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INTERNAL LITHIUM COORDINATION BY A π-BOND IN 7-LITHIONORBORNADIENE

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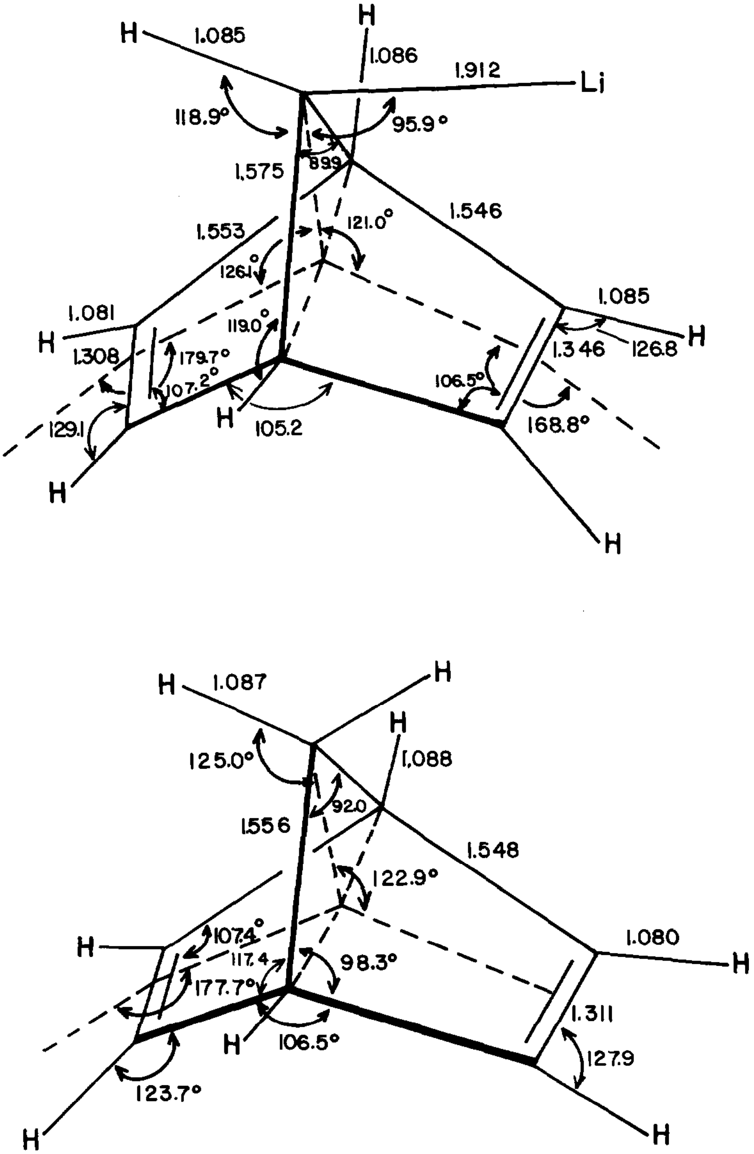
Summary: The STO-3G optimized structure of 7-lithionorbornadiene indicates that the lithium is strongly coordinated to the neighboring π bond in the unsolvated species.

In connection with a study of molecular distortions and stereoselectivities of cycloadditions of 7-substituted norbornadienes,[1-3] we had the occasion to optimize the structure of 7-lithionorbornadiene, using ab initio calculations with the STO-3G basis set and gradient techniques.[4] These results indicate a substantial ability of a properly situated π-bond to coordinate lithium in organolithiums.

