|	53.2	51.1	0.0
|D(1,2,3,4)|	53.2	129.7	0.0
|D(1,2,3,5)|	68.5	10.1	119.5
|D(1,2,7,10)|	68.5	70.4	119.5
|D(1,2,7,9)|	171.1	168.6	119.5
|D(1,2,3,6)|	171.1	110.7	119.5
|D(7,2,1,3)|	125.4	128.2	180.0

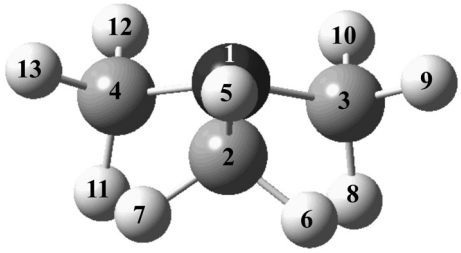
Table S3. Optimized geometries of trimethylamine. Bond distances (in Å) and angle (degree)

Ground state (C_{3v})



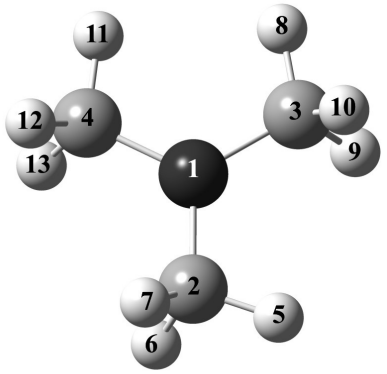
Geometric parameters	B3LYP/cc-pVQZ
R(1,2); R(1,3); R(1,4)	1.451
R(2,6); R(2,7); R(3,9); R(3,10); R(4,12); R(4,13)	1.090
R(2,5); R(3,8); R(4,11)	1.104
A(2,1,3); A(2,1,4); A(3,1,4)	111.8
A(1,2,5); A(1,3,8); A(1,4,11)	112.9
A(6,2,7); A(9,3,10); A(12,4,13)	108.1
A(1,2,6); A(1,2,7); A(1,3,9); A(1,3,10); A(1,4,12); A(1,4,13)	109.9
A(5,2,6); A(5,2,7); A(8,3,9); A(8,3,10); A(11,4,12); A(11,4,13)	108.0

Rotation transition state (C_s)



Geometric parameters	B3LYP/cc-pVQZ
R (1,2)	1.464
R (1,3) (1,4)	1.450
R (2,5)	1.093
R (2,6) (2,7)	1.092
R (3,8) (4,11)	1.104
R (3,10) (4,12)	1.090
R (3,9) (4,13)	1.090
A (2,1,3) (2,1,4)	113.3
A (3,1,4)	112.4
A (1,2,6) (1,2,7)	111.4
A (1,2,5)	111.5
A (5,2,6) (5,2,7)	107.7
A (6,2,7)	106.8
A (1,3,8) (1,4,11)	113.3
A (1,3,9) (1,4,13)	109.8
A (1,3,10) (1,4,12)	110.1
A (9,3,10) (12,4,13)	107.7
A (11,4,13) (8,3,9)	108.0
A (11,4,12) (8,3,10)	107.8

Inversion transition state (C_s)



Geometric parameters	B3LYP/cc-pVQZ
R(1,2)	1.434
R(1,4)	1.434
R(1,3)	1.437
R(2,6); R(2,7); R(4,13); R(4,12)	1.100
R(3,9); R(3,10)	1.099
R(2,5); R(3,8); R(4,11)	1.089
A(2,1,4)	117.3
A(3,1,4)	122.8
A(2,1,3)	120.0
A(1,2,6); A(1,2,7)	112.4
A(1,4,11)	110.3
A(1,4,12); A(1,4,13)	112.4
A(1,2,5)	110.1
A(1,3,10); A(1,3,9)	112.8
A(1,3,8)	109.6
D(3,1,4,11); D(3,1,2,5)	0.0

Table S4. Vibrational frequencies (cm^{-1}) of methylamine

Ground state			
B3LYP/cc-pVQZ	300	833	975
	1055	1173	1348
	1461	1499	1518
	1664	2965	3055
	3089	3496	3570
CCSD(T)/cc-pVTZ	302	877	976
	1066	1187	1359
	1458	1508	1528
	1666	2997	3080
	3116	3499	3580
Rotation transition state			
B3LYP/cc-pVQZ	297i	799	993
	1053	1158	1327
	1464	1495	1522
	1665	3009	3049
	3072	3532	3605
CCSD(T)/cc-pVTZ	350i	914	996
	1066	1166	1338
	1453	1485	1514
	1663	3025	3090
	3104	3496	3575
First order inversion transition state			
B3LYP/cc-pVQZ	672i	101	921
	1114	1169	1287
	1472	1482	1535
	1636	2967	2986
	3085	3659	3779
CCSD(T)/cc-pVTZ	749i	107	918
	1137	1174	1292
	1470	1493	1545
	1642	2993	3027
	3106	3700	3826
Second order inversion transition state			
B3LYP/cc-pVQZ	660i	112i	922
	1109	1170	1290
	1461	1502	1525
	1635	2948	3027
	3065	3660	3778
CCSD(T)/cc-pVTZ	740i	116i	916
	1129	1178	1295
	1462	1508	1537
	1641	2981	3053
	3093	3701	3826

Table S5. Vibrational frequencies (cm^{-1}) of dimethylamine

B3LYP/cc-pVQZ			
Groundstate	230	258	381
	761	938	1036
	1102	1168	1187
	1268	1443	1470
	1477	1488	1495
	1517	1518	2923
	2926	3041	3041
	3089	3089	3525
Rotation transition state	253i	236	391
	699	926	1057
	1106	1159	1187
	1260	1446	1473
	1481	1488	1497
	1515	1522	2925
	2998	3039	3042
	3061	3086	3556
Inversion transition state	591i	180	183
	381	944	1065
	1143	1189	1232
	1277	1453	1471
	1473	1474	1480
	1527	1540	2932
	2943	2943	2953
	3088	3089	3716

Table S6. Vibrational frequencies (cm^{-1}) of trimethylamine

B3LYP/cc-pVQZ			
Groundstate	252	265	265
	357	422	422
	830	1057	1057
	1071	1121	1121
	1208	1306	1306
	1443	1443	1482
	1482	1483	1490
	1502	1511	1511
	2894	2894	2908
	3048	3048	3053
	3089	3093	3093
Rotation transition state	268i	242	246
	331	425	435
	820	1049	1055
	1081	1121	1131
	1183	1305	1306
	1445	1448	1484
	1486	1491	1497
	1501	1511	1513
	2889	2897	2997
	3041	3046	3051
	3058	3088	3091
Inversion transition state	300i	95	108
	134	384	433
	808	1074	1093
	1106	1122	1153
	1170	1331	1391
	1447	1458	1469
	1472	1484	1500
	1514	1528	1541
	2922	2927	2930
	2945	2947	2949
	3086	3090	3098