Computational Investigation on Zr-FI Cation: Understanding the Stability of the Different Configurations

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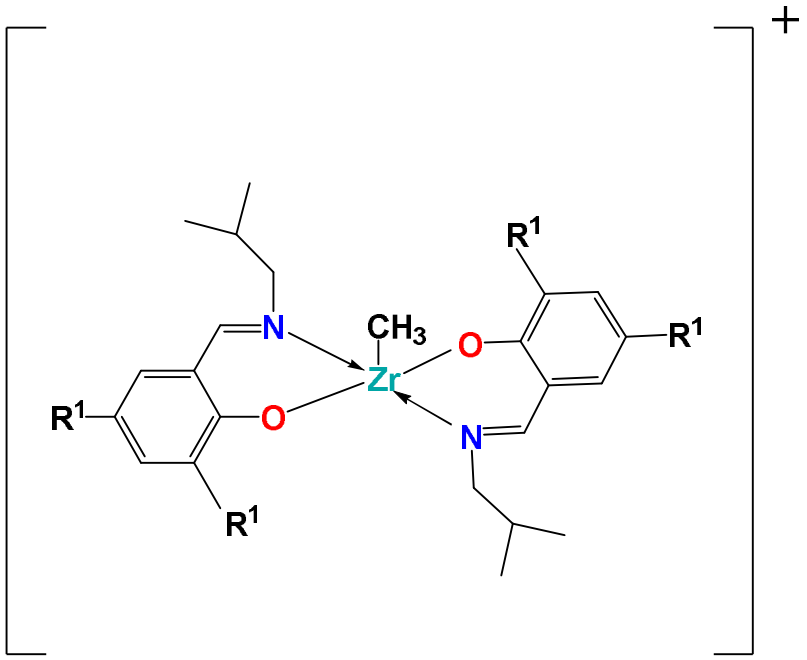
19/VI/2017



R^1= tBu

Zr-Cation

Polymerization Reaction

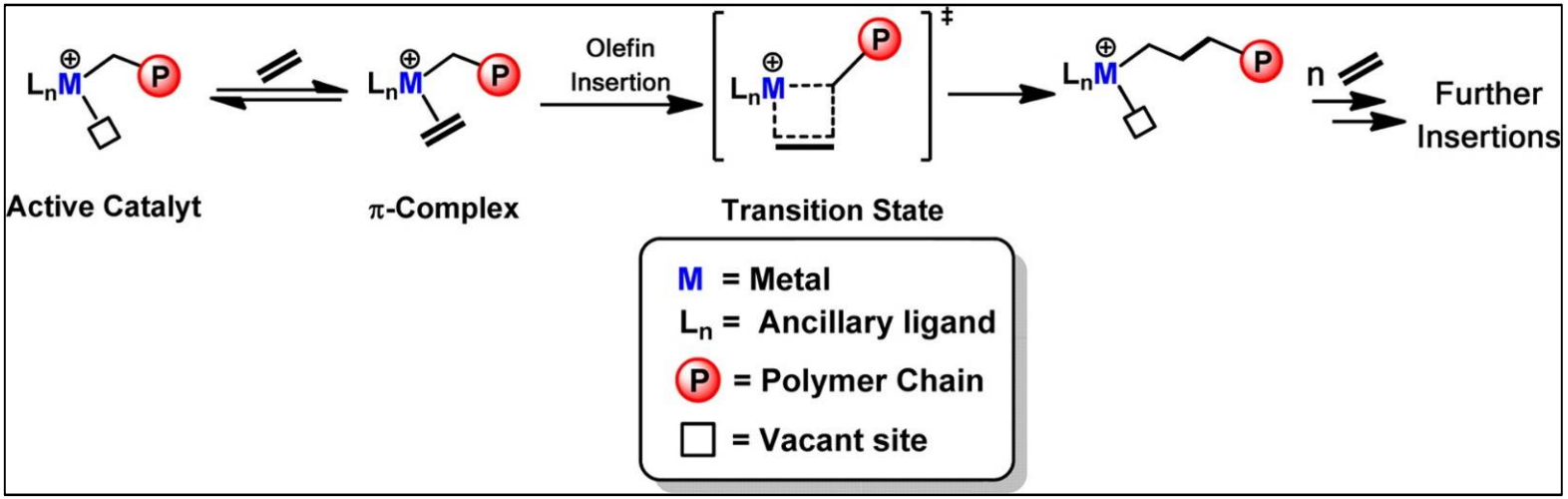


Figure 1: Ethylene Activation and Enchainment Pathway[1]

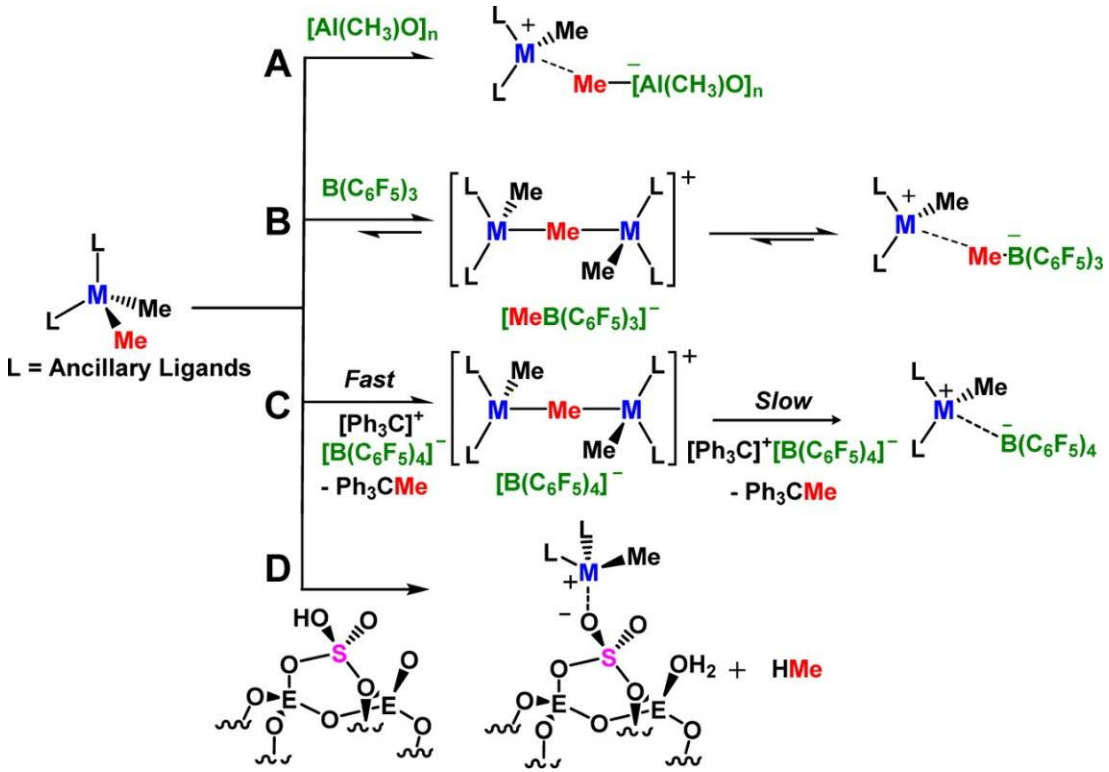
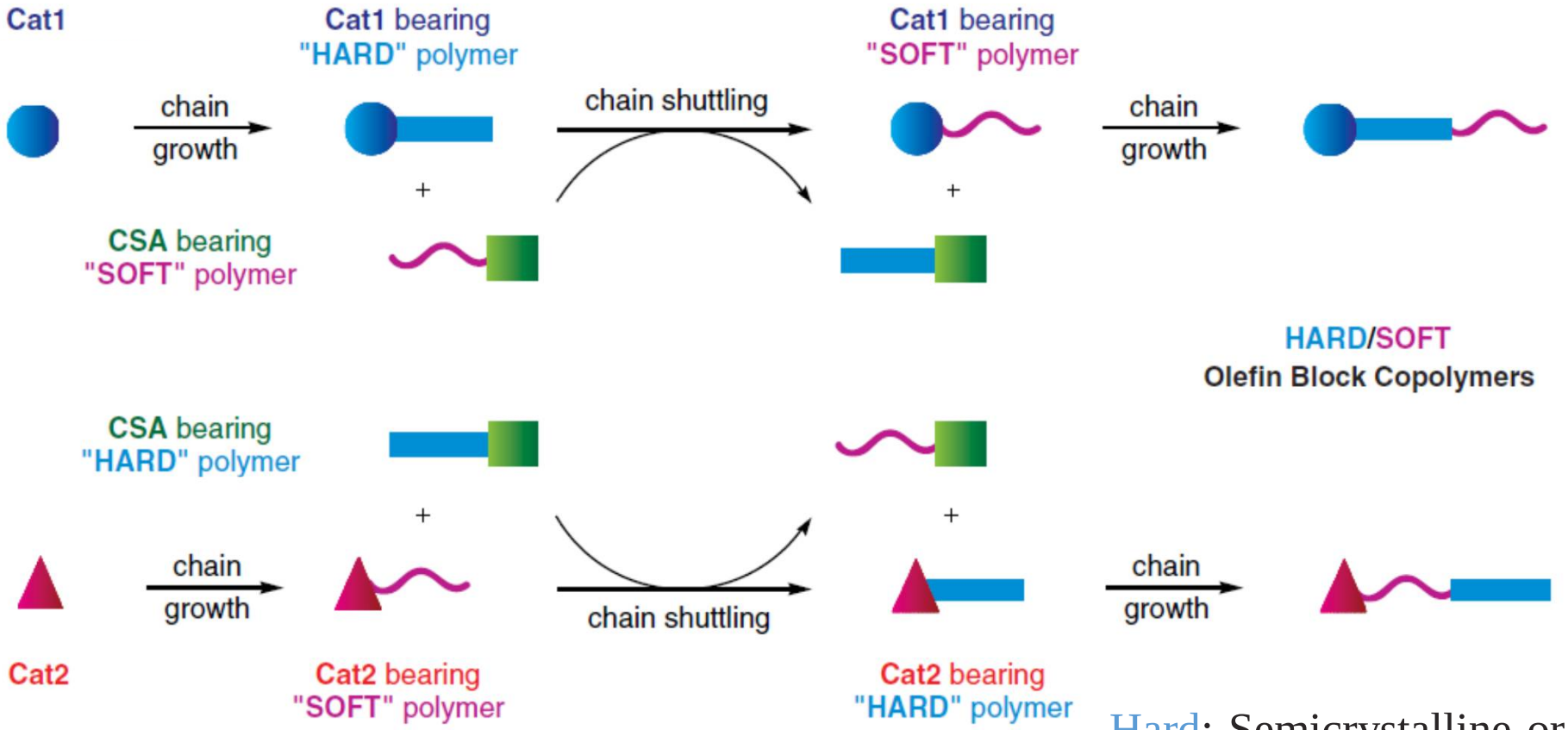
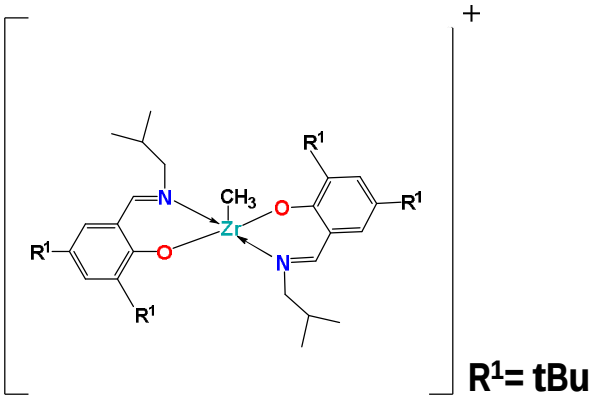


