Benchmarking lithium amide versus amine bonding by charge density and energy decomposition analysis arguments

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Supporting Information

1 Experimental Charge Density Analysis

1.1 Data collection and reduction

The dataset used in this study was measured on a Bruker *D8 Ultra* diffractometer equipped with a molybdenum *Turbo X-Ray Source (TXS)* rotating anode generator and INCOATEC *Helios* mirror optics. A suitable crystal was identified with the help of a X-Temp2 device[1], mounted on the top of a *MiTeGen micromount*™ and placed in a cold stream (100K) of a Bruker *Kryoflex2*.

The data collection strategy was optimised by the *COSMO* plugin[2] of the *APEX2* software suite[3] subsequent to the unit cell determination.

The raw data was integrated with *SAINT v8.37A*[4] with automatic box size refinement enabled. Scaling and absorption correction has been done with SADABS 2015/1[5]. Within SADABS no error model has been applied to the experimental standard uncertainties.

The maximum resolution was determined from the intensity statistics given by XPREP[6] (cf. Table 1). Highest resolution was chosen to 0.45 Å due to the R_{merge} which is above 20%.

R_{merge} and R_{sigma} are defined as followed:

$$R_{merge} = \frac{\sum\left|F_o^2 - < F_o^2 >\right|}{\sum[F_o^2]} \quad \text{and} \quad R_{sigma} = \frac{\sum\left[\sigma\left(F_o^2\right)\right]}{\sum[F_o^2]}$$

Table 1: Intensity statistics given by XPREP after scaling and merging in SADABS 2015/1

Resolution	#Data	#Theory	%Complete	Redundancy	<I>	<I/s>	R_{merge}	R_{sigma}
Inf-1.84	445	445	100	30.62	41.6	71.04	0.0419	0.0102
1.84-1.21	1053	1053	100	36.25	10.6	66.16	0.051	0.0106
1.21-0.95	1540	1540	100	25.84	5.4	54.38	0.0593	0.0124
0.95-0.83	1477	1477	100	15.35	2.3	45.05	0.0513	0.0152
0.83-0.75	1553	1553	100	17.67	1.5	46.95	0.0527	0.0146
0.75-0.7	1380	1381	99.9	18.55	1.6	49.88	0.0452	0.0136
0.7-0.66	1425	1425	100	18.02	1.2	46.19	0.0541	0.015
0.66-0.62	1785	1785	100	16.86	0.9	39.61	0.0644	0.0174
0.62-0.59	1700	1700	100	15.53	0.6	32.19	0.0742	0.0217
0.59-0.57	1298	1298	100	14.77	0.6	29.57	0.0829	0.0239
0.57-0.55	1530	1530	100	14.38	0.4	24.04	0.1079	0.0312
0.55-0.53	1764	1765	99.9	13.76	0.3	19.51	0.1373	0.0399
0.53-0.52	970	970	100	13.22	0.2	16.53	0.1576	0.0472
0.52-0.5	2216	2217	100	11.07	0.2	15.02	0.1517	0.0544
0.5-0.49	1231	1231	100	10.14	0.2	12.42	0.1709	0.067
0.49-0.48	1367	1367	100	9.65	0.2	11.4	0.1866	0.0756
0.48-0.47	1458	1458	100	8.27	0.1	10.49	0.1759	0.0836
0.47-0.46	1567	1567	100	7.11	0.1	9.02	0.18	0.0991
0.46-0.45	1770	1770	100	6.77	0.1	8.48	0.1886	0.1098
0.45-0.44	2023	2080	97.3	6.15	0.1	7.04	0.2202	0.1372
0.54-0.44	13531	13590	99.6	9.1	0.2	11.57	0.1649	0.0739
Inf-0.44	29552	29612	99.8	14.39	1.8	28.19	0.0523	0.0151

For the Independent Atom Model refinement (IAM) an unmerged *.hkl file has been generated. The *.hkl file for the multipole model refinement was also generated with SADABS where symmetry equivalent were merged and negative intensities as well as systematic absent reflections were omitted.

The structure was solved with SHELXT[7] and the refinement was done with SHELXL[8]. Multipole model[9] (MM)refinement has been carried out with the XD2006 software suite.[10,11] Table 2 summarizes crystallographic data after IAM refinement and Multipole Model refinement for compound **1**.

Table 2: Crystallographic data for compound 1

	1	**2**	**3**
CCDC no.	-		
Empirical formula	C_{20} H_{36} Li_2 N_6	$C_{28}H_{44}Li_2N_6$	$C_{40}H_{68}Li_2N_6$
Formula weight	374.43	478.57	646.88
Temperature [K]	100(2)	100(2)	105(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
Unit cell dimensions			
a [Å]	12.793(3)	9.746(2)	13.864(3)
b [Å]	9.709(2)	25.413(3)	30.460(3)
c [Å]	18.672(3)	11.319(2)	9.851(2)
β [°]	94.31(3)	105.55(2).	105.18(2)
Volume Å^3	2312.6(8)	2700.8(8)	4014.9(13)
Z	4	4	4
Absorpt. coeff. [mm^{-1}]	0.065	0.070	0.062
F(000)	816	1040	1424
Theta range [**°**]	1.596 to 53.895.	1.603 to 27.125	1.337 to 26.416
Reflections collected	417443	59474	56034
Independent reflections	28447	5981	8229
R(int)	0.0529	0.0323	0.0376
Completeness to θ = 25.242° [%]	100.0	99.8	99.9
Data / restraints / parameters	28447 / 0 / 261	5981 / 305 / 374	8229 / 3710 / 874
(IAM) Gof	1.091	1.062	1.049
(IAM) *R*1 [$I>2\sigma(I)$]	0.0386	0.0427	0.0452
(IAM) w*R*2 (all data)	0.1338	0.1184	0.1170
(IAM) Largest diff. peak and hole [eÅ^{-3}]	0.582 and -0.212	0.296 and -0.205	0.241 and -0.151
(MM) Gof on F^2	1.5768	-	-
(MM) *R*{F^2} (all data)	0.0224	-	-
(MM) w*R*{F^2} (all data)	0.0258	-	-
(MM) Largest diff. peak and hole [eÅ^{-3}]	-0.130 and 0.117	-	-

1.2 Local coordinate systems

ATOM	ATOM0	Ax1	ATOM1	ATOM2	Ax2	Symm	CHEMCON	K set

ATOM	ATOM0	Ax1	ATOM1	ATOM2	Ax2	Symm	CHEMCON	K set
N(1)	C(1)	X	N(1)	C(4)	Y	_mz		1
N(2)	Li(1)	X	N(2)	C(5)	Y	_mz		6
N(3)	Li(2)	X	N(3)	C(8)	Y	_mz	N(2)	6
N(4)	C(11)	X	N(4)	C(14)	Y	_mz	N(1)	1
N(5)	Li(1)	X	N(5)	C(15)	Y	_mz	N(2)	6
N(6)	Li(2)	X	N(6)	C(18)	Y	_mz	N(2)	6
C(1)	N(1)	X	C(1)	C(2)	Y	_mz		2
C(2)	C(1)	X	C(2)	C(4)	Y	_mz		2
C(3)	C(4)	X	C(3)	C(1)	Y	_mz	C(2)	2
C(4)	N(1)	X	C(4)	C(3)	Y	_mz	C(1)	2
C(5)	C(1)	X	C(5)	N(2)	Y	_mz		7
C(6)	N(2)	Z	C(6)	H(6C)	X	_3m		5
C(7)	N(2)	Z	C(7)	H(7B)	X	_3m	C(6)	5
C(8)	C(4)	X	C(8)	N(3)	Y	_mz	C(5)	7
C(9)	N(3)	Z	C(9)	H(9B)	X	_3m	C(6)	5
C(10)	N(3)	Z	C(10)	H(10C)	X	_3m	C(6)	5
C(11)	N(4)	X	C(11)	C(12)	Y	_mz	C(1)	2
C(12)	C(11)	X	C(12)	C(14)	Y	_mz	C(2)	2
C(13)	C(14)	X	C(13)	C(11)	Y	_mz	C(2)	2
C(14)	N(4)	X	C(14)	C(13)	Y	_mz	C(1)	2
C(15)	C(11)	X	C(15)	N(5)	Y	_mz	C(5)	7
C(16)	N(5)	Z	C(16)	H(16B)	X	_3m	C(6)	5
C(17)	N(5)	Z	C(17)	H(17C)	X	_3m	C(6)	5
C(18)	C(14)	X	C(18)	N(6)	Y	_mz	C(5)	7
C(19)	N(6)	Z	C(19)	H(19C)	X	_3m	C(6)	5
C(20)	N(6)	Z	C(20)	H(20B)	X	_3m	C(6)	5
Li(1)	N(6)	Z	Li(1)	N(4)	X			3
Li(2)	N(2)	Z	Li(2)	N(1)	X			3
H(2)	C(2)	Z	H(2)	C(1)	Y	_cy		4
H(3)	C(3)	Z	H(3)	C(4)	Y	_cy	H(2)	4
H(5A)	C(5)	Z	H(5A)	H(5B)	Y	_cy		4
H(5B)	C(5)	Z	H(5B)	H(5A)	Y	_cy	H(5A)	4
H(6A)	C(6)	Z	H(6A)	H(6C)	Y	_cy		4
H(6B)	C(6)	Z	H(6B)	H(6A)	Y	_cy	H(6A)	4
H(6C)	C(6)	Z	H(6C)	H(6B)	Y	_cy	H(6A)	4
H(7A)	C(7)	Z	H(7A)	H(7B)	Y	_cy	H(6A)	4
H(7B)	C(7)	Z	H(7B)	H(7C)	Y	_cy	H(6A)	4
H(7C)	C(7)	Z	H(7C)	H(7A)	Y	_cy	H(6A)	4
H(8A)	C(8)	Z	H(8A)	H(8B)	Y	_cy	H(5A)	4
H(8B)	C(8)	Z	H(8B)	H(8A)	Y	_cy	H(5A)	4
H(9A)	C(9)	Z	H(9A)	H(9B)	Y	_cy	H(6A)	4
H(9B)	C(9)	Z	H(9B)	H(9C)	Y	_cy	H(6A)	4
H(9C)	C(9)	Z	H(9C)	H(9A)	Y	_cy	H(6A)	4
H(10A)	C(10)	Z	H(10A)	H(10C)	Y	_cy	H(6A)	4
H(10B)	C(10)	Z	H(10B)	H(10A)	Y	_cy	H(6A)	4