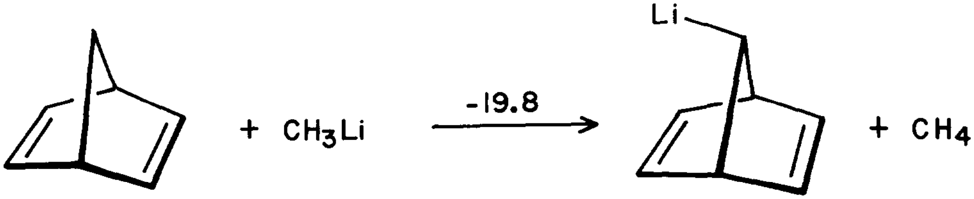
The structure of 7-lithionorbornadiene is shown on the next page, along with that of norbornadiene, optimized independently by Morokuma and Wipff,[5] and by our group.[2] Four features of structure are obvious indications of rather large interactions between the Li atom and the neighboring π-bond. (1) The $C_1C_7C_4$ bridge is tilted toward the lithium side of the molecule by 2°, as compared to norbornadiene. This permits the Li to approach the π-bond more closely. (2) The CC double bond syn to Li is stretched by 0.035 Å versus the STO-3G bond length in norbornadiene, indicative of strong complexation of Li with the double bond. (3) The distance from Li to the syn olefinic carbons is 2.272 Å, only 19% longer than the C_7-Li distance, and only 13% longer than the STO-3G C-Li distance in methyl lithium.[6] (4) The hydrogens of the syn double bond are bent 11.2° below the plane of the double bond, also indicative of substantial Li-alkene interaction.

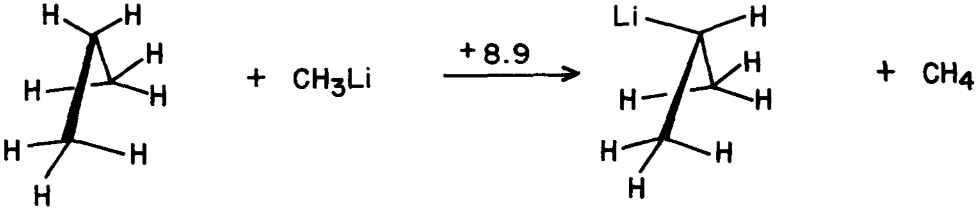


STO-3G Optimized Structures of Norbornadiene and 7-Lithionorbornadiene

The tendency of Li to form polycentric bridges through interactions of a low-lying vacant p orbital with π orbitals is well-documented.[8] The bridging in 7-lithionorbornadiene must arise from the interaction of a symmetric p orbital with the symmetric π orbital of the alkene, accompanied by strong electrostatic interactions[9] between the electropositive Li and relatively electron-rich π cloud of the alkene.

The role of the double bond in coordinating Li can also be assessed from various features of electronic structure. Thus, the total charge (Mulliken) on Li in 7-lithionorbornadiene, **1**, is +0.06, as compared to +0.23 in 2-lithiopropane calculated in the same geometry as the $C_1C_7C_4$ fragment of **1**. Furthermore, there is weak C-Li bonding of C_2 and C_3 with Li (overlap population = 0.05), while the syn double bond is weakened (overlap population = 0.56) as compared to the anti double bond (overlap population = 0.62). The following isodesmic reactions (STO-3G energies in kcal/mol are given over the arrows) indicate that 7-lithonorbornadiene is highly stabilized relative to monomeric methyl lithium. About 30 kcal/mol of stabilization is afforded by internal coordination with the alkene, since the transfer of lithium to propane distorted into the geometry of the $C_1C_7C_4$ bridge of **1** is endothermic.





The theoretical prediction of strong interaction between Li and the π bond provides support to the suggestion by Posner and Lentz that lithium enolates may have significant internal coordination of the lithium by phenyl groups elsewhere in the molecule.[10] Indeed, internal coordination of lithium by heteroatoms is a dominant theme in organolithium chemistry,[11] and computational investigations show that α-heteroatoms can provide substantial stabilization[12] of carbanions. Although 7-lithionorbornadiene is perhaps an extreme case of coordination of lithium to a π-bond, and the internal coordination of lithium would undoubtedly be attenuated in solution, we feel that this result does provide dramatic computational evidence for the potential of internal coordination in stabilization of organolithiums. Finally, we should mention that 7-lithionorbornadiene has been prepared in solution,[13] and is a useful intermediate for synthesis.

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