S8: Comparison of multipole models for [{2−(Me₃Si)₂C(Li)C₅H₄N}₂] with different flexibility.

- **Model 1:**

  as described in S1 and S2

- **Model 2:**

  as Model 1 but without chemical constraints and without imposing selection picking rules for the multipoles.

Topological analysis and geometrical parameters of the agostic fragment

Unit	Distance [Å]	$\rho(\mathbf{r}_c)$ [e/Å³]	$\nabla^2\rho(\mathbf{r}_c)$ [e/Å⁵]	Ellipticity ε
Li···N_a	1.9509	0.210(2)	5.202(2)	0.02
Li−C1	2.2050	0.142(2)	2.515(1)	0.10
C1−Si2	1.8592(4)	0.855(15)	1.83(3)	0.17
Si2−C7	1.8946(6)	0.686(17)	4.81(3)	0.04
C7−H7c	1.0981	1.72(5)	−13.06(11)	0.09

- **Model 3:**

  as Model 1 but with hexadecapole refinement, in addition.

Topological analysis and geometrical parameters of the agostic fragment

Unit	Distance [Å]	$\rho(\mathbf{r}_c)$ [e/Å³]	$\nabla^2\rho(\mathbf{r}_c)$ [e/Å⁵]	Ellipticity ε
Li···N_a	1.9510	0.210(4)	5.110(4)	0.06
Li−C1	2.2049	0.147(4)	2.449(3)	0.33
C1−Si2	1.8591(4)	0.870(17)	1.93(3)	0.24
Si2−C7	1.8940(6)	0.733(18)	4.97(3)	0.08
C7−H7c	1.0981	1.74(5)	−15.81(15)	0.10