ATOM	ATOM0	Ax1	ATOM1	ATOM2	Ax2	Symm	CHEMCON	K set
H(10C)	C(10)	Z	H(10C)	H(10B)	Y	_cy	H(6A)	4
H(12)	C(12)	Z	H(12)	C(11)	Y	_cy	H(2)	4
H(13)	C(13)	Z	H(13)	C(14)	Y	_cy	H(2)	4
H(15A)	C(15)	Z	H(15A)	H(15B)	Y	_cy	H(5A)	4
H(15B)	C(15)	Z	H(15B)	H(15A)	Y	_cy	H(5A)	4
H(16A)	C(16)	Z	H(16A)	H(16B)	Y	_cy	H(6A)	4
H(16B)	C(16)	Z	H(16B)	H(16C)	Y	_cy	H(6A)	4
H(16C)	C(16)	Z	H(16C)	H(16A)	Y	_cy	H(6A)	4
H(17A)	C(17)	Z	H(17A)	H(17C)	Y	_cy	H(6A)	4
H(17B)	C(17)	Z	H(17B)	H(17A)	Y	_cy	H(6A)	4
H(17C)	C(17)	Z	H(17C)	H(17B)	Y	_cy	H(6A)	4
H(18A)	C(18)	Z	H(18A)	H(18B)	Y	_cy	H(5A)	4
H(18B)	C(18)	Z	H(18B)	H(18A)	Y	_cy	H(5A)	4
H(19A)	C(19)	Z	H(19A)	H(19C)	Y	_cy	H(6A)	4
H(19B)	C(19)	Z	H(19B)	H(19A)	Y	_cy	H(6A)	4
H(19C)	C(19)	Z	H(19C)	H(19B)	Y	_cy	H(6A)	4
H(20A)	C(20)	Z	H(20A)	H(20B)	Y	_cy	H(6A)	4
H(20B)	C(20)	Z	H(20B)	H(20C)	Y	_cy	H(6A)	4
H(20C)	C(20)	Z	H(20C)	H(20A)	Y	_cy	H(6A)	4

1.3 XD refinement strategy

Abbreviations: M: monopoles; D: dipoles; Q: quadrupoles; O: octupoles; H: hexadecapoles, U: Uij, k: kappa, C(atom name): Gram Charlier 3rd order, nosym: no local symmetry constraints, nocon: no chemical constraints.

The scale factor is refined in every step but only mentioned in the first.

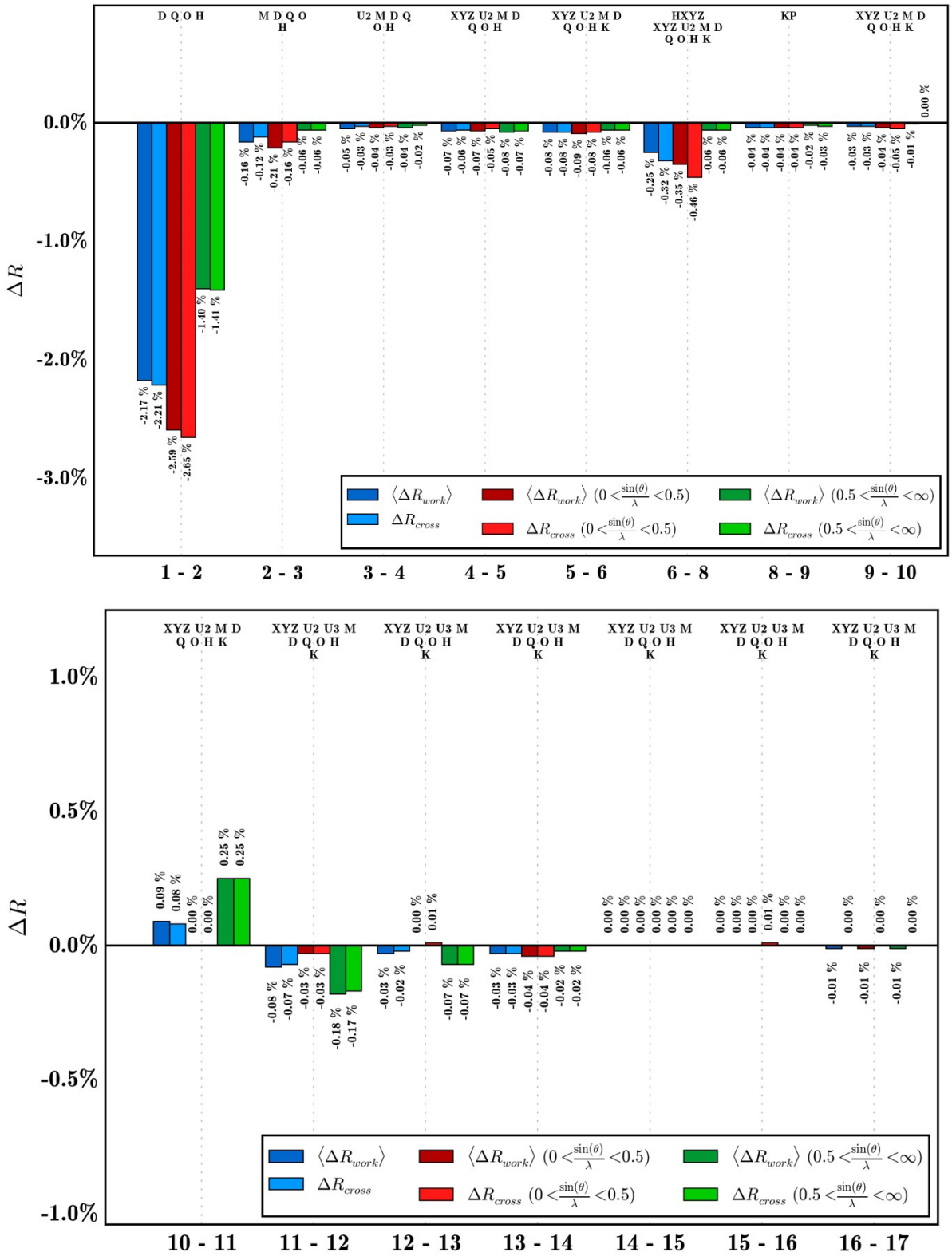
The refinement strategy was validated by R_{cross}.[12]

The new added parameter is marked in red while the last refinement step with model improvement and no overfitting is marked in green.

Step	Parameter	# parameter	# data	data/parameters	σ cut off	R(F^2)
1	Scale factor	1	19480	19480.00	3	5.28
2	DQOH	83	19480	234.70	3	3.10
3	MDQOH	92	19480	211.74	3	2.93
4	UMDQOH	296	19480	65.81	3	2.89
5	XYZUMDQOH	380	19480	51.26	3	2.82
6	XYZUMDQOHκ	385	19480	50.60	3	2.74
7	xyz(H)	109	2285	20.96	3	2.50
8	XYZUMDQOHκ	385	19480	50.60	3	2.53
9	κ‘	6	19480	3246.67	3	2.50
10	XYZUMDQOHκ	385	19480	50.60	3	2.46
11	XYZUMDQOHκ [sig obs = 0]	385	24648	64.02	0	2.55
12	XYZUMDQOHκ C(6,7,9,10,16,17,19,20)	465	24648	53.01	0	2.47
13	XYZUMDQOHκ C(6,7,9,10,16,17,19,20,15)	495	24648	49.79	0	2.45
14	XYZUMDQOHκ C(6,7,9,10,16,17,19,20,15) (nosym N(2))	505	24648	48.81	0	2.42
15	XYZUMDQOHκ C(6,7,9,10,16,17,19,20,15) (nosym N(2),N(1))	515	24648	47.86	0	2.42
16	XYZUMDQOHκ C(6,7,9,10,16,17,19,20,15) (nosym N(2),N(1),C(5))	525	24648	46.95	0	2.42
17	XYZUMDQOHκ C(6,7,9,10,16,17,19,20,15) (nosym all)	563	24648	43.78	0	2.40

The final refinement strategy consists of the steps 1-14.

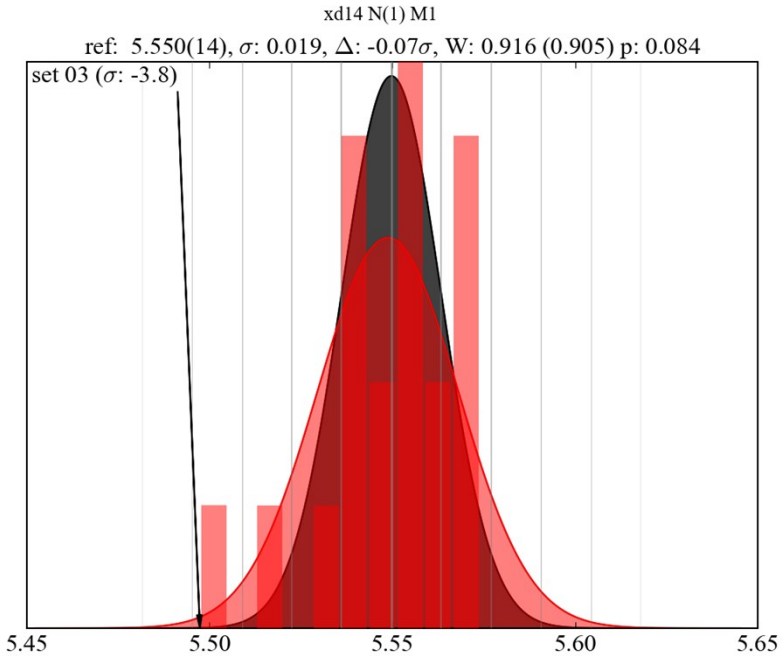
1.4 Cross-validation[12]



