Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information:

Structural Influence of Steric Factors and Donor Functions on Lithium Silylamides in Non-coordinating Solvents

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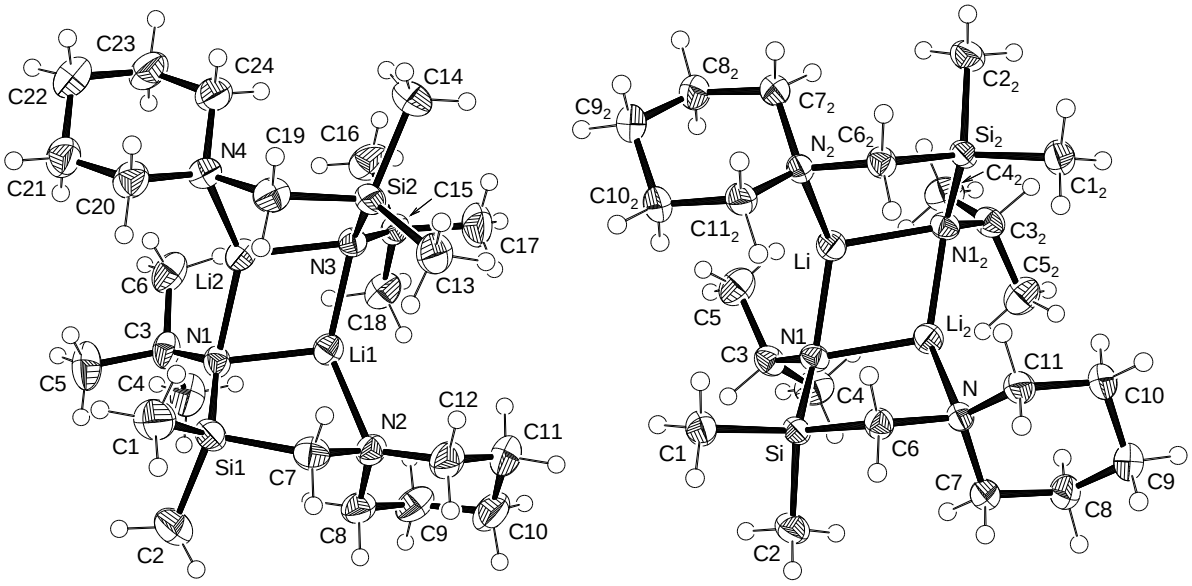
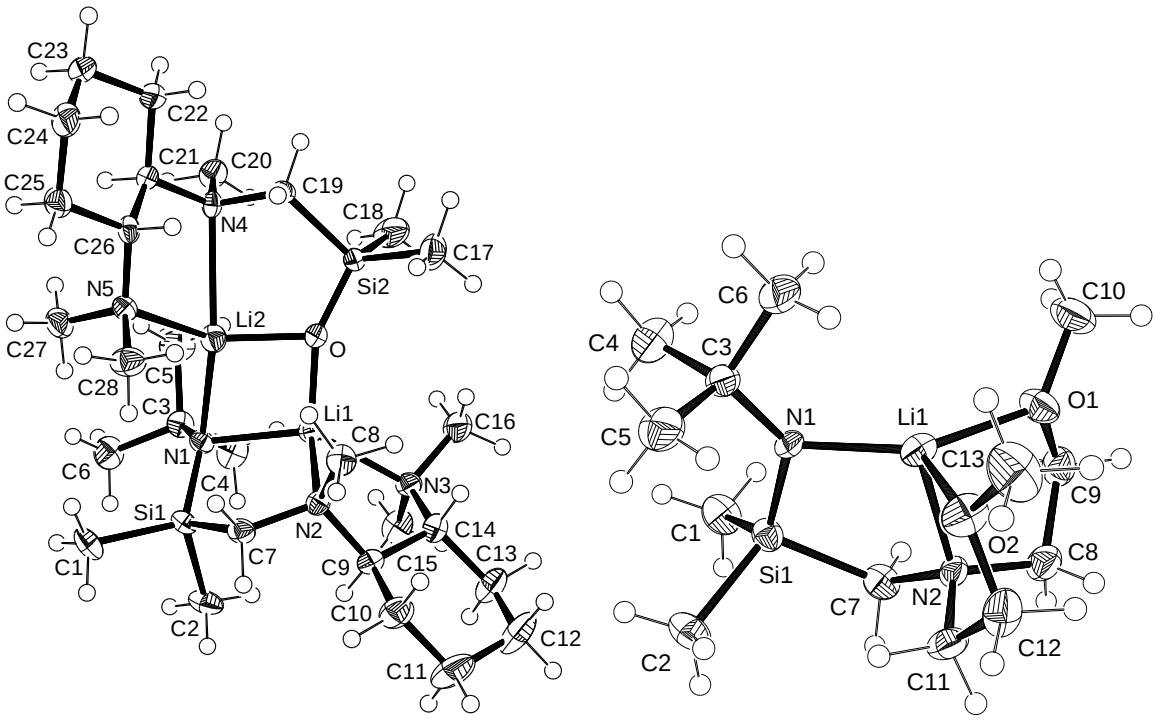
A Crystal Structure Determination of Compounds 2a, 2b, 4 and 6

