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ELECTRONIC STRUCTURE AND BONDING OF ALLYLLITHIUM

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Summary

The results of CNDO/2 calculations have been used to determine the equilibrium geometry for allyllithium which is predicted to be a non-planar "bridge" structure. The lowest energy configuration (LEC) is described in molecular orbital terms which stress the importance of the lithium's position in permitting it to utilize all its valence orbitals in bonding with the allyl moiety. Charge densities, the theoretical dipole moment, and variations of configurations are discussed in relation to the spectroscopic measurements of allyllithium. Utilizing the geometry of the allyllithium monomer (LEC), a proposed dimer configuration is reported which is in feasible agreement with the experimental aggregation properties. The solvent interactions were considered by utilizing two molecules of ammonia as the electron donor with allyllithium. The results of the calculations predict that the solvation of the lithium by ammonia increases the allyllithium fragment separation with concomitant changes in the electron densities and bonding populations.

Introduction

Allylic lithium species have been proposed as possible intermediates in anionic polymerization reactions where organolithium reagents have been used as initiators [1]. Therefore, spectroscopic studies, particularly proton magnetic resonance of several molecules containing the allyllithium component have been made to gain a better understanding of the bonding and structure of this important species [2]. This paper is concerned with the results of molecular orbital calculations using the CNDO/2 approximations [3] with particular interest in the predicted properties compared to experimental values. The CNDO/2 method has been quite successful in calculating properties such as bond angles and to lesser degree, bond lengths [4], and will be employed for predicting the lowest energy configuration for the allyllithium molecule. The wave functions calculated by this method will be utilized to describe the bonding and electronic structure.

Results and discussion

Equilibrium geometry

The following assumptions were made in the calculations to predict the equilibrium geometry of allyllithium: *(1)* C—H bond lengths were chosen as 1.09 Å, *(2)* hydrocarbon bond angles were given values of 109.5 degrees for sp^3 hybridized carbons and *(3)* 120.0 degrees for the sp^2 terminal carbon. All values in the original CNDO/2 parameterization were left unaltered.

Preliminary calculations were made with a lithium—carbon [5] bond distance of 2.20 Å with the molecule in a propylene configuration: however, changing the hybridization on the saturated carbon from an sp^3 to an sp^2, with the lithium coordinates unchanged in this configuration, stabilized the molecule. Also, rotation about the carbon—carbon single bond for the propylene model produced the greatest stability when the lithium was on a line perpendicular to the plane defined by the three carbons. Therefore, a point of interest for the ground state is the location of the lithium atom relative to a planar allylic framework which is given in Fig. 1. Movement of the lithium in the C(1)—C(2) π cloud indicated a more stable configuration was obtained with the lithium located above carbon(2). This increased stabilization is the result of increased bonding between the 2s-orbitals of the four atoms and the π bond of the allyl fragment with the p_x orbital on the lithium atom. Due to the proximity of two partial positive changes, Li^+ and $C(2)^+$, increasing the distance separating the two atoms in the yz plane further stabilized the molecule in a symmetric nonplanar bridge structure. The resulting lowest energy configuration (LEC) is given in Fig. 2 as determined by all possible displacements of the lithium and carbon atoms. Any deviation of the allyl fragment from planarity was found to be less stable. A planar configuration with the lithium atom in the plane of the allyl fragment was found less stable than the nonplanar configuration given in Fig. 2. The separations for the LEC are 2.19 and 2.03 Å for Li—C(1) and Li—C(2) which are slightly smaller than the typical values of 2.36 and 2.12 Å calculated for the unsaturated lithium complex, lithium naphthalide [6].

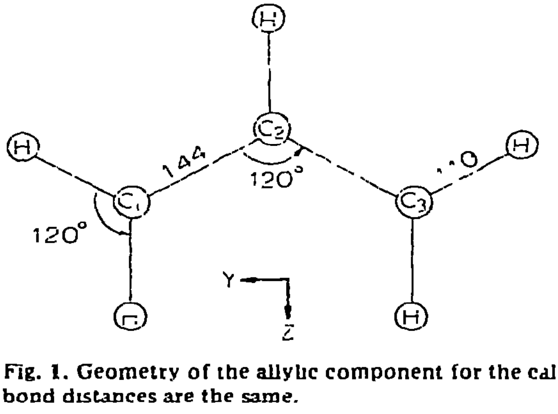


Fig. 1. Geometry of the allylic component for the calculations. All bond angles are 120° and carbon—hydrogen bond distances are the same.