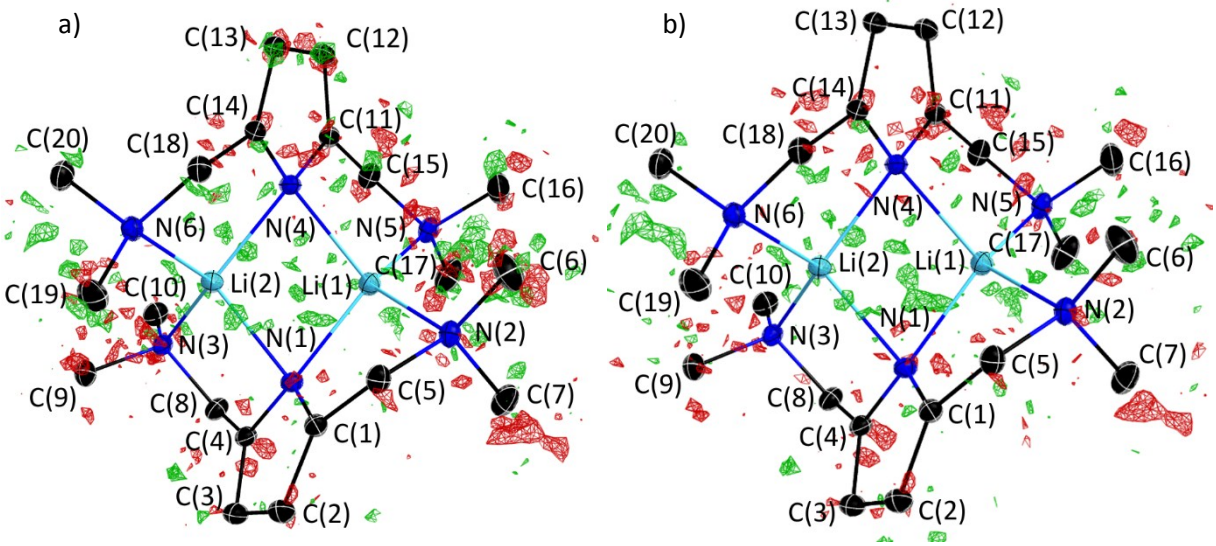
ΔR values for the initial refinement strategy. The refinement steps 15 and 16 add no benefit to the model, while step 17 shows signs of overfitting.

1.5 Parameter distribution of outliers[12]

The distribution of the derived parameters was checked for the 20 different refinements. Only one of 505 parameters shows an outlier with respect to the value v_{total} and the estimated standard uncertainty s_{total} derived from the refinement against all data. Therefore, model bias due to the omission of data can be excluded.



1.6 Residual density before and after anharmonic refinement[13]



Residual density isosurfaces. The green density is positive and red negative, isosurface level 0.079 eÅ^{-3}. (a) before and (b) after anharmonic refinement.

1.7 Kuhs' rule[14]

The table below shows the minimum data resolution required for meaningful refinement of anharmonic thermal parameters (3rd order Gram-Charlier coefficients), for each anisotropic atom.[11]

Atom	Principal M.D.A's (A)			Min. resolution $\sin(\theta)/\lambda$
C(6)	0.216	0.161	0.129	0.79
C(7)	0.193	0.170	0.127	0.81
C(9)	0.168	0.160	0.131	0.85
C(10)	0.172	0.166	0.131	0.83
C(15)	0.178	0.143	0.119	0.89
C(16)	0.205	0.174	0.136	0.76
C(17)	0.236	0.171	0.132	0.74
C(19)	0.195	0.180	0.126	0.79
C(20)	0.179	0.156	0.132	0.84

1.8 Extreme displacements in the map from the equilibrium position of atoms C(6), C(7), C(9), C(10), C(15), C(16), C(17), C(19) and C(20) in Angstroms along reciprocal axial directions. deltaX/Y/Z = -0.8 to 0.8.

Atom	C(6)	C(7)	C(9)	C(10)	C(15)	C(16)	C(17)	C(19)	C(20)
Smallest PDF value	-4.76	-0.76	-0.06	-0.21	-0.58	-0.02	-5.28	-0.14	-0.01
Largest PDF value	32674.48	35273.18	41367.14	38162.51	48319.66	30156.19	27444.01	33119.14	39753.78
Total integrated negative probability [%]	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Integrated volume for negative probability [Å^{-3}]	0.890	0.479	0.576	0.622	0.913	0.410	0.542	0.506	0.608
Total integrated negative probability [%]	100.000	99.998	100.000	100.000	100.00	99.999	99.975	100.000	100.000
Integrated volume for negative probability [Å^{-3}]	3.445	3.857	3.759	3.713	3.422	3.925	3.793	3.829	3.727

1.9 Refined Gram Charlier parameters, in bold values larger than 3 σ

	C(6)		C(7)		C(9)		C(10)		C(15)	
	Value	s.u.	Value	s.u.	Value	s.u.	Value	s.u.	Value	s.u.
C111	0.000034	0.000026	0.000034	0.000018	0.000044	0.000019	**-0.000108**	**0.000021**	-0.000007	0.000018
C222	-0.000043	0.000040	0.00019	0.000059	0.000097	0.000039	**0.000334**	**0.000045**	**0.000371**	**0.000047**
C333	-0.000049	0.000009	-0.00008	0.000007	0.000003	0.000007	0.000006	0.000006	0.000013	0.000005
C112	-0.000252	0.000016	-0.000013	0.000013	**-0.000085**	**0.000013**	**0.000053**	**0.000014**	0.000014	0.000012
C122	-0.000010	0.000018	0.000004	0.000021	0.000031	0.000016	0.000049	0.000019	**-0.000133**	**0.000018**
C113	**-0.000037**	**0.000011**	0.000012	0.000007	-0.000004	0.000007	**0.000037**	**0.000008**	0.000031	0.000006
C133	**-0.000057**	**0.000007**	0.000009	0.000005	0.00001	0.000005	-0.000004	0.000005	0.000007	0.000004
C223	**0.000105**	**0.000012**	**-0.000068**	**0.000016**	-0.000016	0.000011	0.000023	0.000012	0.000031	0.000011
C233	**-0.000104**	**0.000008**	0.000024	0.000008	**0.000028**	**0.000006**	-0.000016	0.000006	**-0.000017**	**0.000005**
C123	**-0.000081**	**0.000008**	-0.000013	0.000007	**0.000042**	**0.000006**	0.000002	0.000006	**-0.000021**	**0.000005**

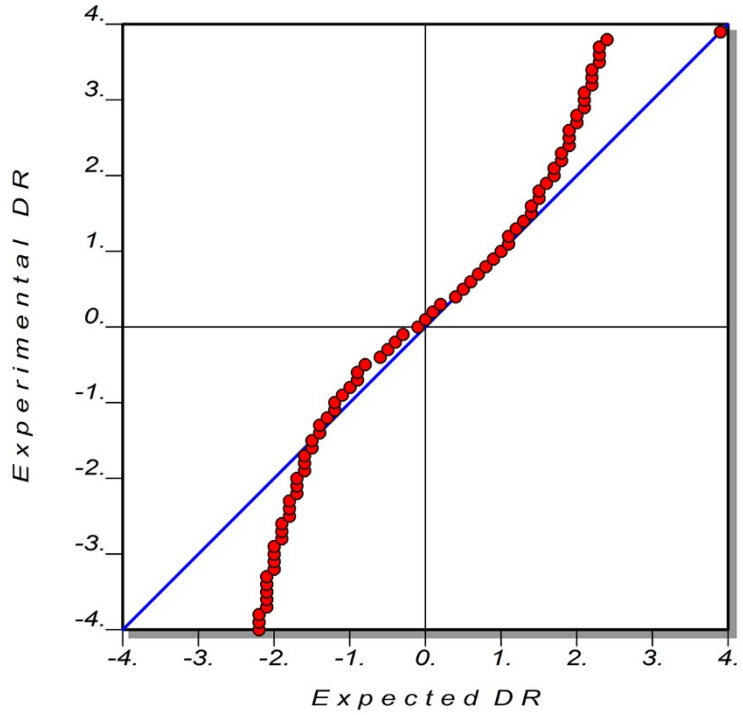
	C(16)		C(17)		C(19)		C(20)	
	Value	s.u.	Value	s.u.	Value	s.u.	Value	s.u.
C111	**-0.000165**	**0.000025**	**-0.000026**	**0.00002**	0.00003	0.000022	0.000046	0.000018
C222	-0.000038	0.000054	**0.001675**	**0.000086**	0.00012	0.000052	0.000004	0.000042
C333	-0.00003	0.000008	0.00006	0.000009	**-0.000032**	**0.000008**	0.000004	0.000008
C112	**0.000089**	**0.000017**	**-0.000134**	**0.000016**	**-0.000087**	**0.000016**	0.000001	0.000012
C122	-0.00007	0.000023	**-0.000159**	**0.000028**	**0.000212**	**0.000021**	**0.000054**	**0.000016**
C113	0.000021	0.000009	-0.000011	0.000008	**-0.000045**	**0.000009**	-0.000012	0.000007
C133	0.000008	0.000007	**-0.000033**	**0.000007**	**-0.000054**	**0.000006**	**0.000018**	**0.000005**
C223	-0.000013	0.000015	**-0.000351**	**0.000023**	0.000015	0.000015	**0.000064**	**0.000012**
C233	**-0.000047**	**0.000008**	0.000008	0.00001	**-0.000031**	**0.000007**	0.000005	0.000007
C123	0.000011	0.000008	0.00003	0.000009	0.000007	0.000008	**-0.000037**	**0.000006**