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 840418 [**2a**], CCDC 840419 [**2b**], CCDC 840420 [**4**] and CCDC 840421 [**6**]. Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; [fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk)



ORTEP plot[1] of **2a** (left) **2b** (right, symmetry operation: –x+1, y, –z+3/2) at 50 % probability level.



ORTEP plot[1] of **4** and **6** at 50 % probability level.

B NMR Spectra

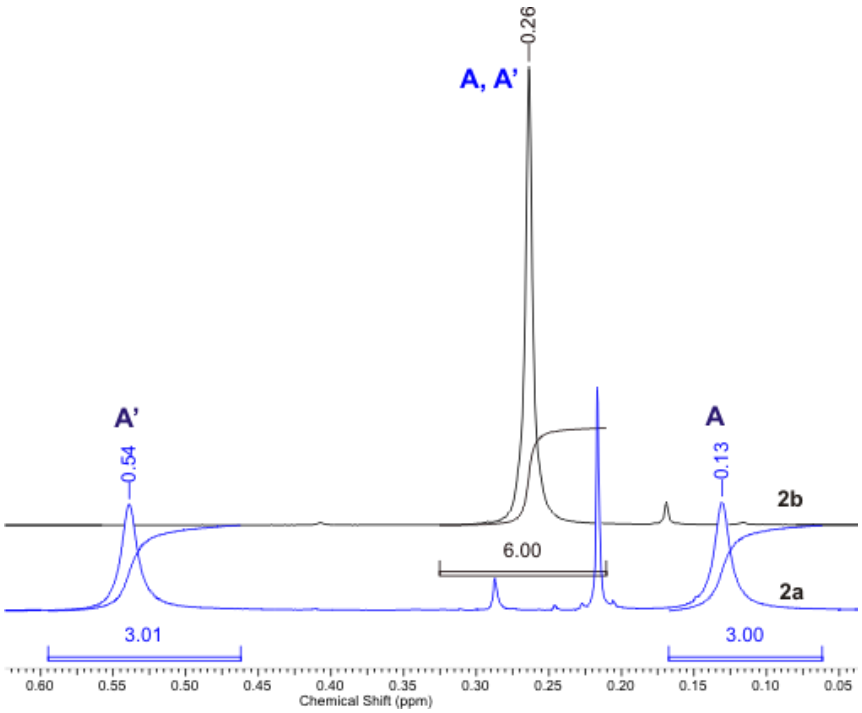


Fig 1 Part of ^{1}H NMR spectrum of compounds **2a** (Bruker DRX 300, C_6D_6) and **2b** (Bruker Avance 400, C_6D_6). The Unlabeled signal in the spectrum of **2a** can be assigned to the decomposition product, the silazane.