Figure 2: Examples of Organo-Group 4 Catalyst Activation Processes with (A) Methylaluminoxanes, (B) Perfluoroarylborane, (C) Perfluoroarylborate, and (D) Sulfated Metal Oxide Cocatalyst/Activator[2]

[1] *J. Chem. Theory Comput.* **2013,** 9, 3491.
[2] *Acc. Chem. Res.* **2014,** 47, 2545; *Chem. Rev.* **2000**, *100*, 1391.

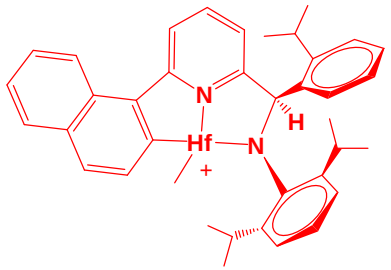
Chain Shuttling Polymerization (CSP)[1]





R^1= tBu

Cat 1



Cat 2

Hard: Semicrystalline or high glass transition temperature

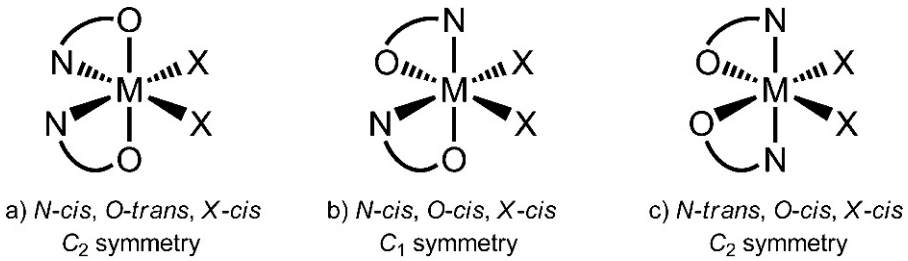
Soft: Amorphous and low glass transition temperature

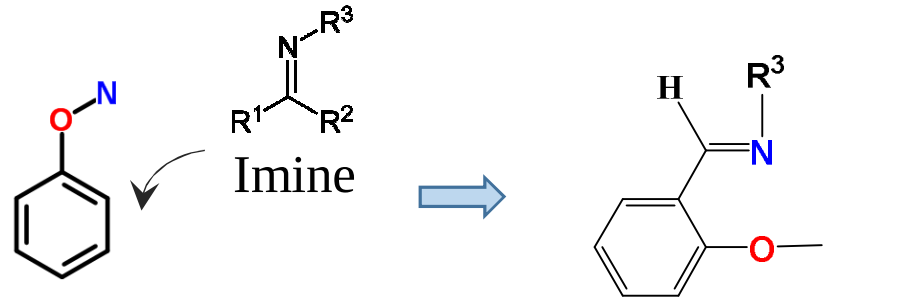
No mechanistic information on the complicated CSP process

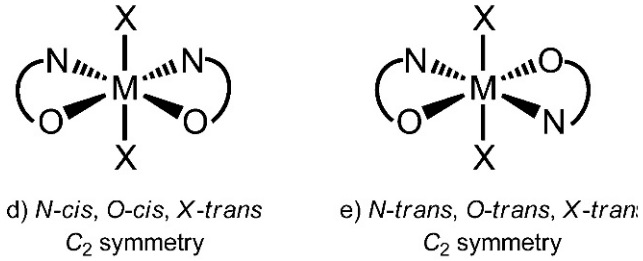
[1] *Science* **2006,** 312, 714.

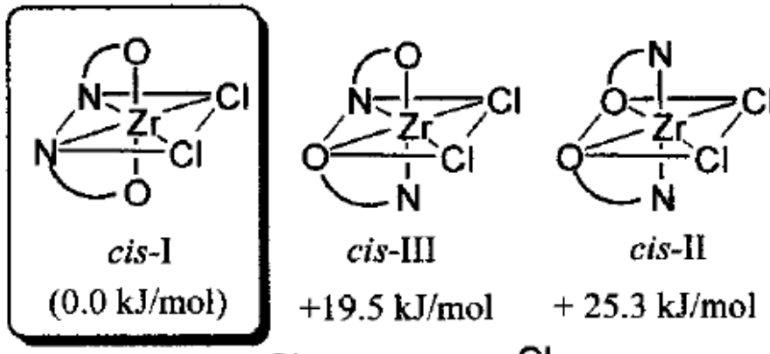
FI Catalyst[1] : Cation 1

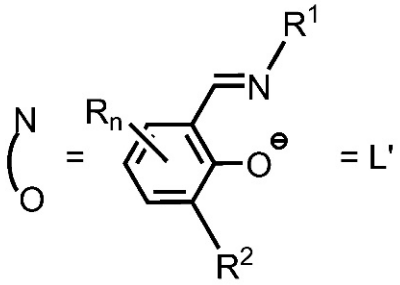
A neutral FI (*Fenokishi-Imin Haiishi*) catalyst is an octahedral complex bearing two bidentate phenoxy-imine ligands (L′; FI ligand) and two X ligands (Scheme 1[1]).





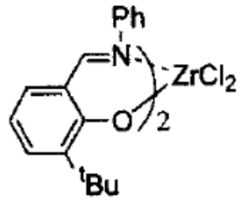






X: alkyl, halides

Scheme 1



complex 1

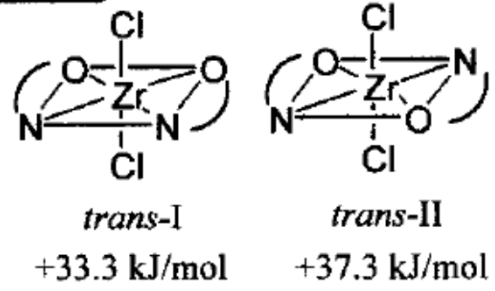
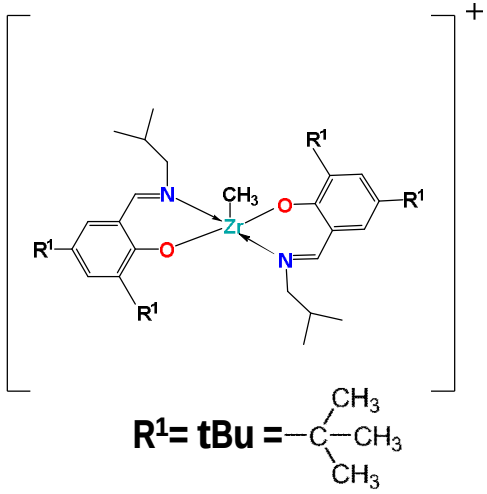


Figure 3: Relative energies of complex 1 isomers: based on isomeric structure cis-I [2]



Cat 1 :FI Cat

[1] *Acc. Chem. Res.* **2009,** 42, 1532.
[2] *J. Am. Chem. Soc.* **2001**, *123*, 6847.

Results and Discussion: Zr-Cation

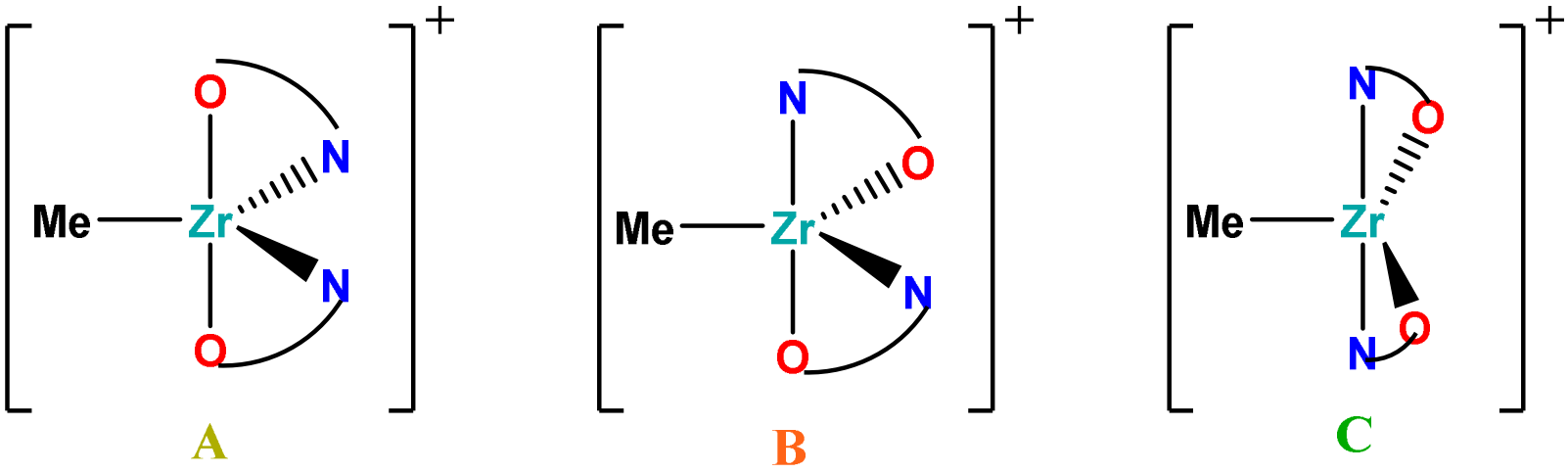
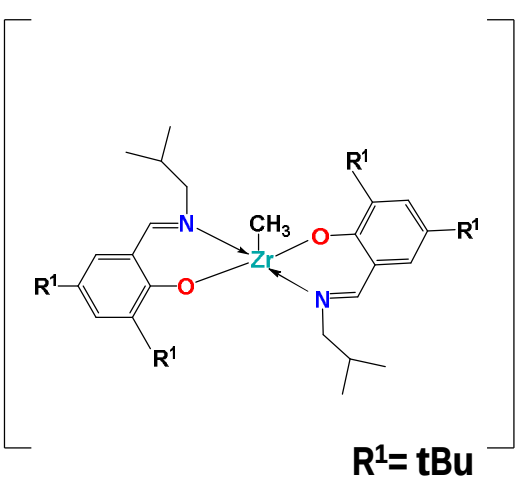