1.10 Differences of Mean-Squares Displacement Amplitudes (DMSDA) along interatomic vectors

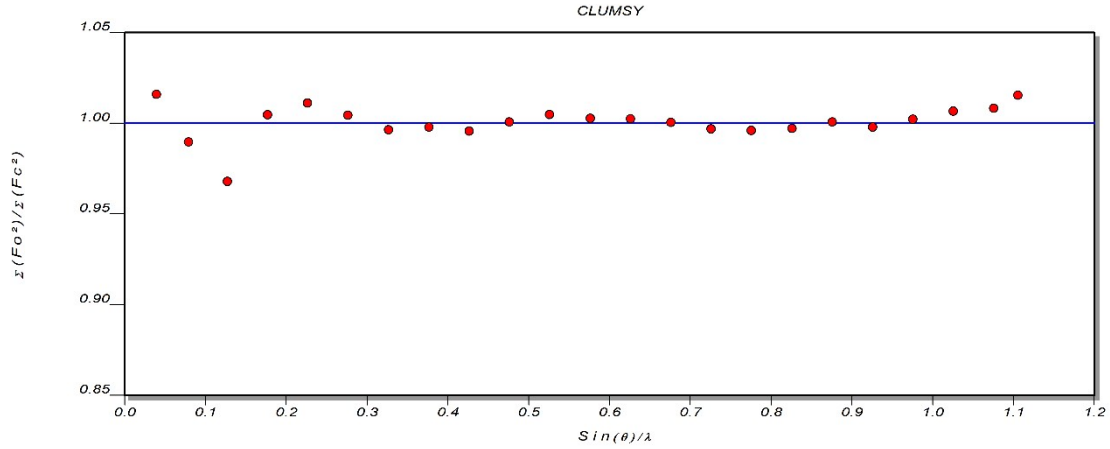
Atom 1	Atom 2	Distance / Å	DMSDA / 10^{-4} Å^2
N(1)	C(1)	1.3745	3
N(1)	Li(2)	2.1212	35
N(1)	C(4)	1.3743	5
N(1)	Li(1)	2.046	31
N(2)	C(5)	1.4804	5
N(2)	Li(1)	2.1165	17
N(2)	C(6)	1.4572	4
N(2)	C(7)	1.4615	2
N(3)	C(8)	1.4809	3
N(3)	Li(2)	2.1169	20
N(3)	C(9)	1.4687	1
N(3)	C(10)	1.4631	4
N(4)	C(11)	1.3731	4
N(4)	Li(2)	2.0363	24
N(4)	C(14)	1.3757	4
N(4)	Li(1)	2.0705	26
N(5)	C(15)	1.4839	2
N(5)	Li(1)	2.1315	11
N(5)	C(16)	1.4628	-1
N(5)	C(17)	1.4567	5
N(6)	C(18)	1.4842	4
N(6)	Li(2)	2.1032	19
N(6)	C(19)	1.462	1
N(6)	C(20)	1.4636	3
C(1)	C(2)	1.3874	4
C(1)	C(5)	1.4954	4
C(2)	C(3)	1.4238	0
C(3)	C(4)	1.3883	-4
C(4)	C(8)	1.4919	3
C(11)	C(12)	1.3872	4
C(11)	C(15)	1.4909	5
C(12)	C(13)	1.4244	-1
C(13)	C(14)	1.3849	-3
C(14)	C(18)	1.4946	3

The Lithium - Nitrogen bonds show significantly higher values for the DMSDA. This is most likely due to the fact that the mass is not considered within the Hirshfeld test. The ratio of the masses of Lithium to Nitrogen is only 1:2. For the bonds of atoms of equal or nearly equal mass the Hirshfeld test is fulfilled.

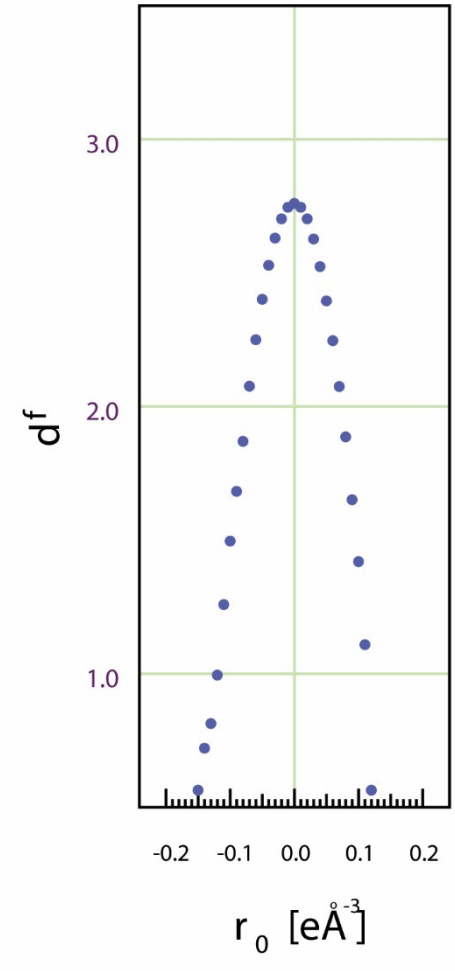
1.11 Normal Probability Plot[15]



1.12 DRK Plots[15]



1.13 Fractal Dimension of the Electron Density[16]



$d^f(0)$ = 2.7605
$\rho_{min}(d=2)$ = -0.0737 eÅ^{-3}
$\rho_{max}(d=2)$ = 0.0740 eÅ^{-3}

ρ_{min}= -0.16 eÅ^{-3}
ρ_{max}= 0.12 eÅ^{-3}
Δρ 0 0.28 eÅ^{-3}

e_{gross} = 27.2 e
e_{net} = 0.0 e

1.14 List of bond critical points

Atom1	Atom2	d1 / Å	d2 / Å	ρ / e Å^{-3}	$\nabla^2\rho$ / e Å^{-5}	λ_1	λ_2	λ_3	ell
C(1)	N(1)	0.5694	0.8051	2.22(1)	-21.19(17)	-18.27	-15.1	12.17	0.21(1)
C(4)	N(1)	0.565	0.8094	2.24	-22.38(18)	-18.7	-15.45	11.77	0.21(1)
LI(1)	N(1)	0.7644	1.2817	0.14(0)	4.08(1)	-0.84	-0.83	5.76	0.02(1)
LI(2)	N(1)	0.7873	1.3339	0.12(0)	3.25(1)	-0.68	-0.65	4.59	0.05(1)
H(2)	C(2)	0.3488	0.7343	1.71	-14.55(21)	-15.85	-15.18	16.49	0.04(1)
H(3)	C(3)	0.3487	0.7343	1.71	-14.56(21)	-15.86	-15.19	16.49	0.04(1)
C(5)	N(2)	0.6281	0.8525	1.77(1)	-15.20(11)	-13.37	-12.98	11.16	0.03(1)
C(6)	N(2)	0.6356	0.8216	1.91(1)	-17.99(12)	-15.29	-14.72	12.02	0.04(1)
C(7)	N(2)	0.6397	0.8218	1.89	-17.41(12)	-15.18	-14.42	12.19	0.05(1)
LI(1)	N(2)	0.7788	1.3377	0.12(0)	3.56(0)	-0.75	-0.73	5.03	0.03(1)
C(8)	N(3)	0.6287	0.8524	1.77	-15.16(11)	-13.39	-12.94	11.17	0.03(1)
C(9)	N(3)	0.6463	0.8225	1.87	-16.66(12)	-14.93	-14.1	12.36	0.06(1)
C(10)	N(3)	0.6411	0.822	1.89	-17.53(11)	-15.1	-14.58	12.15	0.04(1)
LI(2)	N(3)	0.7788	1.3381	0.12	3.55(0)	-0.75	-0.73	5.03	0.02(1)

