

Orbiting of the Lithium Atom in the $[\text{Me}_2\text{Si}(\text{NSiMe}_3)_2]_2\text{InLi}$ Molecule: Theoretical Confirmation

Feliu Maseras* and Agustí Lledós

Unitat Química Física, Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain

A combination of MO calculations on the $[\text{H}_2\text{Si}(\text{NH})_2]_2\text{InLi}$ model and MM calculations on the $[\text{Me}_2\text{Si}(\text{NSiMe}_3)_2]_2\text{InLi}$ molecule confirms previous suggestions of an orbiting movement of the lithium atom, and provides details about the nature of the associated transition states.

It has been recently proposed in an experimental study by Veith and coworkers that the $[\text{Me}_2\text{Si}(\text{NSiMe}_3)_2]_2\text{InLi}$ species undergoes an intramolecular dynamic process consisting of the lithium atom orbiting around the central indium atom.¹ This new development in the chemistry of indium² constitutes one of the first examples of motion of a lithium atom in a molecular environment,³ a process which is well known in solid systems.⁴ In order to shed some more light on the mechanism of this novel process, which is apparently absent in other related species,⁵ we used a combination of *ab initio* molecular orbital (MO) calculations on the $[\text{H}_2\text{Si}(\text{NH})_2]_2\text{InLi}$ model, and molecular mechanics (MM) calculations on the full $[\text{Me}_2\text{Si}(\text{NSiMe}_3)_2]_2\text{InLi}$ system. Similar approaches have been applied successfully to other systems.⁶

For the *ab initio* MO calculations on the $[\text{H}_2\text{Si}(\text{NH})_2]_2\text{InLi}$ system, an effective core potential is used to represent the 46 innermost electrons of the indium atom,⁷ while the basis set is of valence double- ζ quality⁷⁻⁹ with a polarization d shell on the silicon atoms.⁹ The choice of this basis set is the result of preliminary tests at the RHF level with up to five different sets which considered minimal basis,¹⁰ diffuse functions¹¹ and polarization functions in all atoms.¹² The effect of correlation energy is evaluated through MP2 calculations with the same basis set, resulting in only a minor correction to the RHF results.

For the MM calculations¹³ on the complete $[\text{Me}_2\text{Si}(\text{NSiMe}_3)_2]_2\text{InLi}$ system, the skeleton geometry of the corresponding MO-optimized $[\text{H}_2\text{Si}(\text{NH})_2]_2\text{InLi}$ species was used. The non-hydrogen atoms present in $[\text{H}_2\text{Si}(\text{NH})_2]_2\text{InLi}$ are directly frozen. For the hydrogen atoms replaced by bulky substituents, only the bond distances are modified, the N...Si distances being set to 1.72 Å and the Si...C distances set to 1.88 Å. The remaining atoms, six methyl groups and six methyl hydrogen atoms, are completely optimized. MM parameters concerning frozen atoms are set to zero, to avoid double-counting their energy contributions, while program defaults are taken for the other atoms.¹⁴

The geometry optimized at the MP2 level for the $[\text{H}_2\text{Si}(\text{NH})_2]_2\text{InLi}$ complex is presented in Fig. 1. The molecule has C_2 symmetry, with the symmetry axis passing through the

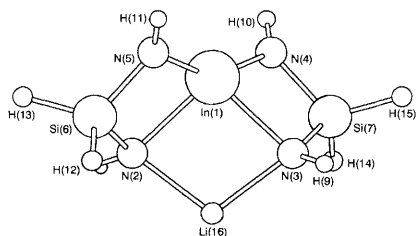


Fig. 1 MP2 optimized structure for the minimum in the model system $[\text{H}_2\text{Si}(\text{NH})_2]_2\text{InLi}$. Selected distances (Å) and angles ($^\circ$), with the corresponding experimental values for $[\text{Me}_2\text{Si}(\text{NSiMe}_3)_2]_2\text{InLi}$ in parentheses: In(1)–N(2) 2.210 (2.223), In(1)–N(3) 2.038 (2.064), N(2)–Li(16) 2.064 (1.995), N(2)–Si(6) 1.769 (1.737), N(4)–Si(7) 1.739 (1.717), In(1)–Li(16) 2.733 (2.748), N(2)–In(1)–N(3) 92.3 (95.2), N(4)–In(1)–N(5) 151.6 (148.4), N(2)–In(1)–N(5) 75.9 (76.2), N(2)–In(1)–N(4) 125.8 (127.3), N(2)–Li(16)–N(3) 105.9 (105.4).

