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Computational Electronic Structure of the Bee Killer Insecticide Imidacloprid

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S1.1 - Theoretical dihedral angles for imidacloprid conformers: IMI1-V, 3C79-V, IMI1-P, IMI2-P, IMI3-P and 3C79-P.

Dihedral (°)	IMI1-V	3C79-V	IMI1-P	IMI2-P	IMI3-P	3C79-P
C1C2C3C4	-0.2	-0.2	-0.1	0.3	0.0	0.0
C6C1C2C3	-0.4	-0.4	0.1	-0.5	0.4	0.3
C4N5C6C1	-0.3	-0.4	0.1	0.1	0.3	0.3
N5C6C1C2	0.7	0.7	-0.2	0.3	-0.6	-0.4
C7C1C2C3	178.1	178.1	178.7	178.0	-178.9	179.3
C7C1C6N5	-177.9	-177.8	-178.7	-178.2	178.7	-179.5
C2C3C4N5	0.5	0.6	0.1	0.1	-0.3	-0.1
C2C3C4Cl17	-179.7	-179.6	180.0	179.8	180.0	179.9
C3C4N5C6	-0.3	-0.3	-0.1	-0.3	0.1	0.0
Cl17C4N5C6	179.9	179.9	180.0	180.0	179.9	180.0
C2C1C7N8	-84.1	-84.1	-71.1	145.9	-49.9	-65.1
C6C1C7N8	94.4	94.3	107.4	-35.7	130.9	113.9
C1C7N8C9	77.7	77.5	87.1	130.6	132.6	89.7
C1C7N8C12	-67.2	-67.3	-64.8	-72.8	-71.3	-63.8
C7N8C12C11	174.7	174.6	177.7	-179.7	-179.4	178.7
C9N8C12C11	25.9	25.8	22.1	-20.0	-20.1	21.7
C7N8C9N10	-161.2	-161.1	-164.6	166.6	166.3	-165.6
C7N8C9N13	16.5	16.6	14.0	-12.4	-12.7	12.8
C12N8C9N10	-12.6	-12.6	-10.0	8.0	8.1	-9.6
C12N8C9N13	165.0	165.0	168.6	-171.1	-170.9	168.9
C9N10C11C12	22.8	22.8	20.7	-20.5	-20.4	20.8
N8C9N10C11	-7.4	-7.4	-7.6	8.8	8.6	-8.0
C11N10C9N13	175.4	175.4	174.0	-172.3	-172.5	173.9
C9N13N14O15	168.8	168.8	177.5	-178.2	-178.3	177.3
C9N13N14O16	-12.0	-12.0	-2.7	2.1	2.0	-2.9
N8C9N13N14	176.5	176.6	176.1	-176.2	-175.9	175.9
N10C9N13N14	-6.5	-6.4	-5.6	4.9	5.3	-6.1
N8C12C11N10	-28.0	-28.0	-24.4	23.1	23.1	-24.3
C4C3C2H18	179.7	179.6	-179.8	-179.5	179.7	-179.7
H19C3C2H18	-0.5	-0.5	-0.1	0.0	179.9	0.1
H18C2C1C6	179.8	179.8	179.8	179.4	-179.3	179.9
H18C2C1C7	-1.7	-1.7	-1.6	-2.2	1.4	-1.0
N5C4C3H19	-179.3	-179.3	-179.7	-179.5	179.8	-179.9
H19C3C2C1	179.7	179.7	179.7	179.9	179.9	179.7
Cl17C4C3H19	0.5	0.5	0.3	0.3	0.0	0.2
C4N5C6H20	179.2	179.2	180.0	179.6	-179.6	-179.8
C2C1C6H20	-178.8	-178.8	-180.0	-179.2	179.3	179.7
C7C1C6H20	2.6	2.7	1.5	2.3	-1.4	0.6
C12N8C7H21	170.1	170.3	173.0	167.8	167.8	174.1
C9N8C7H21	-160.9	-161.1	-35.1	9.4	11.8	-32.4
C2C1C7H21	156.3	156.2	49.4	-94.3	69.4	55.3
C6C1C7H21	-25.3	-25.3	-132.1	84.11	-109.9	-125.7
C12N8C7H22	170.4	170.3	56.3	48.9	50.4	57.5
C9N8C7H22	-44.7	-44.9	-151.7	-107.3	-105.6	-149.0
C2C1C7H22	36.3	36.2	169.2	24.4	-171.3	175.0
C6C1C7H22	-145.2	-145.3	-12.3	-157.2	9.4	-6.0
H23N10C11C12	175.8	175.8	177.4	-176.4	-176.3	176.9
H23N10C9N8	-162.4	-162.4	-165.5	165.9	165.7	-165.3
H23N10C9N13	20.4	20.3	16.1	-15.2	-15.4	16.6
H23N10C11H24	57.9	57.9	59.2	-58.1	63.5	58.7
N8C12C11H24	89.5	89.6	92.6	141.9	141.9	92.8
H26C12C11H24	-29.3	-29.2	-26.1	24.8	24.9	-25.9
H27C12C11H24	-152.9	-152.8	-150.2	-99.2	-99.2	-150.0
C9N10C11H24	-95.2	-95.2	-97.5	-140.6	-140.6	-97.5