Atom1	Atom2	d1 / Å	d2 / Å	ρ / e Å^{-3}	$\nabla^2\rho$ / e Å^{-5}	λ_1	λ_2	λ_3	ell
C(11)	N(4)	0.5682	0.8049	2.22	-21.33(17)	-18.31	-15.14	12.12	0.21(1)
C(14)	N(4)	0.5665	0.8093	2.24	-22.20(18)	-18.65	-15.41	11.86	0.21(1)
LI(1)	N(4)	0.7713	1.2993	0.13	3.78(0)	-0.81	-0.77	5.36	0.05(1)
LI(2)	N(4)	0.7587	1.2776	0.15	4.19(1)	-0.93	-0.91	6.04	0.02(1)
H(12)	C(12)	0.3487	0.7344	1.71	-14.56(21)	-15.86	-15.19	16.49	0.04(1)
H(13)	C(13)	0.3487	0.7344	1.71	-14.57(21)	-15.86	-15.2	16.49	0.04(1)
C(15)	N(5)	0.6313	0.8528	1.76	-14.95(11)	-13.31	-12.88	11.23	0.03(1)
C(16)	N(5)	0.641	0.8219	1.89	-17.23(12)	-15.13	-14.33	12.23	0.06(1)
C(17)	N(5)	0.6354	0.8213	1.91	-17.99(11)	-15.29	-14.73	12.03	0.04(1)
LI(1)	N(5)	0.7837	1.3478	0.12	3.40(0)	-0.71	-0.69	4.81	0.03(1)
C(18)	N(6)	0.6317	0.8527	1.76	-14.91(11)	-13.28	-12.88	11.25	0.03(1)
C(19)	N(6)	0.6409	0.8212	1.89	-17.25(11)	-15.06	-14.4	12.21	0.05(1)
C(20)	N(6)	0.6417	0.822	1.89	-17.34(12)	-15.11	-14.45	12.22	0.05(1)
LI(2)	N(6)	0.7746	1.3287	0.13	3.69(0)	-0.79	-0.76	5.24	0.03(1)
C(2)	C(1)	0.6804	0.7076	2.15(1)	-17.7(12)	-16.82	-12.96	12.08	0.3(1)
C(5)	C(1)	0.7402	0.7552	1.83(1)	-16.45(10)	-13.47	-12.84	9.86	0.05(1)
C(3)	C(2)	0.7122	0.7123	2.03(2)	-16.68(14)	-15.59	-13.01	11.92	0.2(1)
C(3)	C(4)	0.6809	0.708	2.14	-17.64(12)	-16.8	-12.94	12.1	0.3(1)
C(8)	C(4)	0.7379	0.754	1.84	-16.67(10)	-13.57	-12.93	9.84	0.05(1)
H(5A)	C(5)	0.3564	0.7357	1.73(1)	-18.75(7)	-16.34	-15.43	13.02	0.06(1)
H(5B)	C(5)	0.3562	0.7359	1.73	-18.7(8)	-16.37	-15.37	13.04	0.06(1)
H(6A)	C(6)	0.3834	0.6936	1.80(1)	-19.88(6)	-16.63	-15.25	11.99	0.09(1)
H(6B)	C(6)	0.3837	0.6933	1.79	-19.93(6)	-16.65	-15.26	11.98	0.09(1)
H(6C)	C(6)	0.3838	0.6933	1.79	-19.93(6)	-16.65	-15.26	11.98	0.09(1)
H(7A)	C(7)	0.3837	0.6933	1.79	-19.9(5)	-16.63	-15.24	11.98	0.09(1)
H(7B)	C(7)	0.3842	0.6929	1.79	-19.94(6)	-16.65	-15.25	11.96	0.09(1)
H(7C)	C(7)	0.3839	0.6931	1.79	-19.92(6)	-16.65	-15.25	11.97	0.09(1)
H(8A)	C(8)	0.3566	0.7357	1.73	-18.7(7)	-16.29	-15.43	13.03	0.06(1)
H(8B)	C(8)	0.3562	0.7359	1.73	-18.69(8)	-16.37	-15.37	13.04	0.07(1)
H(9A)	C(9)	0.3836	0.6934	1.8	-19.91(6)	-16.64	-15.25	11.98	0.09(1)
H(9B)	C(9)	0.384	0.693	1.79	-19.94(6)	-16.65	-15.25	11.96	0.09(1)
H(9C)	C(9)	0.3841	0.6929	1.79	-19.93(6)	-16.64	-15.25	11.96	0.09(1)
H(10A)	C(10)	0.3836	0.6934	1.8	-19.9(6)	-16.63	-15.25	11.98	0.09(1)
H(10B)	C(10)	0.3838	0.6933	1.79	-19.93(6)	-16.65	-15.26	11.98	0.09(1)
H(10C)	C(10)	0.3838	0.6932	1.79	-19.93(6)	-16.65	-15.25	11.98	0.09(1)
C(12)	C(11)	0.6803	0.7075	2.15	-17.72(12)	-16.83	-12.96	12.07	0.3(1)
C(15)	C(11)	0.7377	0.7533	1.84	-16.68(11)	-13.59	-12.92	9.83	0.05(1)
C(12)	C(13)	0.7124	0.7126	2.02	-16.65(14)	-15.58	-13	11.93	0.2(1)
C(13)	C(14)	0.6791	0.7064	2.16	-17.91(12)	-16.91	-13.02	12.03	0.3(1)
C(18)	C(14)	0.7393	0.7552	1.83	-16.52(10)	-13.51	-12.87	9.86	0.05(1)
H(15A)	C(15)	0.3564	0.7357	1.73	-18.74(7)	-16.33	-15.44	13.03	0.06(1)
H(15B)	C(15)	0.3561	0.736	1.73	-18.68(8)	-16.37	-15.35	13.05	0.07(1)
H(16A)	C(16)	0.3836	0.6934	1.8	-19.92(6)	-16.64	-15.26	11.98	0.09(1)
H(16B)	C(16)	0.3841	0.693	1.79	-19.93(6)	-16.65	-15.25	11.97	0.09(1)
H(16C)	C(16)	0.384	0.693	1.79	-19.93(6)	-16.65	-15.25	11.97	0.09(1)

Atom1	Atom2	d1 / Å	d2 / Å	ρ / e Å^{-3}	$\nabla^2\rho$ / e Å^{-5}	λ_1	λ_2	λ_3	ell
H(17A)	C(17)	0.3834	0.6936	1.8	-19.87(5)	-16.62	-15.24	11.99	0.09(1)
H(17B)	C(17)	0.3838	0.6933	1.79	-19.92(6)	-16.65	-15.26	11.98	0.09(1)
H(17C)	C(17)	0.3839	0.6932	1.79	-19.93(6)	-16.65	-15.26	11.97	0.09(1)
H(18A)	C(18)	0.3567	0.7357	1.73	-18.66(7)	-16.28	-15.42	13.03	0.06(1)
H(18B)	C(18)	0.3561	0.7361	1.73	-18.64(8)	-16.37	-15.32	13.06	0.07(1)
H(19A)	C(19)	0.3834	0.6937	1.8	-19.85(6)	-16.61	-15.24	12	0.09(1)
H(19B)	C(19)	0.384	0.6931	1.79	-19.93(5)	-16.65	-15.25	11.97	0.09(1)
H(19C)	C(19)	0.3838	0.6933	1.79	-19.92(6)	-16.65	-15.25	11.98	0.09(1)
H(20A)	C(20)	0.3836	0.6934	1.8	-19.91(6)	-16.64	-15.25	11.98	0.09(1)
H(20B)	C(20)	0.3839	0.6931	1.79	-19.94(6)	-16.66	-15.25	11.97	0.09(1)
H(20C)	C(20)	0.3839	0.6931	1.79	-19.93(6)	-16.64	-15.26	11.97	0.09(1)

For the electron density ρ the standard deviation of the MM refinement by XD2006 is given, where accessible. Due to the fact that the esd's of the laplacian $\nabla^2\rho$ are underestimated, standard deviations thereof and for the ellipticity have been determined by the method proposed by Krause et al. [12]

Valence shell charge concentrations

		CP1	CP2	CP3	
N(1)	x	3.2398	3.1622	3.2468	
	y	4.7839	4.6565	4.1456	
	z	3.6923	4.41	4.0236	
	ρ / eÅ^{-3}	3.5449	3.5961	3.6318	
	$\nabla^2\rho$ / e Å^{-5}	-63.4738	-63.012	-66.0027	
	λ_1	-14669.44	-12374.65	-12567.9	
	λ_2	-770.55	-1296.61	-1448.87	
	λ_3	-125.86	-860.69	-997.82	
		CP1	CP2	CP3	CP4
N(2)	x	3.7013	3.9584	3.9166	4.3306
	y	6.9515	7.0647	7.5592	7.0775
	z	5.1577	4.5584	5.0167	5.1383
	ρ / eÅ^{-3}	3.3566	3.8819	3.2992	3.3063
	$\nabla^2\rho$ / e Å^{-5}	-56.2626	-79.0748	-51.7152	-51.4214
	λ_1	-11435.12	-16904.82	-10658.43	-10750.39
	λ_2	-1344.62	-1237.2	-1209.74	-1204.96
	λ_3	-881.23	-1083.67	-719.98	-662.98
		CP1	CP2	CP3	CP4
N(3)	x	2.0798	2.2463	2.4703	2.6711
	y	2.3702	3.0322	2.5339	2.5783
	z	1.9563	1.8676	1.4682	2.0949
	ρ / eÅ^{-3}	3.2948	3.8789	3.2899	3.3553
	$\nabla^2\rho$ / e Å^{-5}	-51.2507	-79.0831	-51.6838	-56.2667
	λ_1	-10795.87	-16904.59	-10664.91	-11434.92
	λ_2	-1200.98	-1237.34	-1207.47	-1345.03

	λ_3	-652.35	-1083.62	-722.56	-881.08
		CP1	CP2	CP3	
N(4)	x	1.8785	2.3739	2.4281	
	y	6.6949	6.214	6.7061	
	z	1.698	1.8988	1.3583	
	ρ / eÅ^{-3}	3.63	3.545	3.5977	
	$\nabla^2\rho$ / e Å^{-5}	-65.9848	-63.4732	-63.0282	
	λ_1	-12572.99	-14669.42	-12370.17	
	λ_2	-1448.2	-770.55	-1297.16	
	λ_3	-997.3	-125.88	-861.16	
		CP1	CP2	CP3	CP4
N(5)	x	4.9615	4.9217	5.2492	5.5094
	y	6.7425	6.8579	7.2888	6.7032
	z	1.8494	1.1986	1.5441	1.4564
	ρ / eÅ^{-3}	3.8816	3.3516	3.3034	3.2984
	$\nabla^2\rho$ / e Å^{-5}	-79.0771	-56.24	-51.3683	-51.7194
	λ_1	-16904.9	-11440.4	-10765.45	-10658.93
	λ_2	-1237.24	-1343.88	-1203.96	-1209.64
	λ_3	-1083.62	-881.07	-658.72	-719.74
		CP1	CP2	CP3	CP4
N(6)	x	-0.3381	-0.0957	0.2312	-0.3896
	y	5.0714	5.5968	5.0226	5.1273
	z	3.0852	2.7669	2.7281	2.4434
	ρ / eÅ^{-3}	3.2873	3.352	3.8813	3.3027
	$\nabla^2\rho$ / e Å^{-5}	-51.5092	-56.2322	-79.0789	-51.4817
	λ_1	-10717.87	-11442.46	-16905.28	-10735.26
	λ_2	-1204.53	-1343.95	-1237.02	-1203.35
	λ_3	-704.72	-880.19	-1083.73	-672.3

2 Computational Details

Geometry optimizations were performed using the Gaussian 09 optimizer[17] together with TurboMole V7.0.[18] energies and gradients. All geometry optimizations were computed using the functional BP86[19] functional in combination with the def2-TZVPP basis set.[20] In the case of BP86 the dispersion interactions were estimated using the D3 approximations of Grimme with Becke-Johnson (BJ) damping.[21] The stationary points were located with the Berny algorithm[22] using redundant internal coordinates. Analytical Hessians were computed to determine the nature of stationary points (one and zero imaginary frequencies for minima)[23] and to calculate unscaled zero-point energies (ZPEs) as well as thermal corrections and entropy effects using the standard statistical-mechanics relationships for an ideal gas.[24]

The NBO partial charges[25] were computed with GENNBO5.9[26] at the BP86+D3(BJ)/def2-TZVPP level of theory. The analysis of the electron density with the Atoms-in-Molecules (AIM) method was performed at the BP86+D3(BJ)/def2-TZVPP level with the AIMAll program package. [27a]

For the bonding analyses we calculated the molecules using the gradient corrected functional BP86[19] in conjunction with the Grimme dispersion corrections (BP86+D3(BJ))[21] using uncontracted Slater-type orbitals (STOs) as basis functions.[28] The latter basis sets for all elements have triple-ζ quality augmented by two sets of polarization functions (ADF-basis set TZ2P+). This level of theory is denoted BP86+D3(BJ)/TZ2P+. An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.[29] The calculations were performed with the program package ADF2013.01.[30]

The interatomic interactions were investigated by means of an energy decomposition analysis (EDA, also termed extended transition state method - ETS) developed independently by Morokuma[31] and by Ziegler and Rauk.[32] The bonding analysis focuses on the instantaneous interaction energy ΔE_{int} of a bond A–B between two fragments A and B in the particular electronic reference state and in the frozen geometry of AB. This interaction energy is divided into three main components [Eq. (1)].