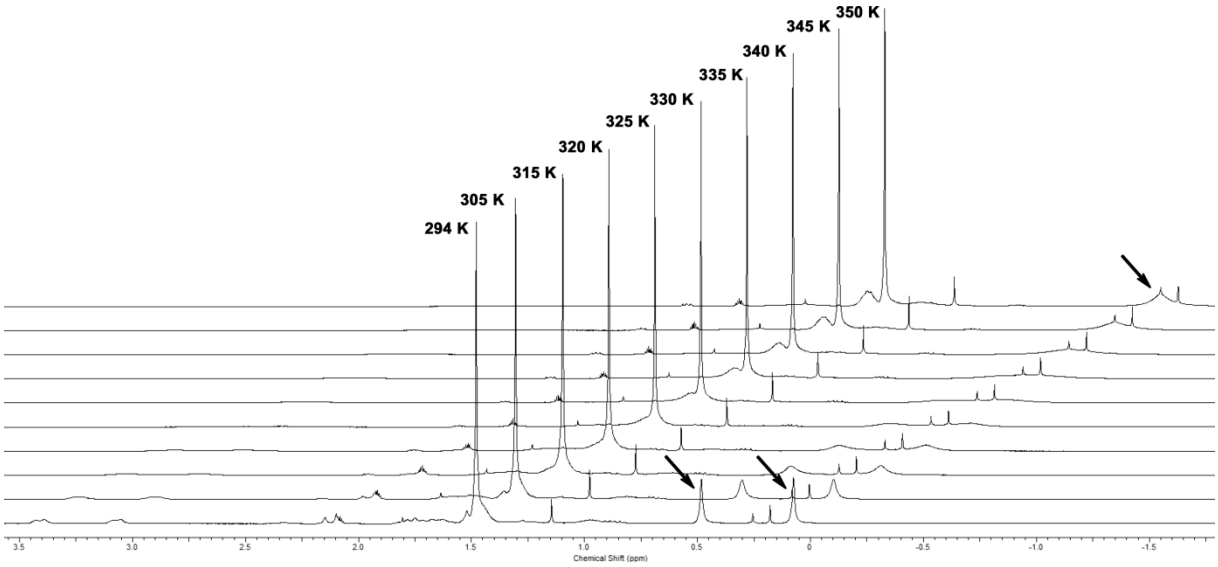


Fig 2 ^{1}H NMR spectra of compound **2a** at different temperatures (Bruker DPX 300, toluene-d_8).

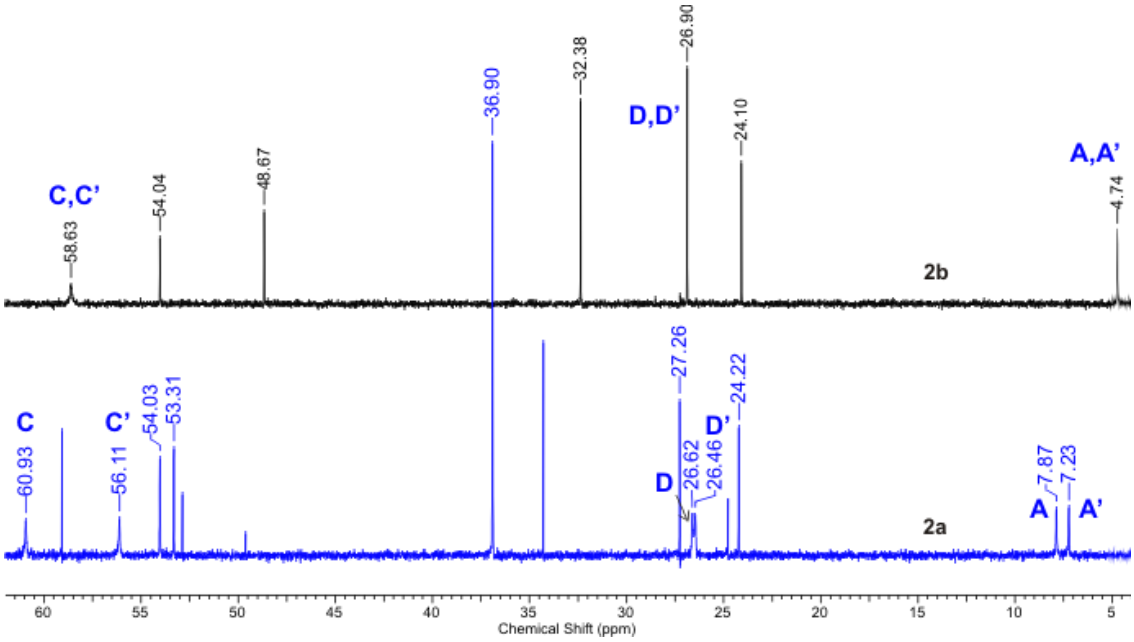


Fig 3 ^{13}C NMR spectra of compounds **2a** (Bruker DRX 300, C_6D_6) and **2b** (Bruker Avance 400, C_6D_6). The Unlabeled signals in the spectrum of **2a** can be assigned to the decomposition product, the silazane.

C Computational Studies

All calculations were modelled after the molecular structures in the crystal. The Optimisation of all structures was performed with Gaussian 03 Revision E.01 at the B3LYP/6-31+G(d) level.[2] The electronic charge distribution of compound **6** was calculated with Gaussian 98 Revision A.9 at the B3LYP/6-31+G(d) level. Harmonic vibrational frequency analyses showed no imaginary frequencies for all stationary points. Fig. 3 shows the calculated energy difference of C_2- and C_i-symmetrical dimers. The total (SCF) and zero-point energies (ZPE) of all compounds are listed in table 1, the coordinates of the optimised structures are listed in Tables 2-4.