S1.1 - continuation

Dihedral (º)	IMI1-V	3C79-V	IMI1-P	IMI2-P	IMI3-P	3C79-P
H23N10C11H25	-64.2	-64.2	-62.4	-58.1	-50.1	-63.0
N8C12C11H25	-146.9	-146.8	-143.2	-94.0	-94.0	-143.1
H26C12C11H25	94.4	94.4	98.1	149.0	149.0	98.2
H27C12C11H25	-29.3	-29.2	-26.0	24.9	24.9	-25.9
C9N10C11H25	142.8	142.7	140.8	97.8	97.9	140.9
C7N8C12H26	-65.1	-65.1	-61.9	-60.8	-60.5	-60.9
C9N8C12H26	146.12	146.2	142.5	99.9	98.8	142.2
H26C12C11N10	-146.8	-146.8	-143.2	-93.9	-93.9	-143.0
C7N8C12H27	56.4	56.5	59.2	60.0	60.2	60.1
C9N8C12H27	-92.2	-92.3	-96.4	-140.3	-140.5	-96.8
N10H23O16N14	-1.2	-1.2	7.0	-8.0	-7.7	6.5
H27C12C11N10	89.6	89.6	92.8	141.9	141.9	92.9

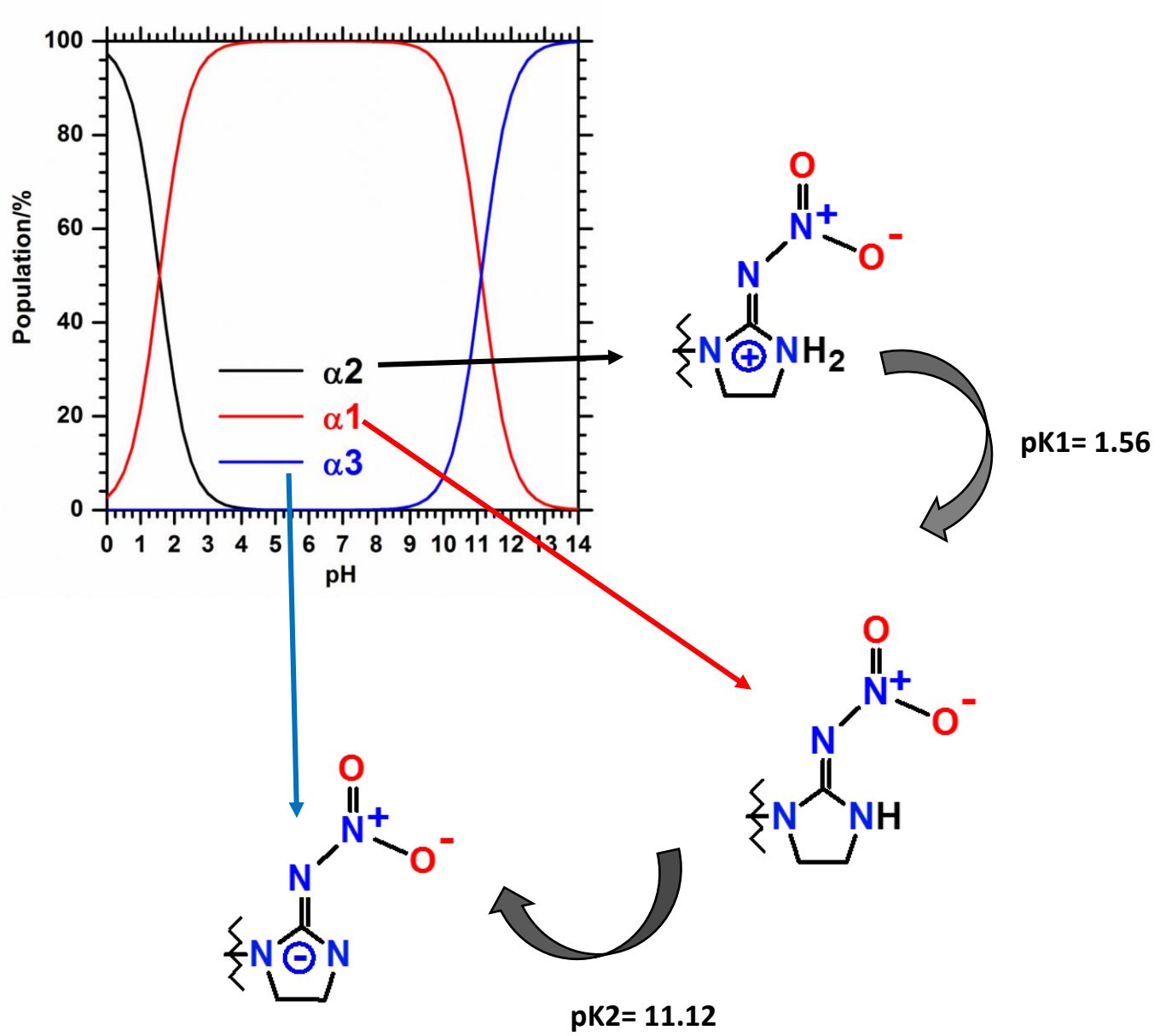
S1.2 - Theoretical bond lengths for imidacloprid conformers: IMI1-V, 3C79-V, IMI1-P, IMI2-P, IMI3-P and 3C79-P.

Bond (Å)	IMI1-V	3C79-V	IMI1-P	IMI2-P	IMI3-P	3C79-P
C1C2	1.399	1.399	1.397	1.393	1.396	1.397
C2C3	1.384	1.384	1.384	1.386	1.384	1.384
C3C4	1.395	1.395	1.392	1.390	1.393	1.393
C4Cl17	1.745	1.745	1.754	1.753	1.753	1.753
C4N5	1.313	1.313	1.313	1.314	1.312	1.312
C6N5	1.335	1.335	1.339	1.337	1.339	1.339