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} + \Delta E_{disp} \qquad (1)$$

The term ΔE_{elstat} corresponds to the quasiclassical electrostatic interaction between the unperturbed charge distributions of the prepared atoms and is usually attractive. The Pauli repulsion ΔE_{Pauli} is the energy change associated with the transformation from the superposition

of the unperturbed electron densities $\rho_A + \rho_B$ of the isolated fragments to the wavefunction $\Psi^0 = N\hat{A}[\Psi_A\Psi_B]$, which properly obeys the Pauli principle through explicit antisymmetrization ($\hat{A}$ operator) and renormalization (N = constant) of the product wavefunction. ΔE_{Pauli} comprises the destabilizing interactions between electrons of the same spin on either fragment. The orbital interaction ΔE_{orb} accounts for charge transfer and polarization effects. The ΔE_{orb} term can be decomposed into contributions from each irreducible representation of the point group of the interacting system. Since dispersion corrected functional is used, the dispersion correction is added to the total interaction energy. Further details on the EDA/ETS method[33] and its application to the analysis of the chemical bond[34] can be found in the literature.

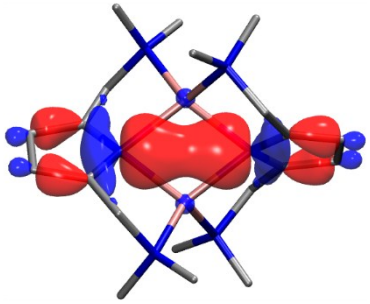
The EDA-NOCV[35] method combines charge (NOCV) and energy (EDA) decomposition schemes to decompose the deformation density which is associated with the bond formation, Δρ, into different components of the chemical bond. The EDA-NOCV calculations provide pairwise energy contributions for each pair of interacting orbitals to the total bond energy. NOCV (Natural Orbital for Chemical Valence)[36] is defined as the eigenvector of the valence operator, $\hat{V}$, given by Equation (2):

$$\hat{V}\Psi_i = v_i\Psi_i \qquad (2)$$

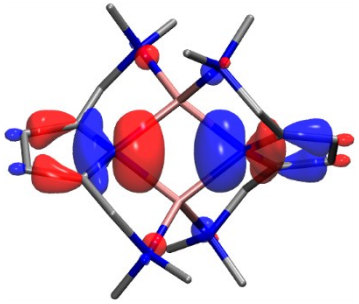
In the EDA-NOCV scheme the orbital interaction term, ΔE_{orb}, is given by Equation (3):

$$\Delta E_{orb} = \sum_k \Delta E_k^{orb} = \sum_{k=1}^{\frac{N}{2}} v_k \left[-F_{-k,-k}^{TS} + F_{k,k}^{TS}\right] \qquad (3)$$

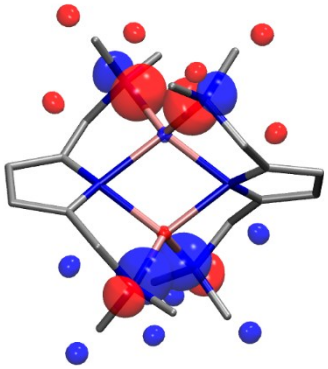
in which $F_{-k,-k}^{TS}$ and $F_{k,k}^{TS}$ are diagonal transition state Kohn-Sham matrix elements corresponding to NOCVs with the eigenvalues $-\nu_k$ and ν_k respectively. The ΔE_k^{orb} term of a particular type of bond are assigned by visual inspection of the shape of the deformation density, $\Delta\rho_k$. The EDA-NOCV scheme thus provides both qualitative ($\Delta\rho_{orb}$) and quantitative (ΔE_{orb}) information about the strength of orbital interactions in chemical bonds, also in molecules with C1 symmetry.[37]



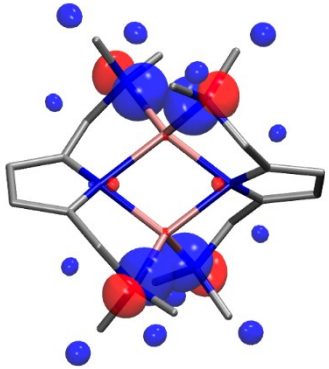
HOMO-9 (ε =-6.93 eV)



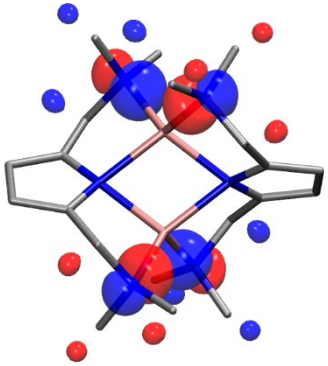
HOMO-8 (ε =-6.16 eV)



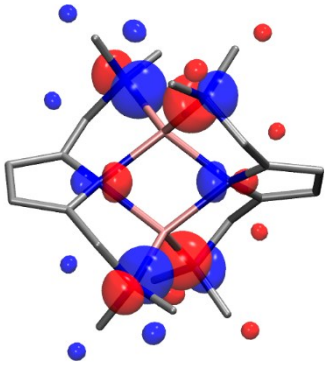
HOMO-7 (ε =-5.95 eV)



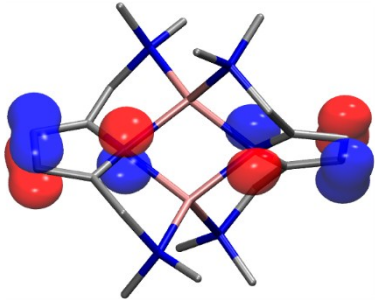
HOMO-6 (ε = -5.91eV)



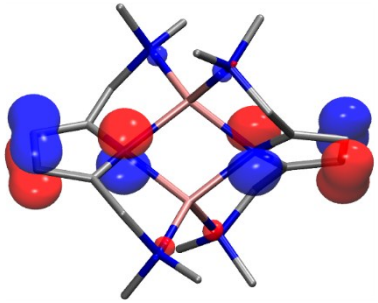
HOMO-5 (ε =-5.79 eV)



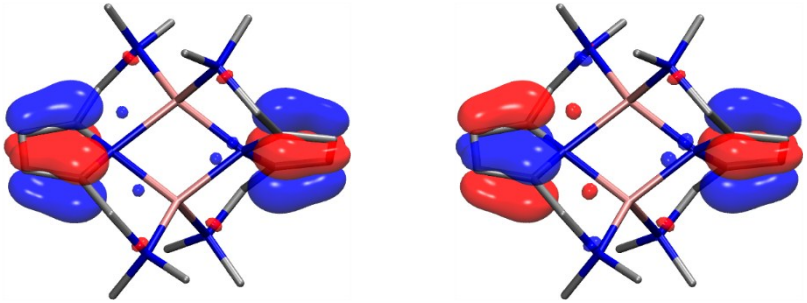
HOMO-4 (ε =-5.74 eV)



HOMO-3 (ε =-5.03 eV)

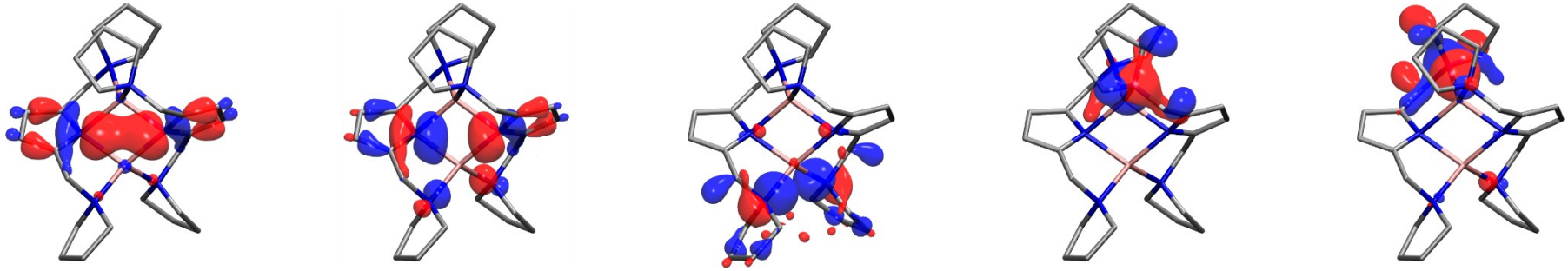


HOMO-2 (ε = -4.89 eV)

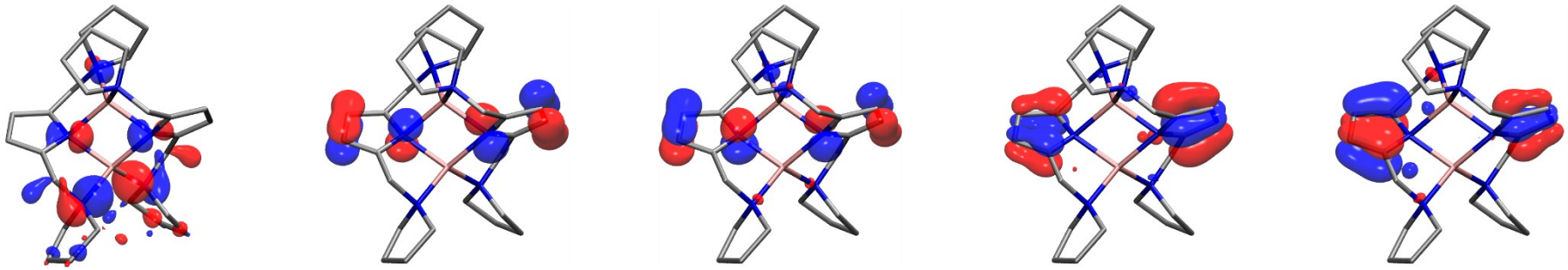


HOMO-1 (ε = -4.29 eV) HOMO (ε = -4.23 eV)

Figure S1. Molecular orbitals of compound **1** and their energies (in eV) at the BP86+D3(BJ)/def2-TZVPP level of theory. Hydrogen atoms were omitted for clarity.

