Isomers of Alkali Metal (Methylbenzyl)allylamides: A Theoretical Perspective

Supplementary Information

Luke Wylie[a], Matthew Flynn[a], Victoria L. Blair[a], Philip C. Andrews[a] and Ekaterina I. Izgorodina[a*]

[a] School of Chemistry, Monash University, Wellington rd, Clayton VIC 3800, Australia

*Katya.Pas@monash.edu

Supplementary Information 6 Tables, 1 Figure:

Table S1: Configuration analysis of each step of isomerisation using M06-2X/cc-pVDZ in kJ mol^{-1}

Isomer	Configuration	Relative Enthalpy
Allyl-Amide	initial	14.09
Allyl-Amide	a1	14.31
Allyl-Amide	a1b2	105.71
Allyl-Amide	a1b2c3	74.83
Allyl-Amide	a1b2c3d2	74.63
Allyl-Amide	a1b2d2	80.28
Allyl-Amide	a1c2	17.56
Allyl-Amide	a1c2d2	7.81
Allyl-Amide	a1c3	12.54
Allyl-Amide	a1c3d2	15.07
Allyl-Amide	a1d2	13.27
Allyl-Amide	a2b2	25.01
Allyl-Amide	a2b2c3	20.08
Allyl-Amide	a2b2c3d2	21.85
Allyl-Amide	a3b2	0.00
Allyl-Amide	a3b2c3	4.42
Allyl-Amide	a3b2c3d2	6.46
Allyl-Amide	a3b2d2	3.40
Aza-Allyl	initial	0.73
Aza-Allyl	a1	1.01
Aza-Allyl	a1b2	6.92
Aza-Allyl	a1b2d2	6.83
Aza-Allyl	a1c2	16.77
Aza-Allyl	a1c2d2	16.74
Aza-Allyl	a1d2	0.00
Aza-Allyl	a2b2	6.84
Aza-Allyl	a2b2c2	37.37
Aza-Allyl	a2b2c2d2	27.92
Aza-Allyl	a2b2d2	7.05
Aza-Allyl	a2c2	16.69
Aza-Allyl	a2c2d2	16.68
Aza-Allyl	a2d2	1.74
Aza-Allyl	a3	0.26
Aza-Allyl	a3c2	16.74
Aza-Allyl	a3c2d2	16.74
Aza-Allyl	a3d2	0.06
Aza-Enolate	initial	0.00
Aza-Enolate	a1	0.00
Aza-Enolate	a1b2c2	2.17
Aza-Enolate	a1b2c3	12.45
Aza-Enolate	a1b3	3.20

Aza-Enolate	a1b3c2	10.23
Aza-Enolate	a1b3c3	13.64
Aza-Enolate	a1c2	2.31
Aza-Enolate	a1c3	7.40
Aza-Enolate	a2	0.00
Aza-Enolate	a2b2c2	2.16
Aza-Enolate	a2b2c3	12.45
Aza-Enolate	a2b3c2	10.19
Aza-Enolate	a2c2	2.53
Imine	a1	3.49
Imine	a1b2	41.44
Imine	a1b2c2	188.64
imine	a1b2c3	22.34
imine	a1c2	5.11
imine	a1c3	0.00
imine	a2	4.19
imine	a2b2	25.13
imine	a2b2c2	43.05
imine	a2b2c3	24.69
imine	a2c2	5.44
imine	a2c3	0.52
imine	a3	6.00
imine	a3b2c2	41.36
imine	a3b2c3	27.30
imine	a3c2	4.26
imine	a3c3	2.34

Table S2: Lowest energy configuration analysis using M06-2X/cc-pVTZ with Li, Na and K complexes in kJ mol^{-1}

		Li		Na		K	
Isomer	Configuration	Relative Enthalpy	Relative Gibbs Free Energy	Relative Enthalpy	Relative Energy	Relative Enthalpy	Relative Energy
Allyl-amide	a1c2d2	0.0	0.0	0.0	0.0	0.0	1.7
Allyl-amide	a3b2	3.5	4.0	9.3	10.4	17.0	17.4
Allyl-amide	a3b2c3	3.2	4.2	1.5	1.4	2.1	0.0
Allyl-amide	a3b2d2	4.8	3.5	8.9	6.2	14.7	12.5
Aza-allyl	a1b2	22.3	26.5	29.1	38.8	34.8	36.5
Aza-allyl	a1b2d2	22.4	33.2	29.8	42.1	34.4	35.9
Aza-allyl	a1d2	2.4	11.6	0.4	2.4	3.5	4.5
Aza-allyl	a2b2	21.6	26.3	27.6	35.8	34.4	35.8
Aza-allyl	a2b2d2	22.9	27.9	27.5	36.6	34.4	36.0
Aza-allyl	a2d2	4.8	10.7	1.0	7.1	1.5	3.2
Aza-allyl	a3	0.0	0.0	0.0	0.0	0.0	0.0
Aza-enolate	a1	0.6	0.5	0.0	0.0	0.0	0.0
Aza-enolate	a1b2c2	7.2	4.9	10.2	10.8	9.6	9.5
Aza-enolate	a1c2	0.0	0.2	1.4	4.6	2.8	3.7
Aza-enolate	a1c3	1.5	0.0	5.1	8.2	2.2	2.3
Aza-enolate	a2b2c2	7.2	4.9	10.2	10.9	9.7	9.4
Aza-enolate	a2c2	0.7	0.7	1.7	4.4	2.1	2.0
imine	a1	0.0	0.0	0.3	1.3	0.0	0.0
imine	a1c2	3.7	4.1	2.6	2.0	1.8	1.8
imine	a1c3	14.7	11.0	4.3	0.2	1.6	1.5
imine	a2	0.3	0.6	0.0	0.0	0.1	0.3
imine	a2c2	3.9	4.9	2.6	2.0	1.8	1.9
imine	a2c3	15.3	13.8	6.0	4.0	1.4	1.4