C1C6	1.390	1.390	1.389	1.391	1.388	1.388
C1C7	1.511	1.511	1.512	1.512	1.510	1.512
C7N8	1.460	1.460	1.456	1.449	1.451	1.455
C9N8	1.364	1.364	1.351	1.349	1.349	1.350
C12N8	1.461	1.461	1.465	1.465	1.464	1.465
C9N10	1.348	1.348	1.338	1.339	1.339	1.338
C9N13	1.319	1.319	1.340	1.339	1.339	1.340
C11N10	1.460	1.460	1.465	1.465	1.465	1.465
C11C12	1.531	1.532	1.532	1.532	1.532	1.532
N13N14	1.372	1.372	1.344	1.343	1.343	1.344
N14O15	1.207	1.207	1.223	1.223	1.223	1.223
N14O16	1.231	1.231	1.235	1.235	1.235	1.235
H18C2	1.085	1.085	1.085	1.085	1.085	1.085
H19C3	1.081	1.081	1.081	1.081	1.081	1.081
H20C6	1.088	1.088	1.086	1.086	1.086	1.086
H21C7	1.092	1.092	1.091	1.095	1.095	1.091
H22C12	1.089	1.089	1.089	1.090	1.090	1.089
H24C11	1.094	1.094	1.092	1.092	1.092	1.092
H25C11	1.088	1.088	1.087	1.087	1.087	1.087
H26C12	1.090	1.090	1.089	1.089	1.089	1.089
H27C12	1.097	1.097	1.095	1.095	1.095	1.095
H23N10	1.010	1.010	1.009	1.008	1.008	1.008
H23O16	1.983	1.982	2.005	2.002	2.002	2.006

S1.3 - Theoretical angles for imidacloprid conformers: IMI1-V, 3C79-V, IMI1-P, IMI2-P, IMI3-P and 3C79-P.