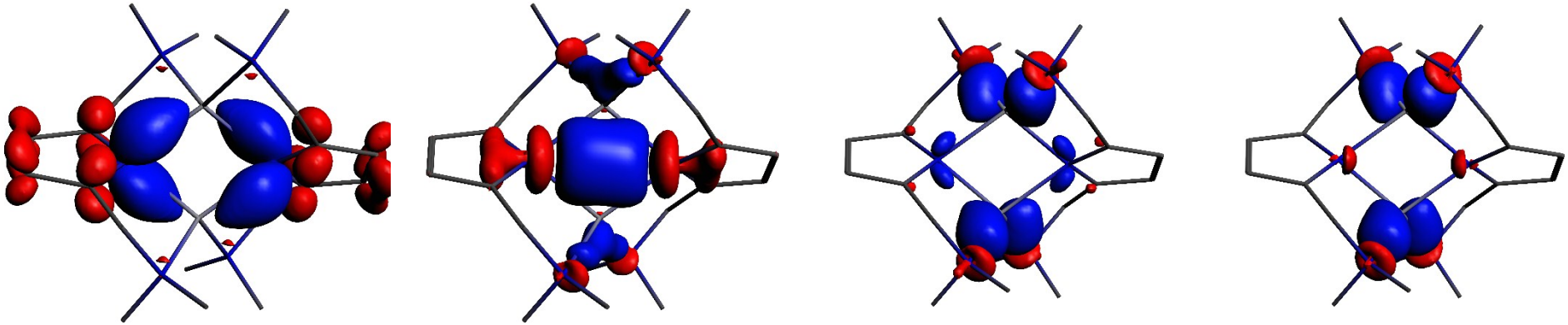


HOMO-8 (ε = -6.79 eV) HOMO-7 (ε = -6.06 eV) HOMO-6 (ε = -5.88 eV) HOMO-5 (ε = -5.71 eV) HOMO-4 (ε = -5.68 eV)

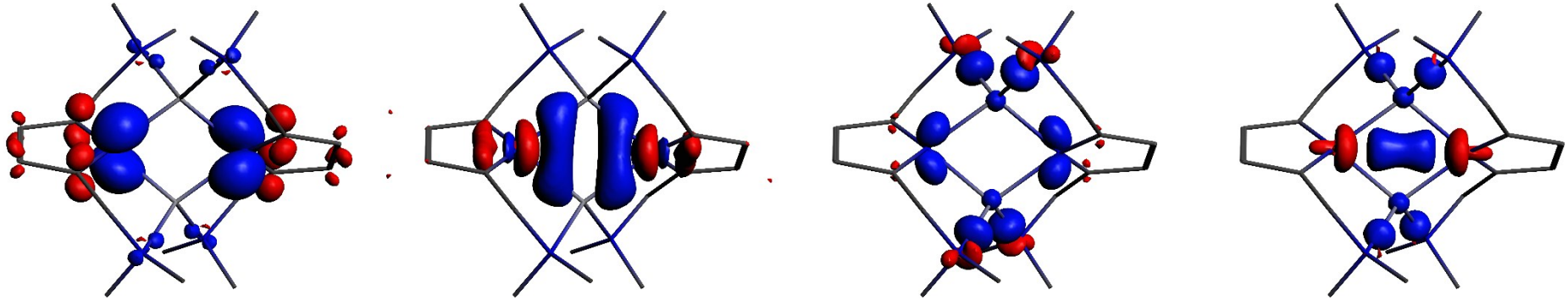


HOMO-3 (ε = -5.66 eV) HOMO-2 (ε = -4.93 eV) HOMO-1 (ε = -4.80 eV) HOMO (ε = -4.19 eV) HOMO (ε = -4.13 eV)

Figure S2. Molecular orbitals of compound **1** and their energies at the BP86+D3(BJ)/def2-TZVPP level of theory. Hydrogen atoms were omitted for clarity.

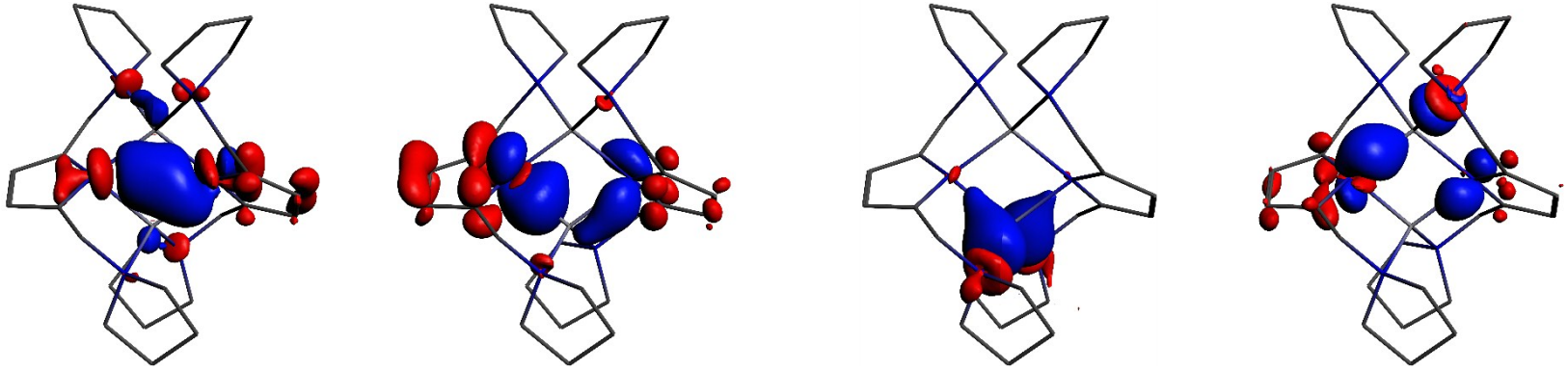


ΔE_1=-19.7; $|\nu_1|$=0.32 ΔE_2=-20.4; $|\nu_2|$=0.30 ΔE_3=-16.3; $|\nu_3|$=0.27 ΔE_4=-15.2; $|\nu_4|$=0.26

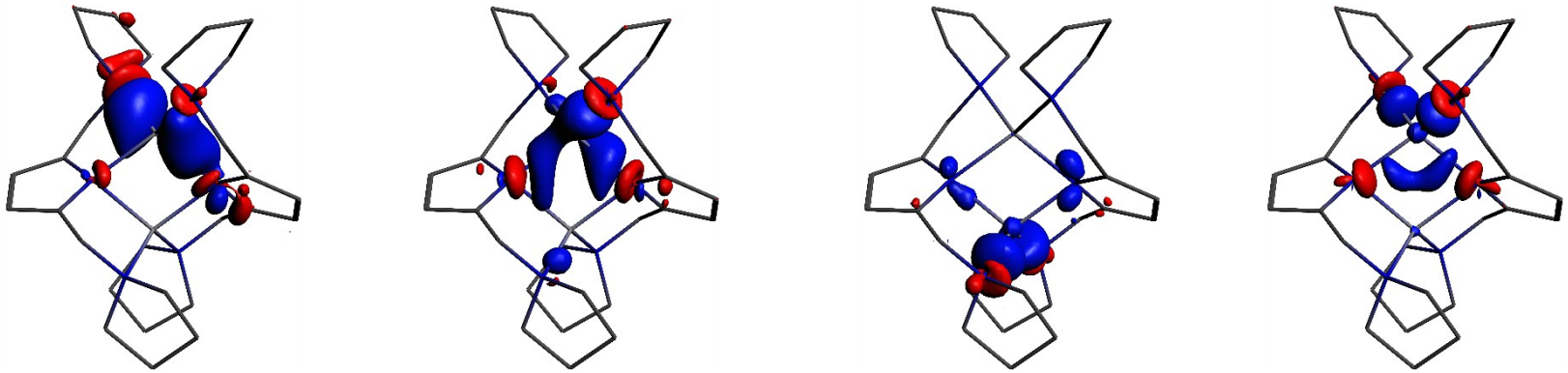


ΔE_5=-14.9; $|\nu_5|$=0.25 ΔE_6=-14.1; $|\nu_6|$=0.23 ΔE_7=-10.9; $|\nu_7|$=0.21 ΔE_8=-8.4; $|\nu_8|$=0.18

Figure S3. Plot of deformation densities $\Delta\rho$ of the pairwise orbital interactions between $(Py)_2^{2-}$ and Li_2^{2+} in **1**, associated energies ΔE (in kcal/mol) and eigenvalues v (in a.u.). The red color shows the charge outflow, whereas blue shows charge density accumulation.



ΔE_1=--21.3; $|\nu_1|$=0.31 ΔE_2=-19.7; $|\nu_2|$=0.30 ΔE_3=-16.1; $|\nu_3|$=0.27 ΔE_4=-13.9; $|\nu_4|$=0.23



ΔE_5=-14.0; $|\nu_5|$=0.23 ΔE_6=-12.4; $|\nu_6|$=0.22 ΔE_7=-10.4; $|\nu_7|$=0.21 ΔE_8=-7.7; $|\nu_8|$=0.16

Figure S4. Plot of deformation densities $\Delta\rho$ of the pairwise orbital interactions between $(Ligand)_2^{2-}$ and Li_2^{2+} in **2**, associated energies ΔE (in kcal/mol) and eigenvalues v (in a.u.). The red color shows the charge outflow, whereas blue shows charge density accumulation.