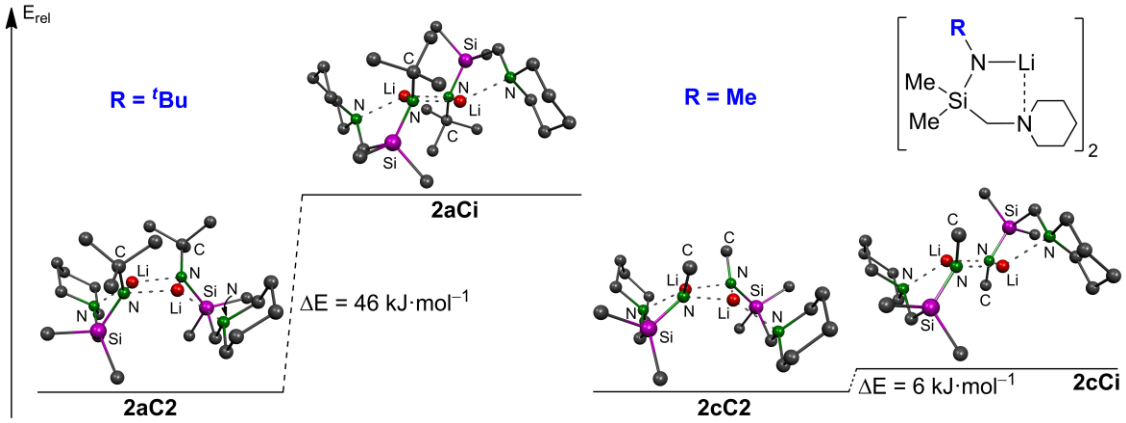


Fig. 3 Calculated energy difference of C_2- and C_i-symmetrical lithium silylamide dimers.

Table 1 Calculated energies of computed structures.

Compound	SCF [Hartree]	ZPE [Hartree]
2aC2	−1760.38655716	−1759.62148000
2aCi	−1760.36947880	−1759.60377100
2cC2	−1524.50543994	−1523.91170200
2cCi	−1524.50476013	−1523.90953500
6	−1071.11809926	−1070.67919100

Table 2 Coordinates of computed structures **2aC2** and **2aCi**.