Figure 4 : The possible isomers



Zr-Cation

Cation	Energy (a.u.)	Relative energy w.r.t. **C** (kcal/mol)
A	**-1829.324149**	**2.05**
B	**-1829.320242**	**4.50**
C	**-1829.327418**	**0.00**

#(Int=Ultrafine)

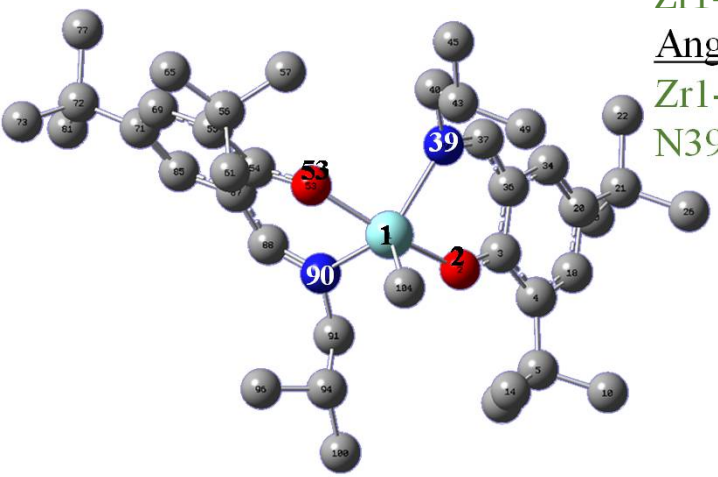
- All calculations are done with Gaussian 09 version D0.1 software.
- The optimization of the structure has been done at M06 level of theory followed by frequency calculation.
- The effective core potential (ECP) and LANL2DZ with added f polarization functions are used for Zr. All other atoms use 6-31G** basis set => **a1**

Results and Discussion: Developing Force field parameter for Zr-Cation A

First MM: The atomic charges were assigned by Merz-Singh-Kollman method by performing single-point QM calculation of the optimized structure. The VdW radius[1] for Zr is considered as 1.75.

In order to obtain QM (M06_a1 level) potential energy curves, scan calculations for three bonds and seven angles have been performed.

Ten times repetition of MM force field have been done and finally the best fitted MM energy (with QM energy) have considered for MD simulation.



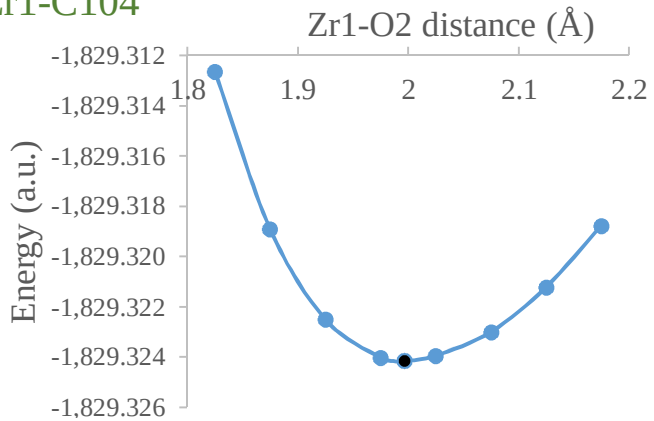
Distance scans × 3

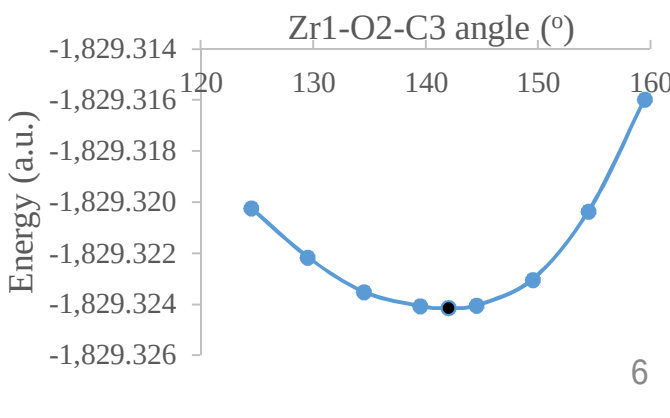
Zr1-O2, Zr1-N39 and Zr1-C104

In total, 77 conformations

Angle scans × 7

Zr1-O2-C3, Zr1-N39-C37, O2-Zr1-N39, O2-Zr1-O53, O2-Zr1-C104, N39-Zr1-N90, N39-Zr1-C104





[1] *Dalton Trans.* **2008**, 2832.