Angle (°)	IMI1-V	3C79-V	IMI1-P	IMI2-P	IMI3-P	3C79-P
C1C2C3	119.2	119.2	119.5	119.7	119.6	119.6
C6C1C2	117.4	117.4	117.6	117.6	117.7	117.6
C2C1C7	121.8	121.8	121.4	121.2	121.1	121.3
N5C6C1	124.1	124.1	123.7	123.6	123.6	123.6
C1C7N8	112.8	112.8	112.2	111.8	111.0	112.3
C2C3C4	117.5	117.5	117.0	116.9	116.9	117.0
C3C4Cl17	118.6	118.6	118.5	118.7	118.5	118.6
C3C4N5	124.8	124.8	125.2	125.0	125.1	125.2
C4N5C6	116.9	116.9	117.0	117.2	117.1	117.0
C6C1C7	120.8	120.8	121.0	121.3	121.2	121.0
Cl7C4N5	116.6	116.6	116.3	116.3	116.4	116.3
C7N8C9	121.7	121.6	124.2	125.2	125.1	124.4
C7N8C12	120.9	120.9	120.9	121.0	120.9	121.1
C12N8C9	109.1	109.1	109.8	110.2	110.2	109.9
C11N10C9	110.5	110.5	110.7	110.8	110.7	110.7
C9N13N14	117.4	117.4	117.9	118.0	118.0	118.0
N8C9N10	109.3	109.3	109.9	109.8	109.8	109.9
N8C9N13	118.3	118.3	118.0	118.1	118.2	118.0
N8C12C11	101.5	101.5	101.7	101.9	101.8	101.7
N10C9N13	132.4	132.4	132.0	132.0	132.0	132.0
N10C11C12	101.0	101.0	101.3	101.5	101.5	101.3
N13N14O15	115.2	115.2	115.7	115.6	115.6	115.6
N13N14O16	121.2	121.2	122.6	122.6	122.6	122.6
O15N14O16	123.6	123.6	121.8	121.7	121.7	121.8
C1C2H18	119.9	119.9	120.1	120.4	120.1	120.1
C3C2H18	120.9	120.9	120.4	119.9	120.3	120.3
C2C3H19	122.0	122.0	122.1	122.0	122.1	122.1
C4C3H19	120.5	120.5	120.9	121.0	120.9	120.9
C1C6H20	120.3	120.3	120.4	120.3	120.5	120.4
N5C6H20	115.6	115.6	116.0	116.1	116.0	116.0
N8C7H21	107.0	107.0	107.8	109.4	109.5	107.7
N8C7H22	107.3	107.4	107.5	107.8	107.7	107.7
C1C7H21	110.3	110.3	110.8	109.7	110.1	110.0
C1C7H22	110.8	110.8	110.1	110.2	110.3	110.7
H21C7H22	108.4	108.4	108.3	107.9	108.2	108.3
N8C12H26	110.5	110.9	110.7	110.8	110.8	110.7
N8C12H27	110.9	110.5	109.9	109.5	109.5	109.9
N10C11H24	111.2	110.7	110.1	110.0	110.0	110.0
N10C11H25	110.7	111.2	111.0	111.0	111.0	111.0
C9N10H23	118.7	118.7	120.4	120.2	120.2	120.3
C11N10H23	125.2	125.2	124.6	124.5	124.5	124.6
C11C12H26	113.1	113.1	113.1	112.9	112.9	113.1
C11C12H27	111.3	111.3	111.7	112.1	112.1	111.8
H24C11H25	109.6	109.6	109.7	109.7	109.7	109.7
H26C12H27	109.4	109.4	109.5	109.4	109.4	109.5
C12C11H24	111.2	111.2	111.6	111.6	111.6	111.6
C12C11H25	112.8	112.8	112.9	112.8	112.9	112.9

S1.4 - Imidacloprid fractions estimated by the experimental values of pK_1 and pK_2.