2aC2				**2aCi**			
C	2.77900200	0.11258500	-2.44685200	C	0.93797800	-2.44586900	-2.39433000
C	-2.77900200	-0.11258500	-2.44685200	C	-2.04138500	-1.99832700	-1.78449500
C	0.95496000	-2.14838800	-1.70545900	C	-3.94954200	-0.46936400	-1.71601000
C	-0.95496000	2.14838800	-1.70545900	C	-0.60606900	-4.51871700	-0.88289600
C	-0.97243000	-3.61331600	-1.46002700	C	-4.84449500	0.43255500	-0.85891400
C	0.97243000	3.61331600	-1.46002700	C	-3.50344800	-1.92336400	0.15012300
C	3.91620900	-2.08513100	-0.77871200	C	-5.46303500	-0.34016500	0.31316600
C	-3.91620900	2.08513100	-0.77871200	C	-4.36365000	-1.07506600	1.09049700
C	-1.85111300	-4.44790000	-0.52386000	C	1.72170400	-3.04595100	1.60283800
C	1.85111300	4.44790000	-0.52386000	C	0.37425700	-2.28499000	1.69482800
C	-0.97243000	3.94745100	-0.05521000	C	0.53457600	-1.17996000	2.75443500
C	0.97243000	-3.94745100	-0.05521000	C	-0.68591700	-3.25865500	2.27272800
C	1.01759800	5.48513800	0.23885900	N	-2.87808900	-1.11559400	-0.92144600
C	-1.01759800	-5.48513800	0.23885900	N	0.00249400	-1.66289400	0.39229900
C	-0.16581000	4.79783100	0.93084200	Si	-0.35985400	-2.62412100	-1.00278900
C	0.16581000	-4.79783100	0.93084200	Li	-1.20396000	-0.04201100	-0.03547600
C	3.79268100	0.82818200	1.24001600	C	-0.93797800	2.44586900	2.39433000
C	-3.79268100	-0.82818200	1.24001600	C	2.04138500	1.99832700	1.78449500
C	2.44114700	0.16507600	1.60574800	C	3.94954200	0.46936400	1.71601000
C	-2.44114700	-0.16507600	1.60574800	C	0.60606900	4.51871700	0.88289600
C	1.64633400	1.21816500	2.41755100	C	4.84449500	-0.43255500	0.85891400
C	-1.64633400	-1.21816500	2.41755100	C	3.50344800	1.92336400	-0.15012300
C	2.71833800	-1.02923800	2.55250500	C	5.46303500	0.34016500	-0.31316600
C	-2.71833800	1.02923800	2.55250500	C	4.36365000	1.07506600	-1.09049700
H	3.15456100	-0.48073200	-3.29296100	C	-1.72170400	3.04595100	-1.60283800
H	-3.15456100	0.48073200	-3.29296100	C	-0.37425700	2.28499000	-1.69482800
H	-1.91703000	-0.68702200	-2.80878600	C	-0.53457600	1.17996000	-2.75443500
H	1.91703000	0.68702200	-2.80878600	C	0.68591700	3.25865500	-2.27272800
H	1.41133700	-2.81972600	-2.46011900	N	2.87808900	1.11559400	0.92144600
H	-1.41133700	2.81972600	-2.46011900	N	-0.00249400	1.66289400	-0.39229900
H	-0.55654000	-4.26468600	-2.25379100	Si	0.35985400	2.62412100	1.00278900
H	0.55654000	4.26468600	-2.25379100	Li	1.20396000	0.04201100	0.03547600
H	3.56610400	0.83061400	-2.18029900	H	0.57924100	-2.87169700	-3.34246100
H	-3.56610400	-0.83061400	-2.18029900	H	1.21377000	-1.40275700	-2.59292300
H	0.25741800	-1.51300500	-2.26975700	H	1.85750200	-2.98315100	-2.12383300
H	-0.25741800	1.51300500	-2.26975700	H	-2.63986700	-2.87487600	-2.10150000
H	-1.57104100	-2.84321300	-1.95541000	H	-1.82167200	-1.45060100	-2.70755200
H	1.57104100	2.84321300	-1.95541000	H	-4.56667900	-1.24968400	-2.20180500
H	-3.99988900	2.73931300	-1.65805900	H	-3.48280400	0.11293200	-2.51700400
H	3.99988900	-2.73931300	-1.65805900	H	-0.70025700	-4.90471300	-1.90812100
H	2.63654300	4.93594400	-1.11538700	H	0.23476500	-5.04678300	-0.41827100
H	-2.63654300	-4.93594400	-1.11538700	H	-1.51948800	-4.80494300	-0.34840600
H	4.82392500	-1.46921100	-0.75897100	H	-5.62546100	0.86727600	-1.49620400
H	-1.45099900	4.60847300	-0.80465400	H	-4.24925100	1.27005700	-0.47119100
H	1.45099900	-4.60847300	-0.80465400	H	-4.13115000	-2.71279300	-0.30897100
H	0.63903800	6.23949000	-0.46727800	H	-2.70684600	-2.42228100	0.70207000
H	-4.82392500	1.46921100	-0.75897100	H	-6.18606900	-1.07452600	-0.07219800
H	-0.63903800	-6.23949000	-0.46727800	H	-6.02039900	0.33770300	0.97187800
H	-2.35694900	-3.78126900	0.18713500	H	-4.79774900	-1.72540100	1.86095400
H	-3.93646600	2.72738500	0.10824100	H	-3.72685500	-0.34695700	1.61432400
H	2.35694900	3.78126900	0.18713500	H	2.51463000	-2.37626100	1.25183800
H	3.93646600	-2.72738500	0.10824100	H	1.65962200	-3.88245400	0.89866100
H	1.77305000	-3.42328700	0.47155700	H	2.02836200	-3.45409500	2.57624800
H	-1.77305000	3.42328700	0.47155700	H	1.30914500	-0.46803100	2.46409200
H	1.63721500	6.01952600	0.97018600	H	-0.40404200	-0.63025500	2.88686500