Results and Discussion: Developing Force field parameter for Zr-Cation A

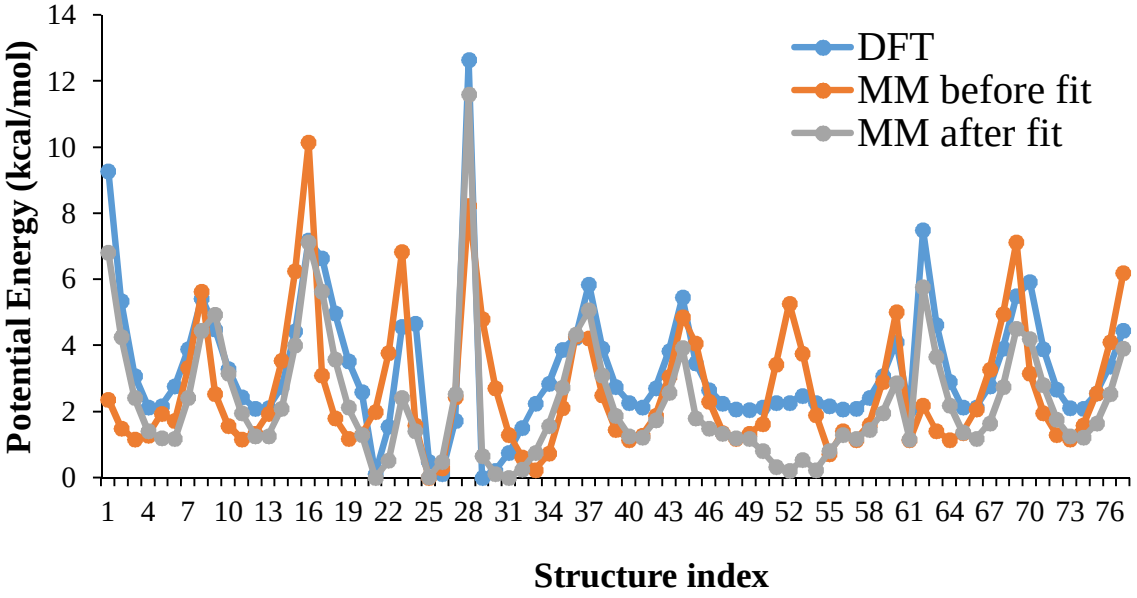


Figure 5: Energetics plot as obtained from developed force field

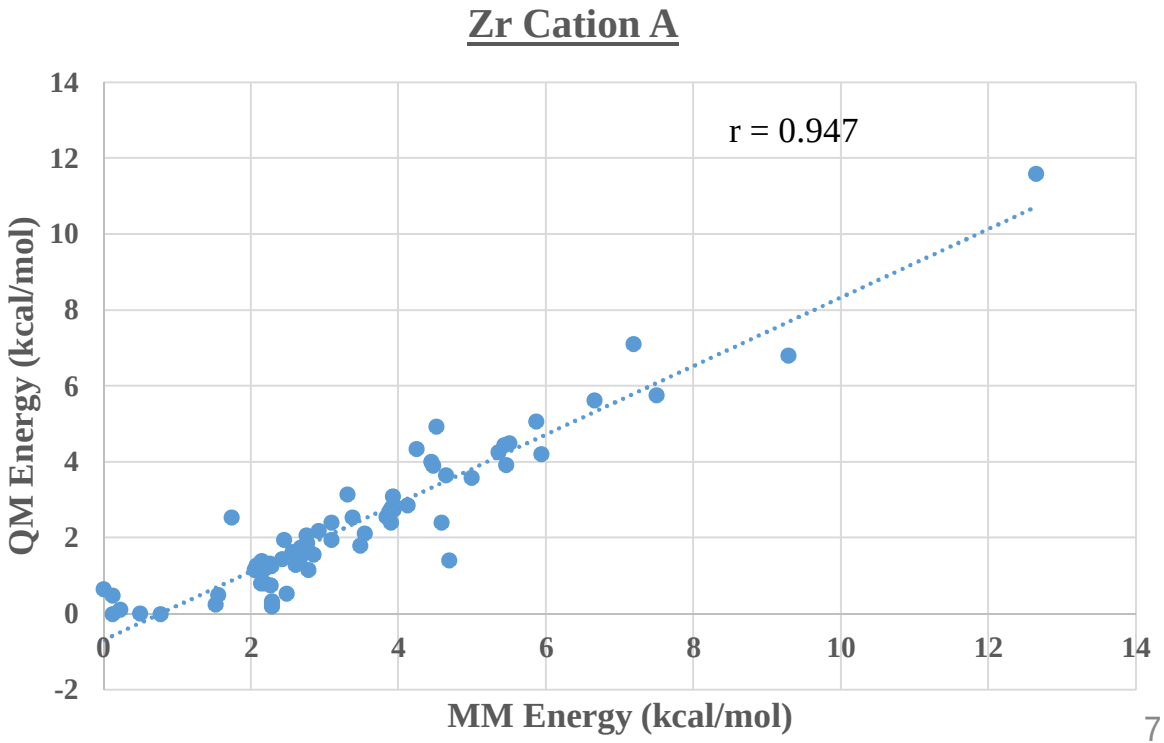
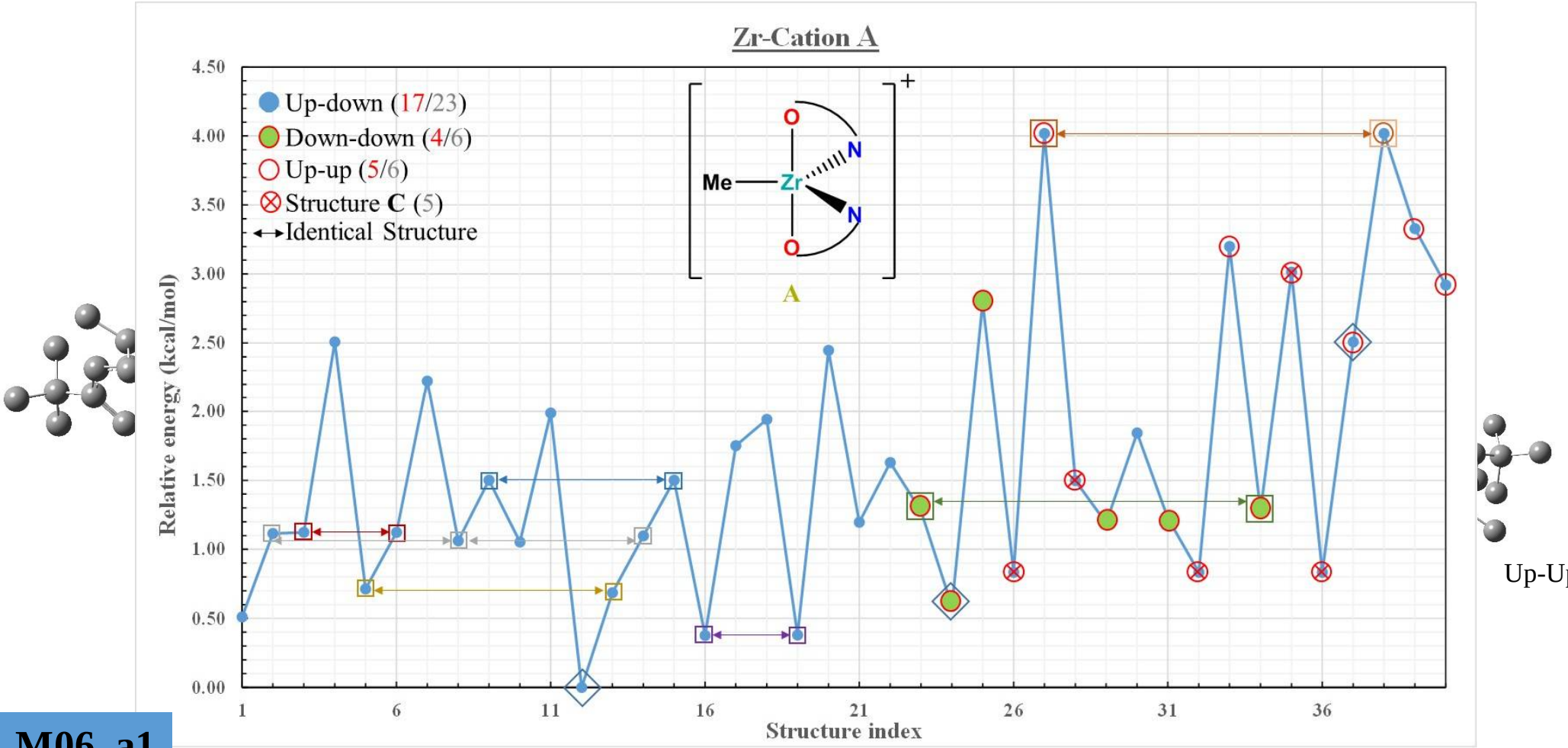


Figure 6: Relation between the QM energy and MM energy by the developed force field

Results and Discussion: MD simulation for Zr-Cation A

First MD and QM: The 40 ns MD calculations were performed at 400 K using AMBER 12 and obtained 20000 configurations. We have divided these 20000 configurations into 40 clusters by K-means clustering. The obtained 40 configurations were further optimized using QM procedure.



Up-Up

M06_a1

*(distinguishable/total)

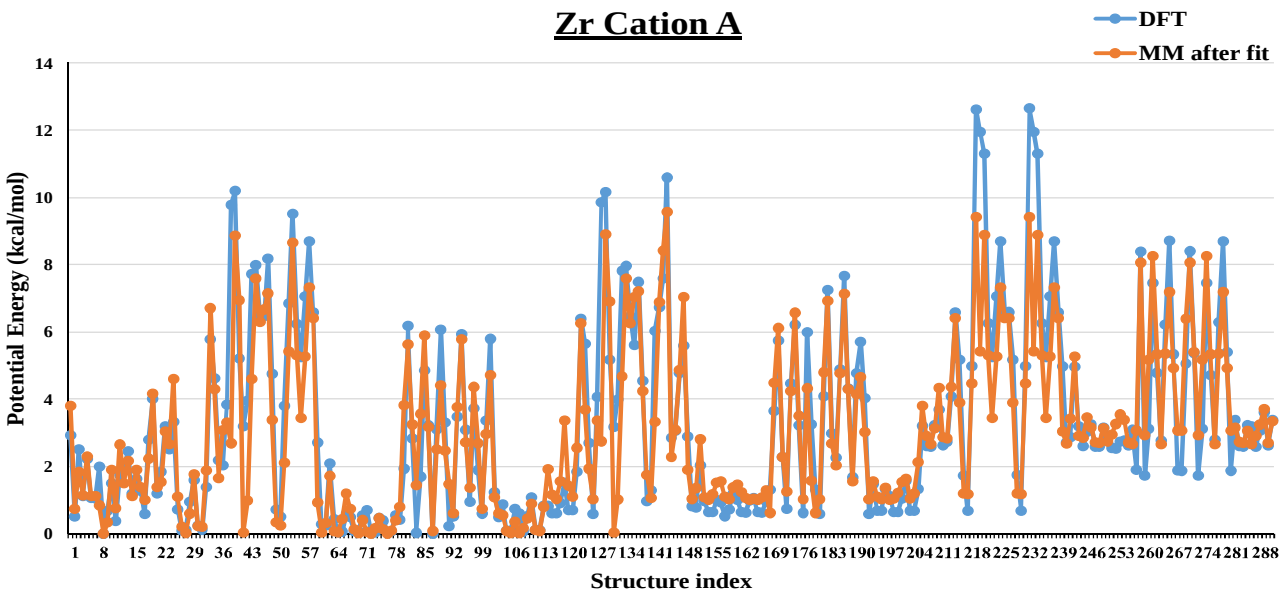
a1 = 6-31G** (LANL2DZ +f polarization functions: Zr)

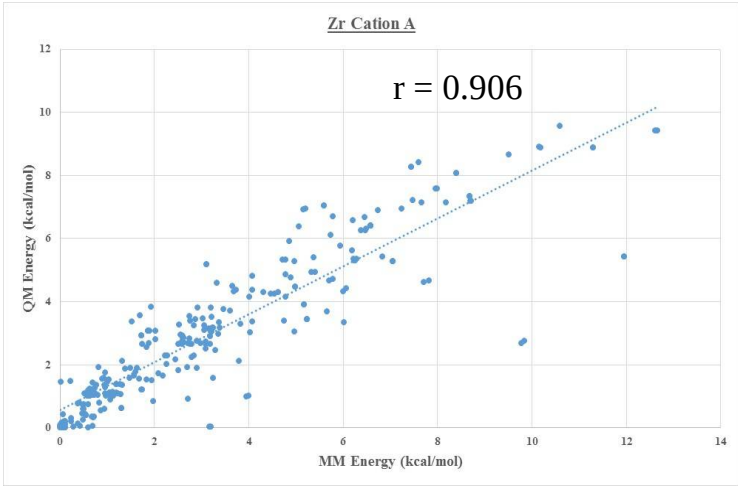
Results and Discussion: Re-perform Force field for Zr-Cation A

Second MM: The repetition of the earlier procedure has been done by performing QM (M06_a1 level) scan calculations for three bonds, seven angles and four dihedral angle have been performed for the most stable three configurations (up-up, up-down and down-down, as obtained earlier). The Merz-Singh-Kollman charge calculation have been performed for all the distinguishable configurations.

In the case of MM calculations all the distinguishable configurations and the scan results are used. So in total 293 conformers are used for MM. Initial parameters are taken from earlier MM calculation.

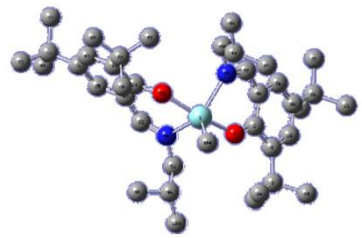
Ten times repetition have been done and finally the best fitted MM energy (with QM energy) have considered for MD simulation.