Table S3: Overall relative energy of isomerisation for each metal isomer from the allyl-amide in kJ mol^{-1}

Step	Metal	Relative Energy
Allyl-Amide	Li	0
Allyl-Amide	Na	0
Allyl-Amide	K	0
Aza-Allyl	Li	-64.0
Aza-Allyl	Na	-75.7
Aza-Allyl	K	-72.2
Imine	Li	-39.8
Imine	Na	-52.6
Imine	K	-69.4
Aza-enolate	Li	-63.7
Aza-enolate	Na	-109.5
Aza-enolate	K	-81.9

Table S4: Partially frozen core interaction energy in kJ mol^{-1} using SRS-MP2/cc-pVTZ

Metal	Step	SRS-MP2 Total Interaction Energy	Electrostatic interaction Energy	Dispersion Interaction Energy
Li	Imine	-1038.1	-1008.4	-29.7
Li	Allyl-amide	-1166.0	-1156.2	-9.9
Li	Aza-allyl	-1114.9	-1113.2	-1.7
Li	Aza-enolate	-1068.0	-1061.6	-6.4
Na	Imine	-878.2	-837.8	-40.4
Na	Allyl-amide	-989.4	-965.3	-24.1
Na	Aza-allyl	-949.2	-931.9	-17.3
Na	Aza-enolate	-897.5	-874.5	-23.0
K	Imine	-781.8	-722.1	-59.7
K	Allyl-amide	-892.6	-832.4	-60.3
K	Aza-allyl	-833.5	-782.1	-51.4
K	Aza-enolate	-794.5	-746.4	-48.1

Table S5: Open core interaction energy in kJ mol^{-1} using SRS-MP2/cc-pVTZ

Metal	Step	SRS-MP2 Total Interaction Energy	Electrostatic interaction Energy	Dispersion Interaction Energy
Li	Imine	-1048.3	-1008.4	-40.0
Li	Allyl-amide	-1174.1	-1156.2	-17.9
Li	Aza-allyl	-1123.9	-1113.2	-10.7
Li	Aza-enolate	-1078.4	-1061.6	-16.7
Na	Imine	-887.9	-837.8	-50.1
Na	Allyl-amide	-999.6	-965.3	-34.3
Na	Aza-allyl	-959.5	-931.9	-27.7
Na	Aza-enolate	-906.1	-874.5	-31.6
K	Imine	-795.4	-722.1	-73.4
K	Allyl-amide	-908.6	-832.4	-76.2
K	Aza-allyl	-845.1	-782.1	-62.9
K	Aza-enolate	-805.6	-746.4	-59.2

Table S6: Natural Bond Order (NBO) of ligand atoms important in the interaction with the metal using HF/cc-pVDZ, atoms labelled as shown in Fig S1

Metal	Step	Cphen-C1 bond	C1-N bond	C1-C2 bond	N-C3 bond	C3-C4 bond	C4-C5 bond	C4-C6 bond
Li	Allyl-amide	1.969	1.978	1.983	1.984	1.974	3.949	1.980
Li	Aza-allyl	1.973	1.979	1.980	1.985	3.906	1.981	1.981
Li	Aza-enolate	1.967	1.983	3.936	1.984	1.976	1.983	1.983
Li	Imine	1.972	1.982	1.983	3.937	1.976	1.983	1.979
Na	Allyl-amide	1.969	1.976	1.984	1.983	1.973	3.950	1.980
Na	Aza-allyl	1.969	1.976	1.982	1.984	3.903	1.981	1.982
Na	Aza-enolate	1.966	1.983	3.934	1.982	1.975	1.982	1.982
Na	Imine	1.972	1.982	1.984	3.934	1.975	1.983	1.980
K	Allyl-amide	1.968	1.973	1.985	1.982	1.974	3.951	1.980
K	Aza-allyl	1.969	1.980	1.975	1.984	3.901	1.981	1.983
K	Aza-enolate	1.966	1.982	3.935	1.982	1.975	1.969	1.982
K	Imine	1.973	1.982	1.986	3.934	1.974	1.982	1.979

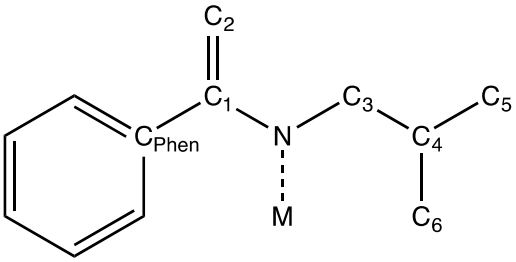

Figure S1: Example of an aza-enolate with atoms labelled as shown in Table S6