H	3.63330300	1.67157900	0.55725300	H	0.82019700	-1.59630800	3.72931200
H	-1.63721500	-6.01952600	0.97018600	H	-0.88672100	-4.10066100	1.60762400
H	-3.63330300	-1.67157900	0.55725300	H	-1.62927300	-2.73389300	2.46329400
H	4.47139600	0.12158800	0.75252600	H	-0.34457700	-3.67317700	3.23102500
H	-4.47139600	-0.12158800	0.75252600	H	-0.57924100	2.87169700	3.34246100
H	-0.83527300	5.53905300	1.38627600	H	-1.21377000	1.40275700	2.59292300
H	0.83527300	-5.53905300	1.38627600	H	-1.85750200	2.98315100	2.12383300
H	0.20059200	4.15991700	1.74689500	H	2.63986700	2.87487600	2.10150000
H	-0.20059200	-4.15991700	1.74689500	H	1.82167200	1.45060100	2.70755200
H	4.30604300	1.20865500	2.13378100	H	4.56667900	1.24968400	2.20180500
H	1.52773000	2.15192100	1.84915200	H	3.48280400	-0.11293200	2.51700400
H	-1.52773000	-2.15192100	1.84915200	H	0.70025700	4.90471300	1.90812100
H	-4.30604300	-1.20865500	2.13378100	H	-0.23476500	5.04678300	0.41827100
H	3.31438400	-1.79696000	2.04898900	H	1.51948800	4.80494300	0.34840600
H	-3.31438400	1.79696000	2.04898900	H	5.62546100	-0.86727600	1.49620400
H	-0.65300200	-0.84729400	2.69777200	H	4.24925100	-1.27005700	0.47119100
H	0.65300200	0.84729400	2.69777200	H	4.13115000	2.71279300	0.30897100
H	-1.77600000	1.49074200	2.87206800	H	2.70684600	2.42228100	-0.70207000
H	1.77600000	-1.49074200	2.87206800	H	6.18606900	1.07452600	0.07219800
H	2.16471000	1.48551800	3.34646100	H	6.02039900	-0.33770300	-0.97187800
H	-2.16471000	-1.48551800	3.34646100	H	4.79774900	1.72540100	-1.86095400
H	3.26626100	-0.71756500	3.45316000	H	3.72685500	0.34695700	-1.61432400
H	-3.26626100	0.71756500	3.45316000	H	-2.51463000	2.37626100	-1.25183800
N	0.13811300	-2.94057900	-0.74705100	H	-1.65962200	3.88245400	-0.89866100
N	-0.13811300	2.94057900	-0.74705100	H	-2.02836200	3.45409500	-2.57624800
N	1.64623300	-0.25199100	0.42255200	H	-1.30914500	0.46803100	-2.46409200
N	-1.64623300	0.25199100	0.42255200	H	0.40404200	0.63025500	-2.88686500
Si	2.33950600	-1.00868200	-0.96180600	H	-0.82019700	1.59630800	-3.72931200
Si	-2.33950600	1.00868200	-0.96180600	H	0.88672100	4.10066100	-1.60762400
Li	-0.18648400	-1.17516800	0.36279600	H	1.62927300	2.73389300	-2.46329400
Li	0.18648400	1.17516800	0.36279600	H	0.34457700	3.67317700	-3.23102500

Table 3 Coordinates of computed structures **2cC2** and **2cCi**.

2cCi				**2cC2**			
C	0.94613300	-2.76576700	-2.56164900	C	-3.35641100	0.25291200	-1.71312600
C	-1.83942700	-1.82405500	-1.86968200	C	3.35641100	-0.25291200	-1.71312600
C	-3.73352800	-0.29278500	-1.65353700	C	-1.22897200	2.35530700	-1.27207900
C	-0.60589600	-4.42163100	-0.55031700	C	1.22897200	-2.35530700	-1.27207900
C	-4.61993300	0.51527000	-0.70063000	C	0.96818100	3.43209300	-1.32633800
C	-3.40808000	-2.03215700	-0.00532700	C	-0.96818100	-3.43209300	-1.32633800
C	-5.31842800	-0.39966700	0.31510500	C	-3.88407900	2.28014500	0.46625000
C	-4.28729800	-1.29704400	1.01217300	C	3.88407900	-2.28014500	0.46625000
C	0.81961900	-2.15682100	1.39754800	C	2.16421000	3.93142700	-0.50991100
N	-2.72795900	-1.09536100	-0.92408300	C	-2.16421000	-3.93142700	-0.50991100
N	0.22933900	-1.57365000	0.18610100	C	0.56799400	-3.92717100	0.47790700
Si	-0.25337700	-2.62417100	-1.08298200	C	-0.56799400	3.92717100	0.47790700
Li	-1.16838100	-0.15360700	0.09509700	C	-1.73157600	-4.98544400	0.51919600
C	-0.94613300	2.76576700	2.56164900	C	1.73157600	4.98544400	0.51919600
C	1.83942700	1.82405500	1.86968200	C	-0.56799400	-4.45037600	1.36355300
C	3.73352800	0.29278500	1.65353700	C	0.56799400	4.45037600	1.36355300
C	0.60589600	4.42163100	0.55031700	C	-2.18608200	-0.17263700	2.01589600
C	4.61993300	-0.51527000	0.70063000	C	2.18608200	0.17263700	2.01589600
C	3.40808000	2.03215700	0.00532700	H	-3.89544600	0.91356100	-2.40730000
C	5.31842800	0.39966700	-0.31510500	H	3.89544600	-0.91356100	-2.40730000
C	4.28729800	1.29704400	-1.01217300	H	2.63978500	0.33335900	-2.30375800
C	-0.81961900	2.15682100	-1.39754800	H	-2.63978500	-0.33335900	-2.30375800
N	2.72795900	1.09536100	0.92408300	H	-1.74572700	3.18223200	-1.79802300
N	-0.22933900	1.57365000	-0.18610100	H	1.74572700	-3.18223200	-1.79802300