Cartesian coordinates xyz and electronic energy at the BP86+D3(BJ)/def2-TZVPP level of theory

1

E(BP86+D3(BJ)/def2-TZVPP)= -1128.0789026830

N	-0.000240	1.599799	-0.000614
N	2.302682	0.859514	-1.608893
N	-2.302928	0.860293	1.608292
N	0.000051	-1.599797	0.000517
N	2.303382	-0.859155	1.608193
N	-2.303368	-0.860774	-1.607537
C	0.533682	2.426461	-0.964864
C	0.351292	3.765438	-0.620242
C	-0.351884	3.765833	0.617568
C	-0.534206	2.427078	0.963082
C	1.243011	1.783165	-2.109112
C	2.787196	-0.023610	-2.669819
C	3.403594	1.634035	-1.027010
C	-1.243414	1.784500	2.107809
C	-3.404000	1.634173	1.025858
C	-2.787260	-0.022136	2.669881
C	0.534574	-2.426445	0.964445
C	0.352562	-3.765425	0.619632
C	-0.350996	-3.765846	-0.617959
C	-0.533919	-2.427092	-0.963163
C	1.244054	-1.783115	2.108577

C	3.404328	-1.633356	1.025945
C	2.787964	0.023946	2.669108
C	-1.243743	-1.784581	-2.107550
C	-2.788459	0.021524	-2.668887
C	-3.403924	-1.635069	-1.024680
Li	1.247728	0.000132	-0.000151
Li	-1.247873	-0.000123	0.000170
H	0.680042	4.631764	-1.188450
H	-0.680667	4.632523	1.185202
H	0.554038	1.160720	-2.706430
H	1.671812	2.543464	-2.791188
H	3.248086	0.536259	-3.508246
H	1.951771	-0.617979	-3.062006
H	3.537969	-0.713467	-2.262736
H	3.916751	2.255596	-1.788121
H	4.142390	0.955613	-0.580843
H	3.005547	2.299951	-0.251147
H	-0.554320	1.162612	2.705566
H	-1.672333	2.545225	2.789336
H	-3.917287	2.256170	1.786526
H	-4.142655	0.955277	0.580175
H	-3.006090	2.299621	0.249525
H	-3.248239	0.538270	3.507900
H	-1.951714	-0.616052	3.062497
H	-3.537908	-0.712435	2.263321
H	0.681800	-4.631736	1.187582
H	-0.679650	-4.632550	-1.185648
H	0.555090	-1.160898	2.706141
H	1.673212	-2.543391	2.790455
H	3.917825	-2.254875	1.786861
H	4.142851	-0.954713	0.579660
H	3.006240	-2.299285	0.250117
H	3.249191	-0.535925	3.507347
H	1.952501	0.618071	3.061586
H	3.538478	0.714026	2.261925
H	-0.555071	-1.162398	-2.705485
H	-1.672668	-2.545361	-2.789013
H	-3.249582	-0.539018	-3.506735
H	-1.953296	0.615764	-3.061830
H	-3.539191	0.711533	-2.261987
H	-3.917304	-2.257221	-1.785159
H	-4.142636	-0.956456	-0.578662
H	-3.005456	-2.300407	-0.248537

2

E(BP86+D3(BJ)/def2-TZVPP)= -1437.9131668600

N	1.403285	3.332769	9.086374
Li	1.108288	4.282546	7.306684
C	0.321148	3.900613	9.722530
N	-0.934439	4.636984	7.738325
C	0.694664	4.411531	10.966128
H	0.047676	4.907937	11.684755
Li	1.889340	1.932206	7.718536
N	3.605680	1.573703	8.877455
C	2.080795	4.121792	11.114327
H	2.710965	4.353482	11.969369
C	2.472096	3.470993	9.942890
N	1.653444	2.874969	5.947145

C	3.791400	2.907823	9.526929
H	4.287080	3.532750	8.763203
H	4.475824	2.864337	10.393602
N	0.866955	0.305934	6.862040
C	3.240832	0.548028	9.882573
H	2.773254	-0.297387	9.354358
H	2.505420	0.965118	10.580664
N	2.593952	5.625067	6.629131
C	4.564610	0.094590	10.548066
H	4.728172	0.626994	11.493191
H	4.544431	-0.976720	10.782912
C	4.872301	1.056983	8.321907
H	5.405650	1.855826	7.792086
H	4.629625	0.274399	7.587525
C	5.661557	0.451467	9.509215
H	6.246397	-0.422827	9.197851
H	6.369338	1.181858	9.921229
C	-0.990602	3.868177	9.007876
H	-1.234465	2.829216	8.731726
H	-1.809576	4.241061	9.651454
C	-1.207524	6.078605	7.923346
H	-0.329259	6.580780	8.347257
H	-2.036663	6.212112	8.646200
C	2.346859	3.710925	5.099402
C	2.020729	3.442612	3.769707
H	2.417811	3.943194	2.890412
C	1.090838	2.364735	3.798644
H	0.629909	1.873676	2.945154
C	0.890341	2.056393	5.145137
C	0.069806	0.993518	5.797464
H	-0.810448	1.408023	6.319091
H	-0.313983	0.289432	5.037293
C	1.895904	-0.571284	6.256528
H	2.667102	-0.769211	7.016751
H	2.368729	-0.052419	5.414023
C	1.178031	-1.889286	5.871385
H	0.890992	-1.882380	4.812648
H	1.833334	-2.756266	6.020445
C	-0.073599	-1.929315	6.788838
H	-0.104003	-2.825941	7.420091
H	-0.996065	-1.922687	6.194469
C	0.043028	-0.640415	7.640144
H	-0.921947	-0.182738	7.891372
H	0.567468	-0.853411	8.583833
C	3.294624	4.687250	5.717208
H	4.032392	4.147867	6.334577
H	3.856590	5.244305	4.943352
C	1.995567	6.777273	5.919177
H	1.059379	6.477874	5.430844
H	2.680251	7.120411	5.118761
C	1.829516	7.876224	6.995405
H	2.286578	8.812046	6.650512
H	0.777484	8.095938	7.209861
C	2.565143	7.321839	8.240315
H	3.131113	8.089971	8.780399
H	1.859713	6.866317	8.950085
C	3.456578	6.229078	7.659905
H	4.374330	6.661618	7.209265

H	3.748552	5.475520	8.400353
C	-1.623442	6.592715	6.525179
H	-0.878632	7.268960	6.090635
H	-2.563270	7.154451	6.594024
C	-1.796482	5.310997	5.671790
H	-2.665874	5.354386	5.005222
H	-0.907759	5.126769	5.051396
C	-1.907936	4.208309	6.719803
H	-2.933865	4.161928	7.141492
H	-1.643491	3.216166	6.335780

4[M]

E(BP86+D3(BJ)/def2-TZVPP)= -660.9882853494

Li	-0.503182	-1.117501	-0.627205
Li	0.520374	0.660404	1.035914
N	-1.417464	0.499334	0.476998
N	1.430870	-0.531145	-0.517727
C	-2.491247	-0.268135	0.885984
C	-3.677820	0.165188	0.291455
H	-4.670464	-0.252128	0.436644
C	-3.323213	1.271973	-0.528544
H	-3.992620	1.883493	-1.127973
C	-1.942736	1.439440	-0.381487
C	1.936905	0.273226	-1.514446
C	3.317429	0.443808	-1.372172
H	3.973934	1.010925	-2.026967
C	3.692529	-0.303217	-0.221353
H	4.691101	-0.412816	0.192679
C	2.517049	-0.881758	0.261015
H	1.278117	0.692871	-2.272544
H	2.392845	-1.516593	1.138059
H	-2.350848	-1.103123	1.572078
H	-1.296865	2.177410	-0.853622
N	-0.173086	-3.081445	0.089000
H	-0.365371	-3.359431	1.051923
H	0.844327	-3.005960	-0.007684
H	-0.473726	-3.857667	-0.502066
N	1.722820	2.335878	0.877018
H	1.317442	3.158363	0.428175
H	2.400301	1.940257	0.205685
H	2.259408	2.674934	1.676051
N	-1.724985	-1.074572	-2.295864
H	-2.403607	-0.384906	-1.935350
H	-2.258369	-1.898343	-2.575575
H	-1.334065	-0.676409	-3.150766
N	0.219179	0.060997	3.042493
H	-0.800079	0.142054	2.974119
H	0.522363	0.702342	3.776682
H	0.425838	-0.880650	3.377250

5[M]

E(BP86+D3(BJ)/def2-TZVPP)= -660.9817607042

Li	-0.000000	1.277500	0.000000
Li	-0.000000	-1.277500	-0.000000
N	1.614375	0.000000	0.000000
N	-1.614375	0.000000	0.000000
C	2.452788	0.000001	1.097604

C	3.793372	0.000014	0.710165
H	4.660881	0.000025	1.364603
C	3.793372	-0.000014	-0.710165
H	4.660881	-0.000025	-1.364603
C	2.452788	-0.000001	-1.097604
C	-2.452788	0.000001	-1.097604
C	-3.793372	0.000005	-0.710165
H	-4.660881	0.000009	-1.364603
C	-3.793372	-0.000005	0.710165
H	-4.660881	-0.000009	1.364603
C	-2.452788	-0.000001	1.097604
H	-2.045490	0.000002	-2.109650
H	-2.045490	-0.000002	2.109650
H	2.045490	0.000002	2.109650
H	2.045490	-0.000002	-2.109650
N	-0.000000	-2.399827	1.745801
H	-0.827088	-2.109527	2.271899
H	0.827088	-2.109527	2.271899
H	-0.000000	-3.420155	1.731807
N	0.000000	2.399826	1.745803
H	0.827088	2.109525	2.271900
H	-0.827088	2.109525	2.271900
H	0.000000	3.420154	1.731809
N	0.000000	-2.399826	-1.745803
H	0.000000	-3.420154	-1.731809
H	0.827088	-2.109525	-2.271900
H	-0.827088	-2.109525	-2.271900
N	-0.000000	2.399827	-1.745801
H	-0.000000	3.420155	-1.731807
H	-0.827088	2.109527	-2.271899
H	0.827088	2.109527	-2.271899

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