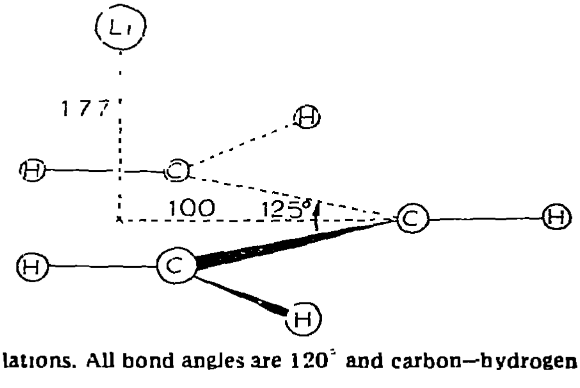


Fig. 2. The predicted geometry for allyllithium, where the lithium atom is located above the plane of the allyl and between the projection of the carbon and hydrogen atoms.

Crystallographic studies have been made by Brooks and Stucky [7] for tetramethylethylenediamine lithium triphenylmethane complex which contains a component analogous to the allyllithium anionic moiety. The portion of the molecular complex analogous to allyllithium is a nonplanar, nonsymmetrical bridge structure with lithium terminal carbon internuclear distances of 2.51 and 2.49 Å and a lithium—carbon(2) distance of 2.23 Å. The geometry predicted for allyllithium is the same as the corresponding component of the complex except for slightly smaller lithium carbon separations and a plane of symmetry for allyllithium. Therefore, the CNDO/2 results are encouraging since the LEC *converged* on this geometry assuming only the C—H bond distances and the standard hybridized carbon bond angles.

Bonding description

Within the CNDO approximations only the valence electrons are considered; thus allyllithium has the nine lowest energy molecular orbitals occupied. The degree of participation of the lithium in each molecular orbital (MO) varies and in certain MO's the contribution is negligible. In Table 1 are given the coefficients (greater than 0.10), not including the hydrogen coefficients. The molecular wavefunctions are numbered according to their increasing eigenvalues [i.e., $\psi(1)$ is the most stable MO]. $\psi(1)$ and $\psi(6)$ are mostly σ bonding MO's between lithium and the three carbons whereas the lithium coefficients in $\psi(3)$ exhibit a greater degree of bonding with C(2). In $\psi(2)$ and $\psi(9)$ the lithium p_y orbital has overlap values of 0.26 and 0.16 with the terminal carbon $2s$ and $2p_x$ orbitals, respectively. Because of the large coefficients of lithium p_y atomic orbital in $\psi(2)$ and $\psi(9)$, it is of major importance in the overall bonding (see Fig. 3). Evident in these molecular orbitals of allyllithium is the utilization of all low-energy orbitals on lithium to increase its bonding with the allyl moiety. Using Mulliken's population analysis [8], the overlap population values for lithium—C(1) and lithium—C(2) are 0.37 and 0.34 relative to 0.83 and 0.65 for carbon—carbon and C(2)—H(5), respectively. Assuming that the strength of the bond between two atoms varies with the overlap population, the bond strength of the lithium—carbon bonds would be predicted to be about one half that of the carbon—carbon or C(2)—H(5) bonds.

A CNDO/2 calculation was also made for the allyl anion using the same geometry for the hydrocarbon framework as in the LEC of allyllithium. The following was noted in the MO's and their eigenvalues: *(1)* the relative ordering of the MO's according to their energy values of the allyl anion and allyllithium