Si	0.25337700	2.62417100	1.08298200	H	0.56300300	4.25797100	-1.94340900
Li	1.16838100	0.15360700	-0.09509700	H	-0.56300300	-4.25797100	-1.94340900
H	0.52966900	-3.37497200	-3.37676200	H	-4.09171900	-0.45045700	-1.29921100
H	1.19006300	-1.77954100	-2.98008100	H	4.09171900	0.45045700	-1.29921100
H	1.89111500	-3.23448300	-2.25512700	H	-0.78748200	1.73323500	-2.06392300
H	-2.42074500	-2.57588100	-2.43958700	H	0.78748200	-1.73323500	-2.06392300
H	-1.49860400	-1.09053300	-2.61458000	H	1.28483100	2.63992700	-2.01362800
H	-4.36171500	-0.96043800	-2.27541100	H	-1.28483100	-2.63992700	-2.01362800
H	-3.20076800	0.37797400	-2.33544000	H	4.28888200	-3.00507300	-0.25297600
H	-1.06072300	-4.98746800	-1.37457700	H	-4.28888200	3.00507300	-0.25297600
H	0.32725200	-4.93546200	-0.28303700	H	-2.91910900	-4.34062000	-1.19359300
H	-1.27658100	-4.49873900	0.31408700	H	2.91910900	4.34062000	-1.19359300
H	-5.35612400	1.08005900	-1.28711000	H	-4.71790500	1.63682100	0.77790100
H	-3.99900500	1.25282100	-0.17284700	H	1.01612100	-4.76630900	-0.09007800
H	-4.02726900	-2.74192400	-0.58880100	H	-1.01612100	4.76630900	-0.09007800
H	-2.64496200	-2.61896400	0.51302900	H	-1.40993900	-5.89761800	-0.00538200
H	-6.05318400	-1.02998100	-0.20791900	H	4.71790500	-1.63682100	0.77790100
H	-5.87680500	0.19258600	1.05100500	H	1.40993900	5.89761800	-0.00538200
H	-4.78381800	-2.03554400	1.65476800	H	2.62829700	3.07743700	0.00309700
H	-3.64965900	-0.68630500	1.66842700	H	3.55790600	-2.83764600	1.35290900
H	-0.52966900	3.37497200	3.37676200	H	-2.62829700	-3.07743700	0.00309700
H	-1.19006300	1.77954100	2.98008100	H	-3.55790600	2.83764600	1.35290900
H	-1.89111500	3.23448300	2.25512700	H	-1.36077300	3.49768000	1.09631900
H	2.42074500	2.57588100	2.43958700	H	1.36077300	-3.49768000	1.09631900
H	1.49860400	1.09053300	2.61458000	H	-2.57570900	-5.27011700	1.15985100
H	4.36171500	0.96043800	2.27541100	H	2.57570900	5.27011700	1.15985100
H	3.20076800	-0.37797400	2.33544000	H	-0.17383200	-5.23205600	2.02558800
H	1.06072300	4.98746800	1.37457700	H	0.17383200	5.23205600	2.02558800
H	-0.32725200	4.93546200	0.28303700	H	-0.92584800	-3.63786400	2.01286700
H	1.27658100	4.49873900	-0.31408700	H	0.92584800	3.63786400	2.01286700
H	5.35612400	-1.08005900	1.28711000	N	-0.10006200	2.88610600	-0.46122400
H	3.99900500	-1.25282100	0.17284700	N	0.10006200	-2.88610600	-0.46122400
H	4.02726900	2.74192400	0.58880100	N	-1.55206800	0.34217500	0.79753600
H	2.64496200	2.61896400	-0.51302900	N	1.55206800	-0.34217500	0.79753600
H	6.05318400	1.02998100	0.20791900	Si	-2.49371000	1.23500900	-0.32032000
H	5.87680500	-0.19258600	-1.05100500	Si	2.49371000	-1.23500900	-0.32032000
H	4.78381800	2.03554400	-1.65476800	Li	0.25613000	1.13230600	0.59658600
H	3.64965900	0.68630500	-1.66842700	Li	-0.25613000	-1.13230600	0.59658600
H	0.22408700	-2.98048600	1.83030600	H	2.62451700	-0.61411300	2.65652000
H	1.83989600	-2.56253300	1.25579600	H	2.99556500	0.90743300	1.83763500
H	0.90261000	-1.40311500	2.19848800	H	1.44953700	0.68863000	2.66104400
H	-1.83989600	2.56253300	-1.25579600	H	-2.62451700	0.61411300	2.65652000
H	-0.90261000	1.40311500	-2.19848800	H	-2.99556500	-0.90743300	1.83763500
H	-0.22408700	2.98048600	-1.83030600	H	-1.44953700	-0.68863000	2.66104400