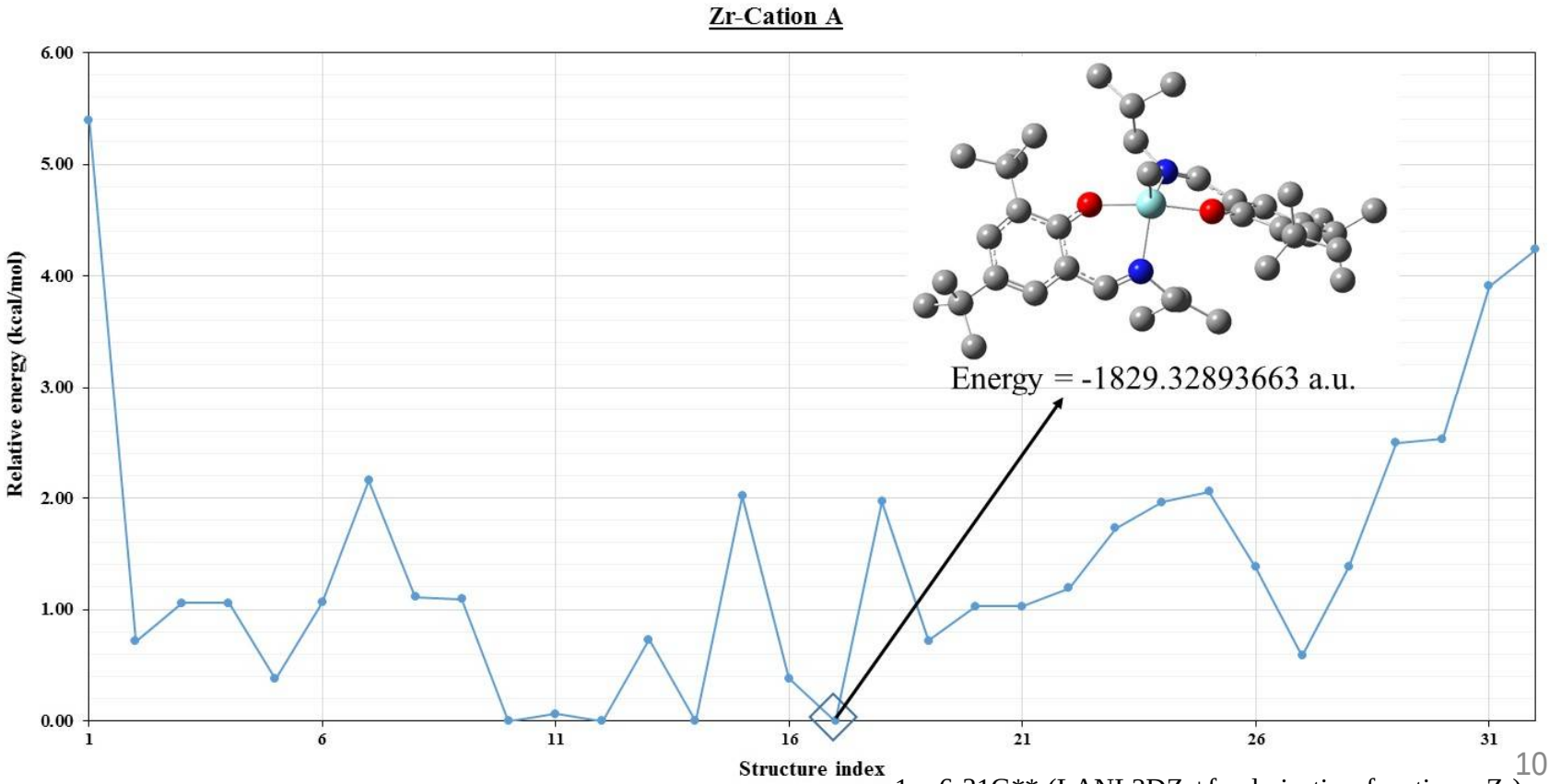


Results and Discussion: Re-perform MD and QM for Zr-Cation A

Second MD and QM: Likewise, earlier the 40 ns MD calculations were performed and obtained 40 clusters by K-means clustering. The obtained 40 configurations were further optimized using QM (M06_a1 level) procedure. Among these 40 configurations, 32 configurations are 'Zr-Cation A' and 8 configurations are 'Zr-Cation C'. Among 32 configurations, the most stable configurations are considered as the most preferable structure for 'Zr-Cation A'.



Energy = -1829.32414922

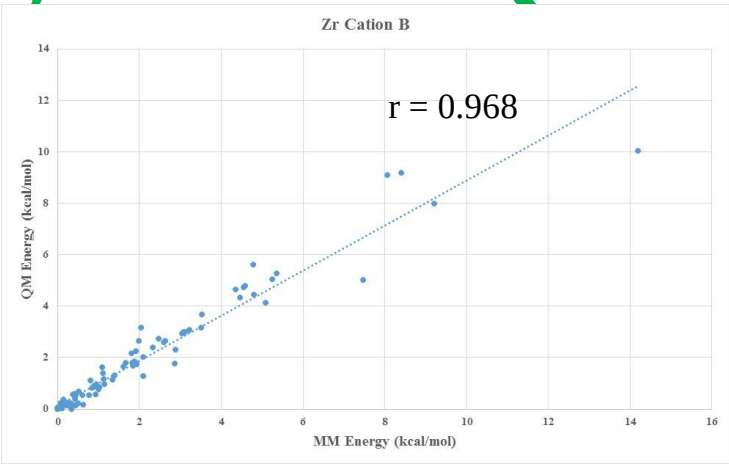


M06_a1

a1 = 6-31G** (LANL2DZ +f polarization functions: Zr)

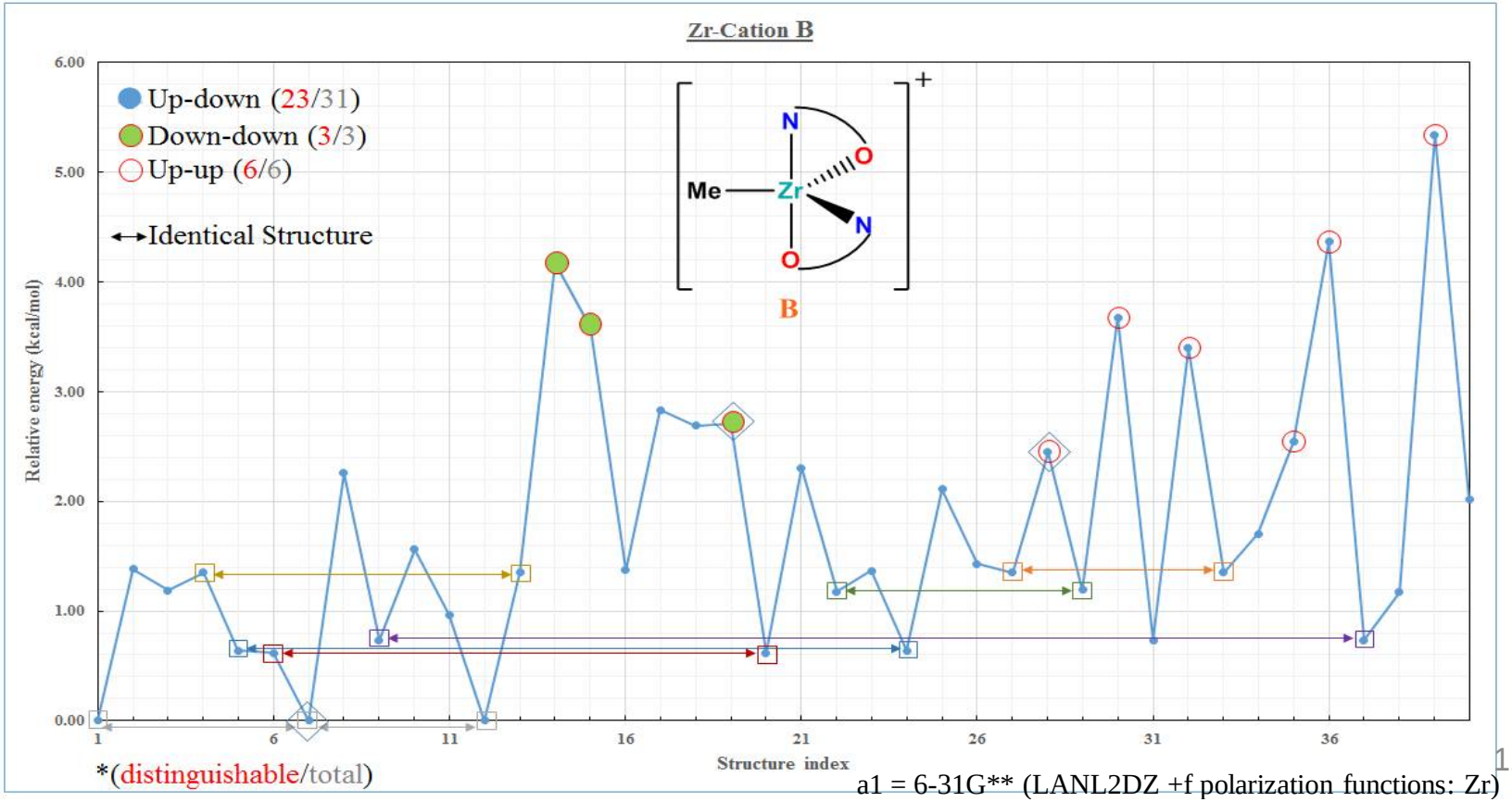
Results and Discussion: Developing Force field parameter, MD and QM for Zr-Cation B

First MM:



In total, 88 conformations

First MD and QM:

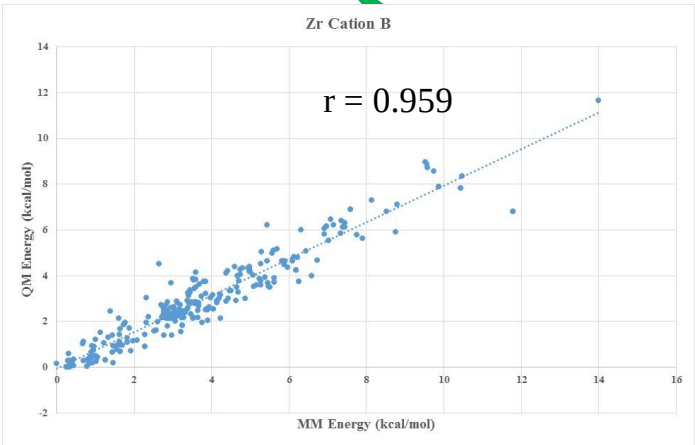


M06_a1

a1 = 6-31G** (LANL2DZ +f polarization functions: Zr)

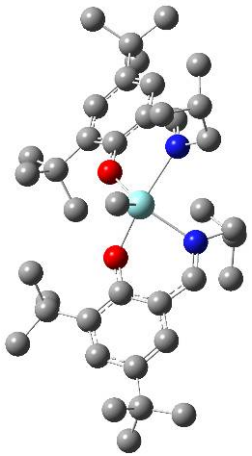
Results and Discussion: Developing Force field parameter, MD and QM for Zr-Cation B

Second MM:

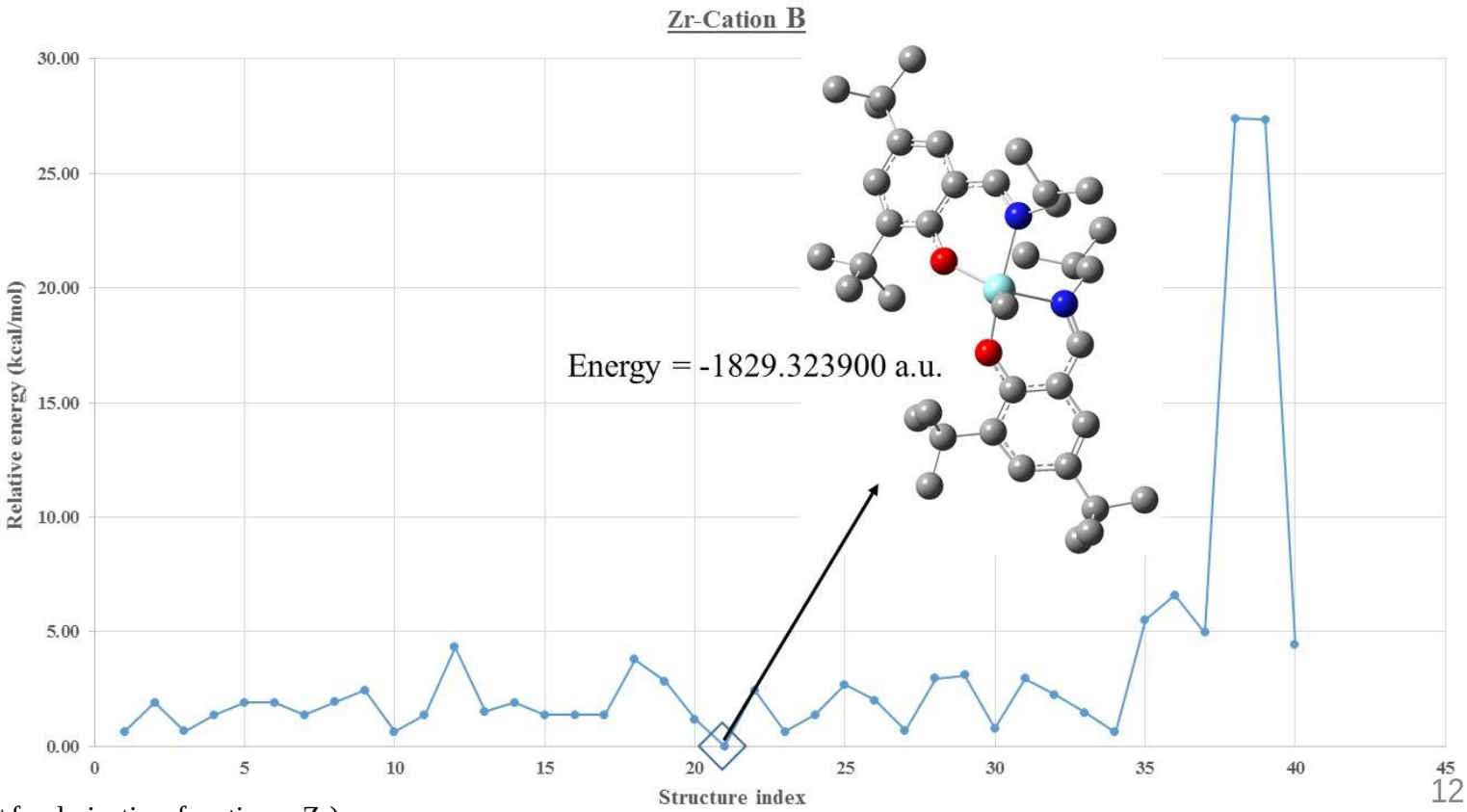


In total, 303 conformations

Second MD and QM:



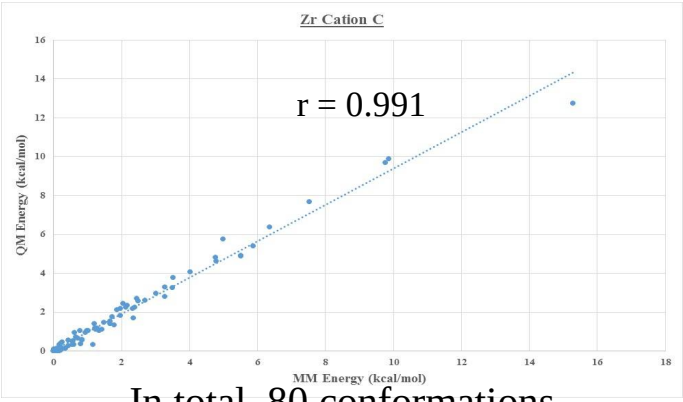
Energy = -1829.32024244



M06_a1 a1 = 6-31G** (LANL2DZ +f polarization functions: Zr)

Results and Discussion: Developing Force field parameter, MD and QM for Zr-Cation C

First MM:

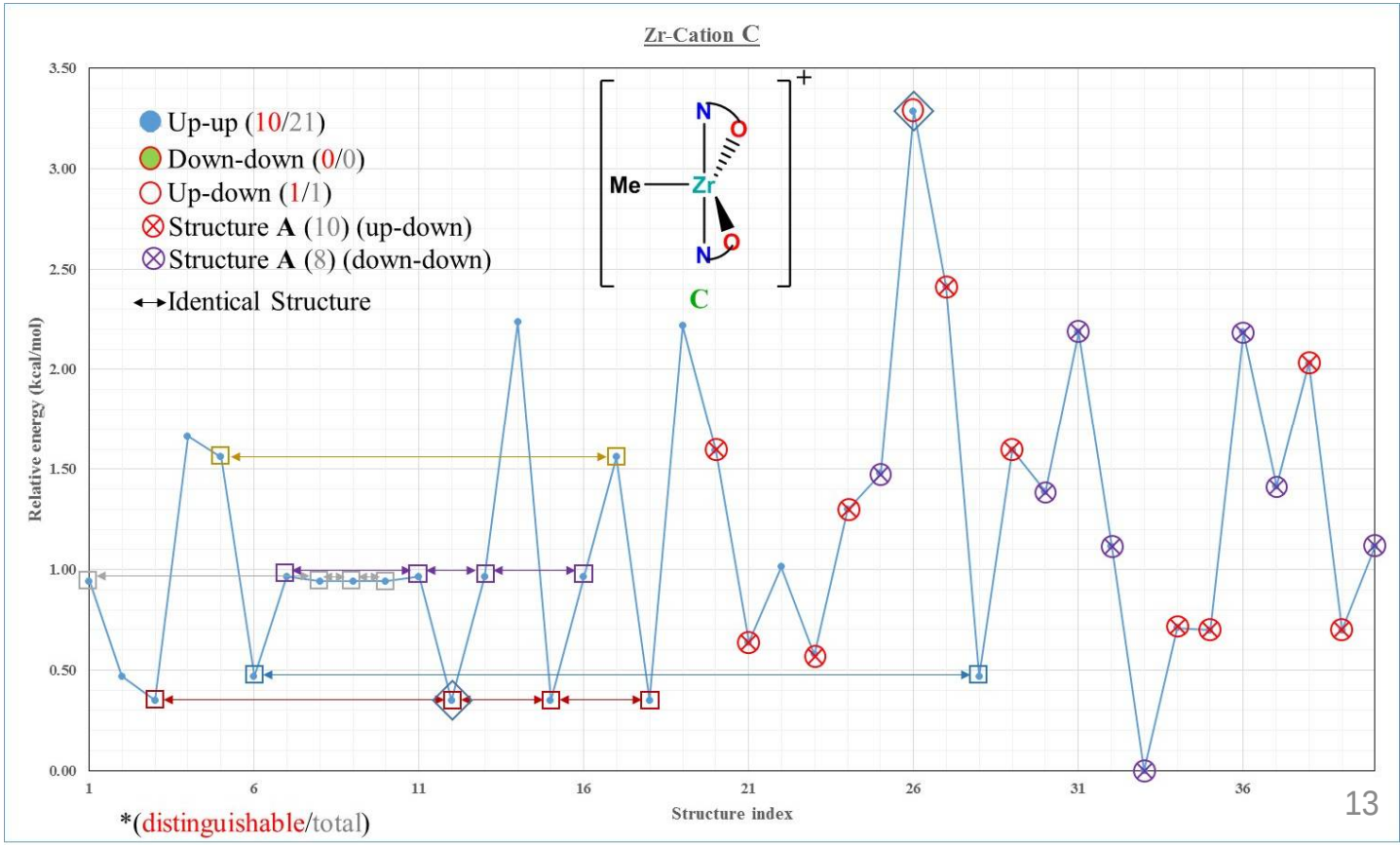


In total, 80 conformations

In order to obtain QM (M06_a1 level) potential energy curves, scan calculations for three bonds and seven angles have been performed.
Ten times repetition have been done and finally the best fitted MM energy (with QM energy) have considered for MD simulation.

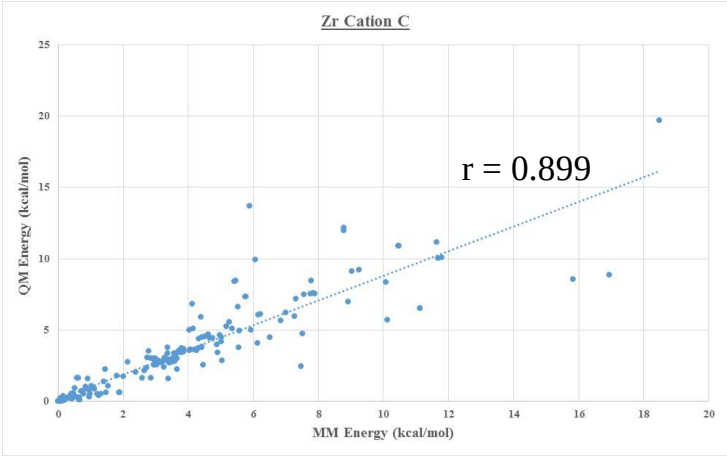
First MD and QM:

The 40 ns MD calculations were performed at 400 K and obtained 20000 configurations. We have divided these 20000 configurations into 40 clusters by K-means clustering. The obtained 40 configurations were further optimized using QM (M06_a1 level) procedure.



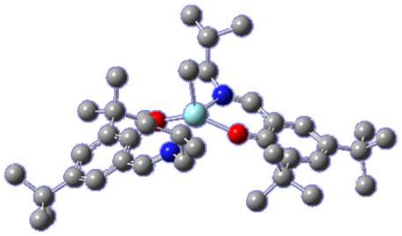
Results and Discussion: Developing Force field parameter, MD and QM for Zr-Cation C

Second MM:

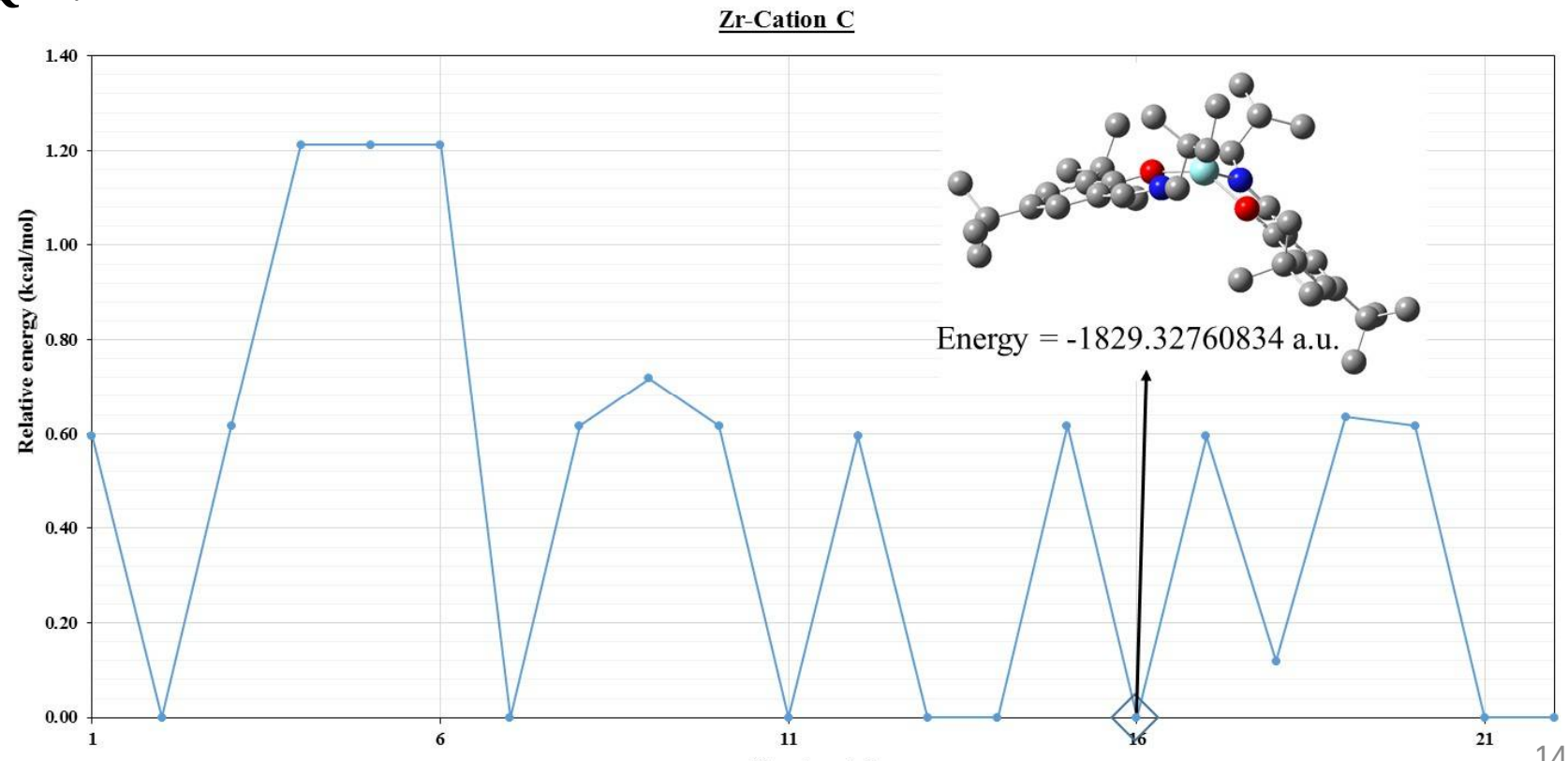


In total, 193 conformations

Second MD and QM:



Energy = -1829.32741824

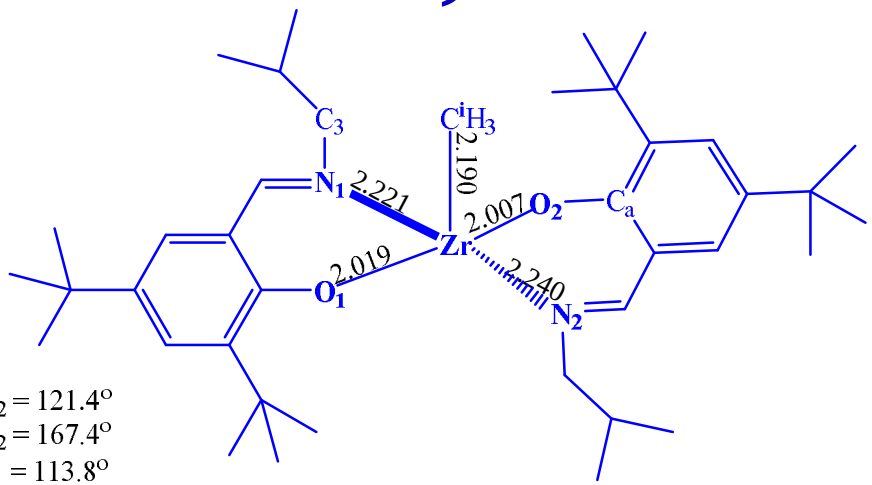


M06_a1

a1 = 6-31G** (LANL2DZ +f polarization functions: Zr)

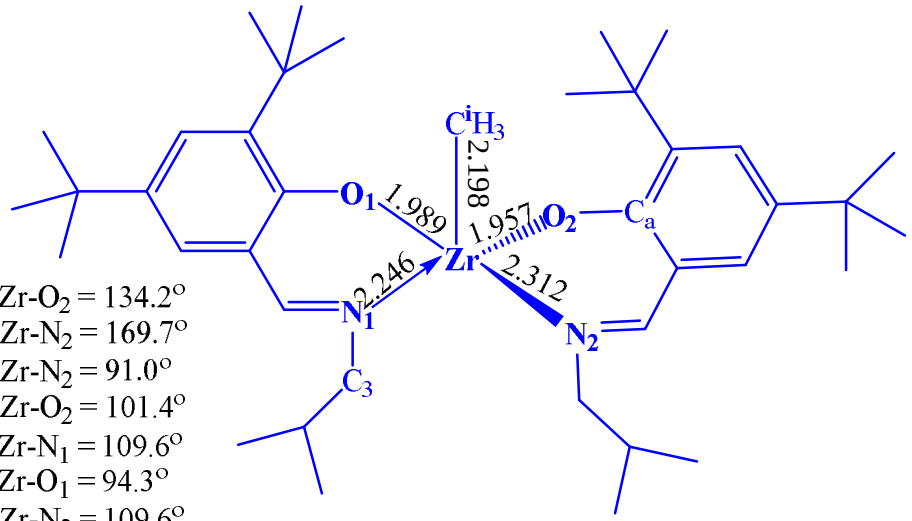
Results and Discussion: Structural Features for Zr-Cation A, B and C

A



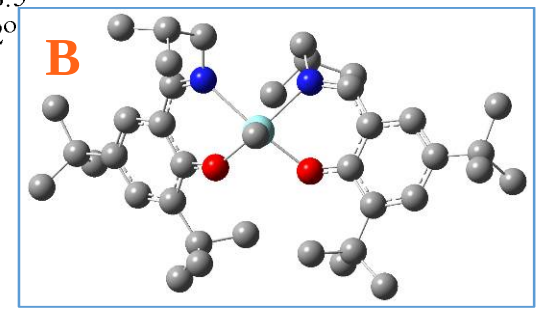
<N_1-Zr-N_2 = 121.4°
<O_1-Zr-O_2 = 167.4°
<C^i-Zr-N_1 = 113.8°
<C^i-Zr-O_1 = 95.3°
<C^i-Zr-N_2 = 124.7°
<C^i-Zr-O_2 = 97.0°
<C_3-N_1-Zr-N_2 (dihedral angle) =119.5°
<Ca-O_2-Zr-O_1 (dihedral angle) = 39.9°
<N_1-O_1-N_2-O_2 (dihedral angle) = -35.2°

B

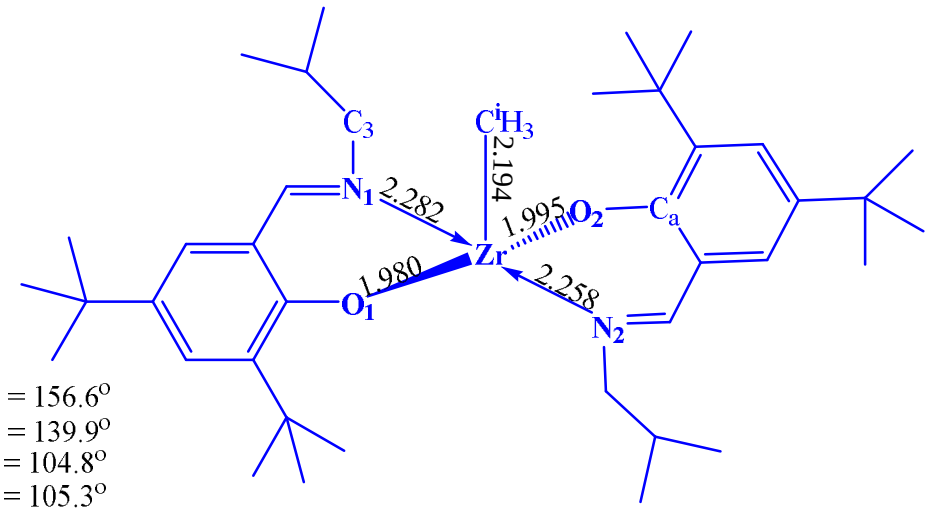


<N_1-Zr-O_2 = 134.2°
<O_1-Zr-N_2 = 169.7°
<N_1-Zr-N_2 = 91.0°
<O_1-Zr-O_2 = 101.4°
<C^i-Zr-N_1 = 109.6°
<C^i-Zr-O_1 = 94.3°
<C^i-Zr-N_2 = 109.6°
<C^i-Zr-O_2 = 115.8°
<C_3-N_1-Zr-N_2 (dihedral angle) =-26.2°
<Ca-O_2-Zr-O_1 (dihedral angle) = -138.5°
<N_1-N_2-O_2-O_1 (dihedral angle) = 23.2°

B

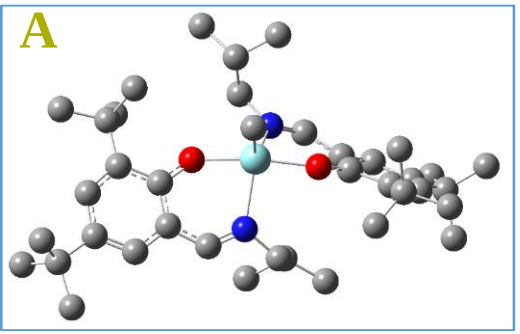


C

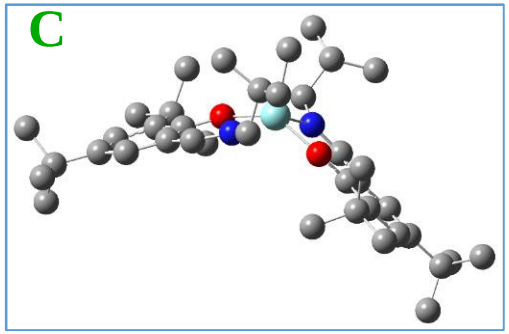


<N_1-Zr-N_2 = 156.6°
<O_1-Zr-O_2 = 139.9°
<C^i-Zr-N_1 = 104.8°
<C^i-Zr-O_1 = 105.3°
<C^i-Zr-N_2 = 98.4°
<C^i-Zr-O_2 = 114.7°
<C_3-N_1-Zr-N_2 (dihedral angle) =117.0°
<Ca-O_2-Zr-O_1 (dihedral angle) = 64.2°
<N_1-O_1-N_2-O_2 (dihedral angle) = 9.5°