TABLE 1

SELECTED VALENCE ORBITALS OF ALLYLLITHIUM

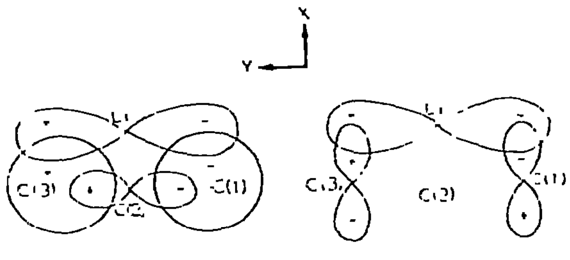
$$\psi(1) = 0.41s(1) + 0.56s(2) + 0.41s(3) + 0.23s(\mathrm{Li}) - 0.26p_x(\mathrm{Li}) + 0.18p_y(1) - 0.18p_y(3) + 0.14p_z(2)$$

$$\psi(2) = -0.48s(1) + 0.48s(3) + 0.44p_y(2) + 0.24p_y(\mathrm{Li})$$

$$\psi(3) = 0.14s(1) - 0.32s(2) + 0.14s(3) - 0.33p_z(1) - 0.45p_z(2) + 0.33p_z(3) + 0.20p_z(\mathrm{Li})$$

$$\psi(6) = 0.18s(\mathrm{Li}) + 0.51p_x(1) + 0.65p_x(2) + 0.51p_x(3) - 0.11p_z(\mathrm{Li})$$

$$\psi(9) = -0.54p_x(1) + 0.54p_x(2) + 0.38p_y(\mathrm{Li})$$



ψ(2) ψ(9)

Fig 3 Molecular orbital sketches of ψ(2) and ψ(9).

remained unchanged, *(2)* in the allyllithium MO's, with few exceptions, (1,2,3,6, and 9) (see Table 1), the carbon atom coefficients exhibited small decreases as compared to their coefficients in the allyl anion, and *(3)* all the occupied MO's except the lowest occupied MO were further stabilized in allyllithium. From the electron densities, the partial charges are −0.36 and +0.10 on C(1) and C(2) in the allyl anion and −0.20 and +0.16 in allyllithium. The partial charge on lithium is +0.12 with the rest of the positive charge dispersed among the hydrogens.

Ionic character

Due to experimental difficulties, limited experimental values are available with which to compare the results of theoretical calculations for allyllithium. The proton magnetic resonance (PMR) spectra is available and is of particular interest as to equivalence of the hydrogen atoms of allyllithium [9]. The room temperature PMR spectra of allyllithium has an AB_4 type spectrum and upon lowering the temperature to −87° an AA′BB′C type spectrum was obtained. The following rapid dynamic equilibrium is suggested to account for the PMR data, that being the intramolecular exchange of the lithium from one terminal carbon to the other [10]. The results of the calculations of the propylene-type

$$LiCH_2{-}CH{=}CH_2 \rightleftarrows CH_2{=}CH{-}CH_2Li$$

arrangement with the Li—C(1) bond distance of 2.10 Å predicts that the LEC described earlier is more stable by 3.9 eV. CNDO/2 calculations under the original parameterization are known to give excessive binding energies, therefore, the energies in this paper are used only in describing relative stabilities [4]. The AB_4 type spectra would be the result of rapid intramolecular exchange in this configuration with rotation about the carbon—carbon single bond and the low temperature spectra would correspond to the geometry of the LEC.

Another configuration considered is that of the lithium atom being involved in an intermolecular exchange between allyl fragments. To account for the PMR data, rotation about the carbon—carbon bonds in allyllithium and allyl anion were also calculated and the rotational barriers are predicted to be 2.5 and 1.9 eV, respectively, the difference between these two configurations being the result of the nuclear—nuclear repulsion for the lithium atom and the allyl fragment. Therefore, assuming the same solvation effects for all three mechanisms, the lowest energy path favors the formation of the allyl anion.

This proposed ionic character is supported by other data. The infrared spectra has a lower than expected carbon—carbon stretching frequency compared to other allyl—metal (Mg, Zn, Cd) compounds [11]. The interpretation of the low temperature PMR spectra by West, Purmont and McKinley concluded that this is not indicative of a covalently bonded allyllithium involved in rapid intramolecular exchange [9]. The calculated dipole moment (a property which CNDO/2 calculations are noted for predicting with good success) for allyllithium is 3.6 debyes, which is indicative of charge separation supporting ionic character.