indium and lithium atoms, in agreement with experimental data for $[\text{Me}_2\text{Si}(\text{NSiMe}_3)_2]_2\text{InLi}$.¹ Optimized geometrical parameters are in excellent agreement with X-ray results, especially taking into account the simple model used. The number and characteristics of the equivalent minima accessible to the system can be discussed in view of this geometry. In order to do that, it is better to consider the complex as formally derived from the interaction of a hypothetical $[\{\text{H}_2\text{Si}(\text{NH})_2\}_2\text{In}]^-$ anion and a Li^+ cation. The optimization experiment on such an anion showed it to have D_{2d} symmetry, with the main symmetry axis passing through the indium and the two silicon atoms, as expected. This anion has four equivalent nitrogen atoms such that an entering lithium cation can interact with any pair of nitrogens, providing they are bound to different silicon atoms. In principle the lithium atom can bridge N(2) and N(3), N(2)–N(4) or N(4)–N(5). So there are four different local minima with the same energy. It can also be seen that there are two different enantiomeric forms, two of the four local minima belonging to each of them.

The existence of these four degenerate local minima and their geometrical relationship strongly suggests the possibility of an intramolecular dynamic process with the net result of rotation of the lithium atom around the indium centre. The other necessary condition is the existence of a low-energy barrier for such a process. This barrier can be theoretically computed as the energy difference between the minimum and the transition state of the process. The geometry of the transition state has been optimized at the MP2 level, Fig. 2. This transition state connects the local minima where the lithium atom bridges N(2)–N(3) (Fig. 1) and N(2)–N(4). This transition state has a C_s symmetry, with the symmetry plane including the In(1), N(2) and Li(16) atoms. Its nature as a transition state is checked through a numerical calculation of the hessian at the RHF level, which yields a single negative eigenvalue (-0.00658 atomic units), as expected for a transition state. Moreover, the associated eigenvector corresponds to the 'orbiting' of the lithium atom, being of A'' symmetry, and having the strongest components in the out-of-plane displacement of the atoms H(8), Li(16) and H(11). Another interesting geometrical feature of this species is

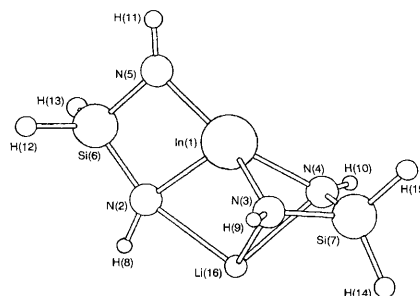


Fig. 2 MP2 optimized structure for the transition state in the model system $[\text{H}_2\text{Si}(\text{NH})_2]_2\text{InLi}$. Selected distances (Å) and angles ($^\circ$): In(1)–N(2) 2.172, In(1)–N(3) 2.140, In(1)–N(5) 2.005, N(2)–Li(16) 2.216, N(3)–Li(16) 2.214, N(2)–Si(6) 1.747, N(3)–Si(7) 1.751, N(5)–Si(6) 1.750, In(1)–Li(16) 2.441, N(2)–In(1)–N(3) 102.9, N(3)–In(1)–N(5) 144.8, N(2)–In(1)–N(5) 76.3, N(2)–Li(16)–N(3) 99.1, N(3)–Li(16)–N(4) 67.6.

that the lithium atom interacts with three nitrogen atoms simultaneously.