S1.4 - Cartesian coordinates to the imidacloprid conformers.

a) IMI1-V

1	C	13.18083	1.356863	0.336871
2	C	12.83812	0.722934	1.535679
3	C	11.93456	1.332965	2.388092
4	C	11.41291	2.5659	1.997244
5	N	11.70783	3.183423	0.876411
6	C	12.57704	2.578365	0.063076
7	C	14.19198	0.763607	-0.61587
8	N	15.56823	1.100971	-0.26364
9	C	16.22077	0.471677	0.756115
10	N	17.27358	1.221073	1.140437
11	C	17.45824	2.347412	0.230475
12	C	16.05351	2.475243	-0.36587
13	N	15.72624	-0.66436	1.207167
14	N	16.43474	-1.31778	2.183932
15	O	15.85283	-2.23154	2.716308
16	O	17.58592	-0.98642	2.466678
17	Cl	10.27945	3.365276	3.056081
18	H	13.28251	-0.23356	1.788356
19	H	11.63408	0.881313	3.323456
20	H	12.79492	3.102184	-0.86503
21	H	14.11743	-0.32281	-0.63116
22	H	14.02088	1.134625	-1.62884
23	H	18.0045	0.788008	1.686029
24	H	18.19569	2.105161	-0.54053
25	H	17.77173	3.240611	0.767384
26	H	16.05841	2.809046	-1.40343
27	H	15.42807	3.149819	0.231568

b) 3C79-V

1	C	13.10433	6.358376	-4.37423
2	C	13.65758	7.614951	-4.10683
3	C	14.67545	8.090641	-4.91474
4	C	15.09939	7.27446	-5.96322
5	N	14.59622	6.094784	-6.24549
6	C	13.61129	5.653284	-5.45921
7	C	12.02136	5.764649	-3.5044
8	N	12.55134	5.07928	-2.32907
9	C	12.9892	5.76782	-1.23567
10	N	13.78663	4.970121	-0.49708
11	C	13.76773	3.60634	-1.0172
12	C	13.33075	3.850995	-2.46454
13	N	12.63067	7.030263	-1.10741
14	N	13.02061	7.68427	0.034091
15	O	12.85938	8.880429	0.021397
16	O	13.48378	7.069622	0.994713
17	Cl	16.38849	7.842057	-6.99325
18	H	13.28964	8.20168	-3.27217
19	H	15.13217	9.057129	-4.75215
20	H	13.20166	4.680189	-5.72091
21	H	11.34211	6.538771	-3.15025
22	H	11.44217	5.030544	-4.06891
23	H	13.97347	5.224991	0.462005
24	H	13.03499	2.997223	-0.47959
25	H	14.74995	3.143301	-0.94538
26	H	12.71801	3.044912	-2.86804
27	H	14.19585	4.014341	-3.11882

c) IMI1-P

1	C	0.995193	0.390552	0.979896
2	C	1.072707	-0.84227	0.326994
3	C	2.269259	-1.2372	-0.24584
4	C	3.343752	-0.35898	-0.13318
5	N	3.308606	0.805704	0.471304
6	C	2.142964	1.171545	1.019142
7	C	-0.29801	0.876083	1.59377
8	N	-1.27868	1.250765	0.584674
9	C	-2.14749	0.388043	0.013042
10	N	-2.67615	0.935098	-1.08722
11	C	-2.28174	2.340698	-1.20719
12	C	-1.03578	2.379526	-0.31738
13	N	-2.30956	-0.81304	0.584682
14	N	-3.23178	-1.63965	0.06255
15	O	-3.31148	-2.74183	0.585718
16	O	-3.95767	-1.3141	-0.88216
17	Cl	4.879119	-0.81932	-0.8445
18	H	0.200595	-1.48556	0.27518
19	H	2.377511	-2.18424	-0.75601
20	H	2.132756	2.137799	1.515184
21	H	-0.74269	0.103438	2.219123
22	H	-0.11196	1.754925	2.213641
23	H	-3.49466	0.530689	-1.51563
24	H	-3.07309	2.986091	-0.81973
25	H	-2.07113	2.599036	-2.24194
26	H	-0.9411	3.307415	0.244354
27	H	-0.12031	2.206151	-0.89347