Vibrational motions

Several vibrational motions of the lithium in allyllithium for the LEC were considered. Three displacements corresponding to the motions considered are given in Fig. 4. A plot of the total energy versus the lithium displacement (increments of 0.02 Å) about the equilibrium geometry predicts that the motion of the lithium perpendicular to the plane of the allyl fragment (a) is the lowest in energy. This motion maintains the greatest degree of bonding even as the lithium atom coordinates are being varied due to the bonding combination of the lithium p_x-orbital with the anti-symmetric combination of the terminal carbon p-orbitals in the highest occupied molecular orbital. Similar vibrational motions have been proposed for lithium naphthalide to account for calculated spin densities obtained from experimental ESR coupling constants [6].

Dimer configurations

Solvent studies indicate dimer formation as well as higher degrees of aggregation depending on the concentration [9]; therefore, it was of interest to determine the predicted geometry of the dimer. Utilizing the LEC of the monomer of allyllithium, various dimer geometries were investigated. One possible dimer arrangement, where a lithium atom from one monomer would be bonded to another lithium of the second monomer, was found to have a negative charge localized on both lithium atoms. This, together with the fact

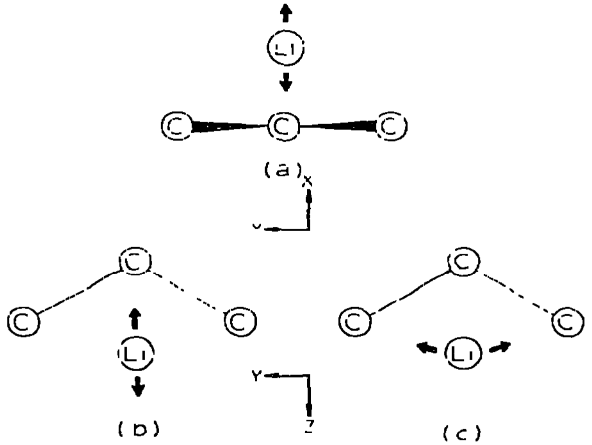
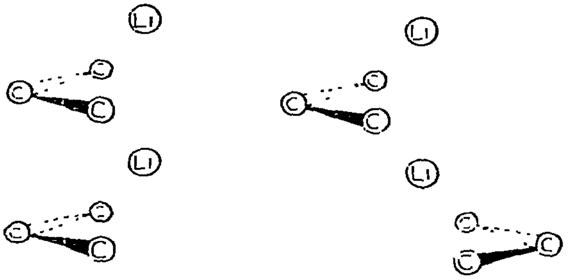


Fig. 4. Vibration motions of the lithium atom: *(a)* motion of lowest energy; perpendicular to the allylic plane; *(b)* motion which increases the overlap with the terminal carbons but increases the interaction of the positive charged lithium and center carbon; *(c)* oscillatory motion which could lead to a propylene-type conformation



"CIS" "TRANS"

Fig. 5. The conformation of the "*cis*" and "*trans*" dimers.

that no lithium containing molecules have shown evidence of direct lithium—lithium bonding, except the lithium molecule, eliminated this geometry from further consideration. In terms of the energies only two possible forms were found significant and are given in Fig. 5. The "*cis*" dimer was predicted to be 4.6 eV more stable than the "*trans*" dimer. The total binding energy was predicted to be 8.4 eV more stable for the "*cis*" dimer compared to the monomer [*i.e.* E(dimer)—2E(monomer)]. For the "*cis*" and "*trans*" dimers, the more stable molecular orbitals are localized on individual allyl monomeric units and the less stable are spread over the entire dimer. This delocalization provides the additional stability of the dimer as compared to the monomers. Studies of allyllithium in higher concentrations in THF have aggregation greater than ten; the "*cis*" dimer can easily be extended by "stacking" additional monomeric units in agreement with this observation.

Solvent interactions

Experimental studies of allyllithium requires a donor solvent such as ethyl ether or tertiary amine to stabilize the reactive species. These solvents are thought to stabilize allyllithium by formation of intimate ion pairs thereby reducing the magnitude of charge on the lithium atom. Calculations of the interactions of solvent molecules with allyllithium are of interest to determine what changes are predicted by comparing the results of the solvated and unsolvated species. These calculations for ethyl ether or tertiary amine exceeds the computational space available; therefore, the solvent effects are investigated by assuming the solvent to be ammonia as the interactions are expected to be similar to the other solvents. This section contains a discussion of the results obtained for allyllithium solvated with two molecules of ammonia. It was necessary to determine the predicted geometry for the complex before the results of the different forms could be compared. The number of possible displacements that could be considered even for this small complex is great, therefore restictions were placed on the number of parameters considered. The parameters considered for the predicted geometry were *(1)* the N—Li—N bond angle, *(2)* the N—Li bond distance, and *(3)* the separation of the solvated lithium from the allyl plane.