The MP2 energy for this transition state is 20.5 kcal mol⁻¹ (1 cal = 4.184 J) above that of the minimum. This computed barrier for the [H₂Si(NH)₂]₂InLi system is in poor agreement with the experimental value of 10.6 kcal mol⁻¹ for [Me₂Si(NSiMe₃)₂]₂InLi.¹ Fortunately, this theoretical result is substantially corrected when the steric effects present in the real

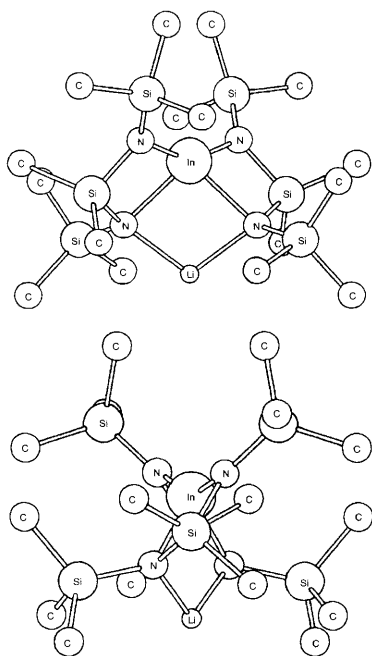


Fig. 3 MM optimized structure for the minimum in the complete [Me₂Si(NSiMe₃)₂]₂InLi system seen from two different orientations. Hydrogen atoms are omitted for clarity.

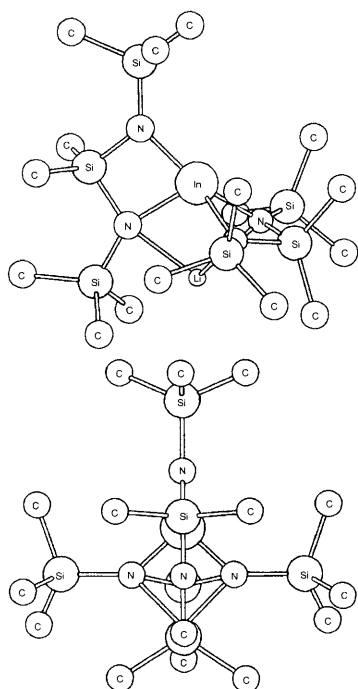


Fig. 4 MM optimized structure for the transition state in the complete [Me₂Si(NSiMe₃)₂]₂InLi system seen from two different orientations. Hydrogen atoms are omitted for clarity.

system are estimated through MM calculations. The steric energy correction associated with the bulky substituents is computed to favour the transition state by 6.4 kcal mol⁻¹. The magnitude and the sign of the steric stabilization value lowers the energy barrier with respect to that of the [H₂Si(NH)₂]₂InLi system, therefore bringing the theoretical result closer to the experimental value. The reasons for this behaviour can be understood by inspection of Figs. 3 and 4. From the second structure of each Fig. it is clear that the transition state allows a less crowded distribution of the bulky substituents. The addition of electronic (MO calculations) and steric (MM calculations) energies computed in this way fails to reproduce exactly the experimental result, but this was to be expected. Some likely sources of error are the inaccuracy in the MM calculation itself, the freezing of the [H₂Si(NH)₂]₂InLi fragment when computing steric contributions, and the eventual contribution of quantum tunnelling effects to the experimental value. It should be also taken into account that the *ab initio* calculations only yield energy differences at 0 K.

In summary, the results contained in this communication confirm the existence of an intramolecular orbiting movement of a lithium atom in the [Me₂Si(NSiMe₃)₂]₂InLi species as had been postulated from NMR data.¹ This orbiting movement goes through four degenerate C₂ local minima (with the lithium atom connecting two nitrogen atoms), and four degenerate C_s transition states (with the lithium connecting three nitrogen atoms). This novel orbiting movement seems to be attributed to a combination of favourable factors which leads to the existence of the degenerate local minima and the low-energy barrier between them. The subtle combination of steric strains associated with this particular combination of fused four-membered rings with bulky substituents on the ligands seems to play a central role.

We acknowledge financial support from the Spanish Dirección General de Investigación Científica y Técnica (DGICYT) under project No. Pb92-0621.

Received, 24th November 1994; Com. 4/07175A

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