A



C



M06_a1

a1 = 6-31G** (LANL2DZ +f polarization functions: Zr)

Method	Zr-Cation	Total Energy (E: a.u.)	Total Energy (E: kcal/mol)	ΔE wrt A (kcal/mol)	E^* = Total Energy + ZPE (a.u.)	E^* (kcal/mol)	ΔE^* wrt A (kcal/mol)	G^* (a.u.)	G^* (kcal/mol)	ΔG^* wrt A (kcal/mol)
M06_a1	A	-1829.328937	-1147920.372	0.00	-1828.387599	-1147329.674	0.00	-1828.471062	-1147382.048	0.00
	B	-1829.323900	-1147917.211	3.16	-1828.382136	-1147326.246	3.43	-1828.466204	-1147378.999	3.05
	C	-1829.327608	-1147919.538	0.83	-1828.385577	-1147328.405	1.27	-1828.469732	-1147381.213	0.83
B2PLYPD3_a1	A	-1826.610132	-1146214.297	0.00	-1825.668794#	-1145623.599	0.00	-1825.752257#	-1145675.973	0.00
	B	-1826.609558	-1146213.937	0.36	-1825.667794#	-1145622.972	0.63	-1825.751862#	-1145675.725	0.25
	C	-1826.613374	-1146216.332	-2.03	-1825.671343#	-1145625.199	-1.60	-1825.755498#	-1145678.007	-2.03
MP2_a1	A	-1824.600016	-1144952.931	0.00	-1823.658678#	-1144362.234	0.00	-1823.742141#	-1144414.607	0.00
	B									
	C	-1824.599250	-1144952.451	0.48	-1823.657219#	-1144361.318	0.92	-1823.741374#	-1144414.126	0.48
B3LYP_b1	A	-1831.841274	-1149496.886	0.00	-1830.899361	-1148905.827	0.00	-1830.987833	-1148961.344	0.00
	B	-1831.841773	-1149497.199	-0.31	-1830.899842	-1148906.129	-0.30	-1830.987350	-1148961.041	0.30
	C	-1831.845801	-1149499.727	-2.84	-1830.903966	-1148908.717	-2.89	-1830.991686	-1148963.762	-2.42
B3LYP-D3_b1	A	-1831.991018	-1149590.852	0.00	-1831.045533	-1148997.551	0.00	-1831.131628	-1149051.577	0.00
	B	-1831.988197	-1149589.082	1.77	-1831.042599	-1148995.710	1.84	-1831.127774	-1149049.158	2.42
	C	-1831.991941	-1149591.431	-0.58	-1831.045901	-1148997.782	-0.23	-1831.130509	-1149050.875	0.70
M052X_b1	A	-1831.568829	-1149325.924	0.00	-1830.609039	-1148723.647	0.00	-1830.693963	-1148776.938	0.00
	B	-1831.567902	-1149325.343	0.58	-1830.608085	-1148723.049	0.60	-1830.693260	-1148776.497	0.44
	C	-1831.572356	-1149328.137	-2.21	-1830.611987	-1148725.497	-1.85	-1830.696162	-1148778.318	-1.38
M06_b1	A	-1830.434302	-1148613.998	0.00	-1829.492947	-1148023.29	0.00	-1829.575779	-1148075.268	0.00
	B	-1830.429797	-1148611.172	2.83	-1829.488629	-1148020.580	2.71	-1829.572897	-1148073.459	1.81
	C	-1830.434430	-1148614.079	-0.08	-1829.492742	-1148023.161	0.13	-1829.576499	-1148075.719	-0.45
M06L_b1	A	-1831.602545	-1149347.081	0.00	-1830.656095	-1148753.176	0.00	-1830.739905	-1148805.767	0.00
	B	-1831.598031	-1149344.249	2.83	-1830.651652	-1148750.387	2.79	-1830.736596	-1148803.691	2.08
	C	-1831.601507	-1149346.430	0.65	-1830.654881	-1148752.414	0.76	-1830.739038	-1148805.223	0.54
M062X_b1	A	-1830.926842	-1148923.072	0.00	-1829.974890	-1148325.713	0.00	-1830.057821	-1148377.753	0.00
	B	-1830.925129	-1148921.997	1.08	-1829.973417	-1148324.789	0.92	-1830.057953	-1148377.836	-0.08
	C	-1830.930256	-1148925.214	-2.14	-1829.977760	-1148327.514	-1.80	-1830.060723	-1148379.574	-1.82
TPSSh_b1	A	-1831.919242	-1149545.811	0.00	-1830.981174	-1148957.166	0.00	-1831.071082	-1149013.584	0.00
	B	-1831.919748	-1149546.129	0.32	-1830.981730	-1148957.514	-0.35	-1831.070401	-1149013.156	0.43
	C	-1831.922808	-1149548.049	2.24	-1830.984937	-1148959.527	-2.36	-1831.073695	-1149015.223	-1.64

a1 = 6-31G** (LANL2DZ +f polarization functions: Zr); b1 = Def2-TZVPP; 'Red Colour' is more stable; #E + Correction (M06_a1)

Results and Discussion: Energetics for Zr-Cation A, B and C

Solvent (Heptane)†:

Method	Zr-Cation	Total Energy (E: a.u.)	Total Energy (E: kcal/mol)	ΔE wrt A (kcal/mol)	E^* = Total Energy + ZPE (a.u.)#	E^* (kcal/mol)#	ΔE^* wrt A (kcal/mol)#	G^* (a.u.)#	G^* (kcal/mol)#	ΔG^* wrt A (kcal/mol)#
M06_a1	A	-1829.383634	-1147954.695	0.00	-1828.442296	-1147363.997	0.00	-1828.525759	-1147416.371	0.00
	B	-1829.378339	-1147951.372	3.32	-1828.436575	-1147360.406	3.59	-1828.520643	-1147413.160	3.21
	C	-1829.380260	-1147952.578	2.12	-1828.438229	-1147361.445	2.55	-1828.522384	-1147414.253	2.12
B3LYP_b1	A	-1831.897759	-1149532.331	0.00	-1830.955846	-1148941.272	0.00	-1831.044318	-1148996.789	0.00
	B	-1831.898178	-1149532.594	-0.26	-1830.956248	-1148941.524	-0.25	-1831.043756	-1148996.436	0.35
	C	-1831.900699	-1149534.176	-1.84	-1830.958864	-1148943.166	-1.89	-1831.046584	-1148998.211	-1.42
B3LYP-D3_b1	A	-1832.047528	-1149626.313	0.00	-1831.102043	-1149033.012	0.00	-1831.188138	-1149087.037	0.00
	B	-1832.044800	-1149624.601	1.71	-1831.099202	-1149031.229	1.78	-1831.184377	-1149084.677	2.36
	C	-1832.045993	-1149625.349	0.96	-1831.099952	-1149031.700	1.31	-1831.184560	-1149084.792	2.25
M052X_b1	A	-1831.625497	-1149361.484	0.00	-1830.665707	-1148759.207	0.00	-1830.750631	-1148812.498	0.00
	B	-1831.623963	-1149360.522	0.96	-1830.664146	-1148758.228	0.98	-1830.749321	-1148811.676	0.82
	C	-1831.626980	-1149362.415	-0.93	-1830.666611	-1148759.774	-0.57	-1830.750786	-1148812.595	-0.10
M06_b1	A	-1830.489064	-1148648.362	0.00	-1829.547710	-1148057.654	0.00	-1829.630542	-1148109.632	0.00
	B	-1830.485327	-1148646.017	2.35	-1829.544159	-1148055.425	2.23	-1829.628427	-1148108.304	1.33
	C	-1830.487757	-1148647.542	0.82	-1829.546069	-1148056.624	1.03	-1829.629826	-1148109.183	0.45
M06L_b1	A	-1831.657362	-1149381.480	0.00	-1830.710912	-1148787.574	0.00	-1830.794722	-1148840.165	0.00
	B	-1831.652380	-1149378.353	3.13	-1830.706001	-1148784.492	3.08	-1830.790945	-1148837.795	2.37
	C	-1831.654507	-1149379.688	1.79	-1830.707882	-1148785.672	1.90	-1830.792039	-1148838.481	1.68
M062X_b1	A	-1830.983494	-1148958.621	0.00	-1830.031542	-1148361.263	0.00	-1830.114473	-1148413.303	0.00
	B	-1830.981261	-1148957.220	1.40	-1830.029549	-1148360.012	1.25	-1830.114085	-1148413.060	0.24
	C	-1830.985126	-1148959.645	-1.02	-1830.032630	-1148361.946	-0.68	-1830.115593	-1148414.006	-0.70
TPSSh_b1	A	-1831.974783	-1149580.664	0.00	-1831.036715	-1148992.018	0.00	-1831.126623	-1149048.436	0.00
	B	-1831.974859	-1149580.712	-0.05	-1831.036841	-1148992.097	-0.08	-1831.125512	-1149047.739	0.70
	C	-1831.976850	-1149581.961	-1.30	-1831.038979	-1148993.439	-1.42	-1831.127737	-1149049.135	-0.70

a1 = 6-31G** (LANL2DZ +f polarization functions: Zr); b1 = Def2-TZVPP; 'Red Colour' is more stable; #E + Correction (Gas)

† SMD approach: Heptane: ε =1.9113

Conclusion

MC/MD calculations were performed in order to gain information about the stability of the three different isomers of Zr-FI Cation.

On the basis of the symmetry of the possible isomers and their relative energies earlier studies[1] have concluded that, in solution, the FI Catalysts predominantly exist as isomer **A**, (i.e., N-cis, O-tarns and Cl-cis arrangement: C_2 symmetry).

However, in the current study, we have observed that this Zr-FI cation seems to exist as a mixture of the isomer **A** and **C**.

The steric demands of the imine substituent may play a crucial role in the stability of the studied Zr-FI cation.

The study clearly shows that, although somewhat distant from the metal centre, the choice of imine substituent is critical to the ligand coordination geometry about the central metal, and points to possible the rational design of metallo-organic complexes for use in catalysis.

[1] *J. Am. Chem. Soc.* **2001**, *123*, 6847; *Acc. Chem. Res.* **2009,** 42, 1532.

Thank You……