Table 3 Coordinates of computed structure **6**.

6							
C	2.16502400	0.04336300	-2.24521700	H	-2.20444000	2.13446900	-1.75631200
C	1.66134500	2.36892300	-2.25358300	H	2.43143200	-2.69596200	0.90375700
C	2.45878400	-1.11433900	-1.29501000	H	-0.68612400	2.98792200	0.11283600
C	-2.75814900	-1.88269100	-1.49452600	H	3.61758700	-0.54493100	1.33363100
C	0.18650900	-1.98819600	-0.82729600	H	-1.89829900	-3.41760200	1.19300600
C	1.82802600	-1.77139000	0.98956100	H	-3.51232100	0.99721900	-1.39698500
C	-2.93291600	1.83514700	-0.99223800	H	0.93204800	-2.02391900	1.56293700
C	2.62673800	-0.73287000	1.77608900	H	-3.62315200	2.67504300	-0.82220900
C	-1.98048200	-2.33783000	1.38731700	H	-3.01733300	-2.14176200	1.69084000
C	-1.43902200	2.65359400	0.84207200	H	3.48126300	1.77244900	2.17906300

C	-2.19318900	1.41175300	0.30474500	H	-0.92773700	2.40743600	1.78253100
C	2.49136400	1.50711700	2.57884800	H	-2.11215200	3.50098500	1.03197500
C	-3.25729200	1.02460100	1.36339100	H	-1.34673400	-2.09988100	2.25215300
H	3.01633000	0.20035900	-2.92552700	H	2.78432700	-1.09504700	2.80350200
H	1.27042900	-0.15335000	-2.85371600	H	1.83405200	2.37832900	2.53442300
H	0.74395300	2.22004700	-2.83907100	H	-3.87389500	0.18789100	1.01081500
H	2.49819000	2.59185300	-2.93088400	H	2.59670200	1.18678800	3.62503300
H	2.61853700	-2.03614500	-1.88333000	H	-2.77089200	0.71457500	2.29611000
H	-2.58183700	-1.37763800	-2.45347400	H	-3.93514100	1.86061500	1.58848600
H	0.15209200	-1.82990000	-1.91223100	N	1.38219800	-1.26708700	-0.31113500
H	-2.69056700	-2.96720500	-1.66644000	N	-1.22353900	0.35515400	0.04509400
H	3.39686900	-0.89381700	-0.77449900	O	1.94940200	1.22094700	-1.46023500
H	1.51953300	3.20660800	-1.56714100	O	1.88470600	0.48604000	1.79852400
H	0.30880200	-3.07952700	-0.68913300	Si	-1.50902800	-1.30205900	-0.16122100
H	-3.79406100	-1.66998800	-1.19799700	Li	0.65834500	0.61915100	0.12533200

[1] ORTEP-3 V2.02 for Windows, L. J. Farrugia, *J. Appl. Cryst* **1997**, *30*, 565.

[2] Gaussian 03 (Revision B.04), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 2003.