d) IMI2-P

1	C	13.10785	1.47269	0.494407
2	C	11.9826	1.622388	-0.31358
3	C	11.00251	2.537835	0.03641
4	C	11.21252	3.272334	1.197745
5	N	12.26334	3.163738	1.979859
6	C	13.19657	2.272761	1.628485
7	C	14.17534	0.452678	0.168343
8	N	15.49591	0.918573	0.539073
9	C	16.39564	0.213972	1.256714
10	N	17.59784	0.797514	1.17679
11	C	17.49842	2.103155	0.519973
12	C	16.17089	1.965526	-0.23162
13	N	15.97772	-0.89601	1.878334
14	N	16.85533	-1.55357	2.654256
15	O	16.43818	-2.5793	3.173051
16	O	18.00897	-1.15337	2.841411
17	Cl	10.00354	4.446754	1.680602
18	H	11.87125	1.029037	-1.21467
19	H	10.11584	2.686171	-0.56396
20	H	14.05999	2.201895	2.282489
21	H	13.9861	-0.47504	0.708617
22	H	14.15669	0.228213	-0.90326
23	H	18.33329	0.533542	1.814211
24	H	18.34315	2.271608	-0.14305
25	H	17.45546	2.895981	1.269767
26	H	16.31356	1.626282	-1.26254
27	H	15.58652	2.884643	-0.23087

e) IMI3-P

1	C	13.04474	1.570681	0.493106
2	C	12.96776	1.547426	1.886494
3	C	11.94649	2.227432	2.526177
4	C	11.03935	2.908543	1.718005
5	N	11.08365	2.956922	0.40732
6	C	12.08096	2.295241	-0.19386
7	C	14.12974	0.820486	-0.24163
8	N	15.43595	1.11825	0.314638
9	C	16.37322	0.2005	0.630564
10	N	17.55046	0.804777	0.834368
11	C	17.39055	2.26088	0.849747
12	C	16.0579	2.428673	0.113246
13	N	16.00885	-1.08777	0.668178
14	N	16.92135	-1.99062	1.0635
15	O	16.55281	-3.1566	1.049814
16	O	18.05949	-1.67318	1.424239
17	Cl	9.728416	3.784008	2.485309
18	H	13.70763	1.002919	2.463691
19	H	11.84716	2.235974	3.602664
20	H	12.10441	2.353065	-1.27767
21	H	13.97133	-0.25425	-0.15634
22	H	14.11576	1.084168	-1.30428
23	H	18.30454	0.30823	1.283486
24	H	18.21805	2.749438	0.341693
25	H	17.32842	2.618919	1.879518
26	H	16.19832	2.606355	-0.95781
27	H	15.4377	3.219536	0.532843

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1	C	13.33623	6.227109	-4.39768
2	C	14.21503	7.235055	-3.9925
3	C	15.24487	7.621512	-4.83247
4	C	15.3413	6.964563	-6.05687
5	N	14.53693	6.0132	-6.46963
6	C	13.54794	5.650619	-5.64278
7	C	12.20684	5.763179	-3.50609
8	N	12.69015	5.126215	-2.29056
9	C	12.95177	5.779771	-1.13821
10	N	13.66405	4.995271	-0.32063
11	C	13.76049	3.637274	-0.86145
12	C	13.46212	3.881795	-2.34355
13	N	12.51475	7.040546	-1.01571
14	N	12.70207	7.661117	0.161587
15	O	12.3333	8.825783	0.210044
16	O	13.20868	7.098002	1.13709
17	Cl	16.62911	7.422434	-7.15417
18	H	14.08603	7.714845	-3.02796
19	H	15.94548	8.399343	-4.56233
20	H	12.89483	4.860358	-6.00068
21	H	11.57826	6.602694	-3.21286
22	H	11.58575	5.038904	-4.03569
23	H	13.7582	5.230382	0.655455
24	H	13.00648	2.99627	-0.39978
25	H	14.74982	3.219963	-0.6926
26	H	12.87612	3.084966	-2.79829
27	H	14.37865	4.036736	-2.92245