Crystal structure data for several compounds containing lithium in an analogous environment to that of the complex has been reported by Stucky and co-workers [7, 12]. This data for fluorenyllithium diquinuclidine was used as the starting point for the determination of the predicted geometry. Certain approximations were made with respect to the solvent—lithium interactions. The allyl fragment was assumed to be unchanged from the unsolvated form. Each ammonia molecule was assumed to be equally separated from the lithium atom with H—N—H bond angles of 107.3° and N—H bond distances of 1.008 Å. The results of the calculations predicts that the N—Li—N bond angle of 109° is more stable than the 123° of fluorenyllithium diquinuclidine due to the size of the groups containing the nitrogen atoms. Using the sp^3 tetrahedral bond angle for the N—Li—N component the N—Li distance was varied to determine the minimum energy. The N—Li bond distance is predicted to be 2.20 Å which is slightly longer than the average value of 2.03 Å for the fluorenyllithium diquinuclidine [12] but very comparable to that bond distance for other complexes.

Since it has been observed experimentally that the solvated form of lithium is more stable than the unsolvated form and the results of the calculations agree with this observation, it is of interest to determine what is predicted for the separation of the solvated lithium atom and the allyl fragment. The results of the calculations predict that this separation is increased by +0.10 Å when the lithium atom of the molecule is solvated by ammonia compared to the unsolvated compound. The changes in electron densities for this lowest energy geometry is given in Fig. 6. The expected effect of the solvent was to decrease the positive charge at the lithium atom. In the unsolvated form a positive charge of +0.12 is predicted while in the solvated form the charge is —0.23 due to the sharing of electron density of the nitrogen atoms. It is of additional interest to determine the changes in bonding between the allyl group in the two forms. Mulliken overlap population values would be expected to be indicative of these changes and the resulting values are given in Table 2. The results indicate that the

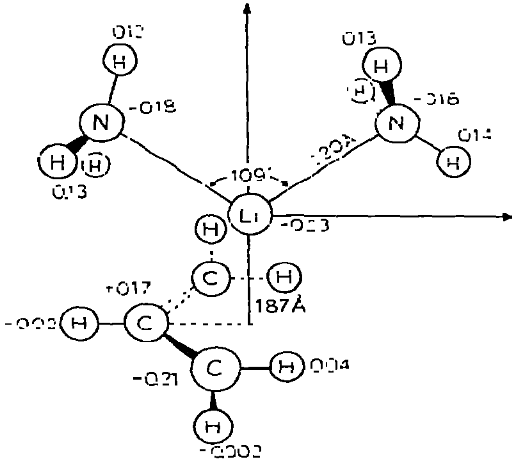


Fig. 6. The predicted geometry for allyllithium solvated with two molecules of ammonia The nitrogen—lithium and allyllithium fragment separations were varied to determine the energy minimum. The numerical values are the predicted electron densities from the calculations.

TABLE 2

OVERLAP POPULATION VALUES FOR SPECIFIC LITHIUM BONDS

Bonds	Unsolvated	Solvated	Differences
Li—C_1	0.37	0.34	0 03
Li—C_2	0 34	0 29	0.05
Li—N_1		0.28	
Li—N_2		0.25	

largest change is for the lithium and the central carbon of the allyl fragment. The difference for the two nitrogen atoms are due to the asymmetry with respect to the allyl fragment (see Fig. 6 for labels).

Conclusions

The results of CNDO/2 molecular orbital calculations predict that the lowest total energy geometry of allyllithium is a nonplanar "bridged" structure. Although the degree of hybridization on the lithium has not been computed, the resulting molecular orbitals reflect that the p_y orbital (in our coordinate system) on lithium is principally involved in the bonding with admixtures of the remaining valence orbitals between lithium and the carbon atoms in this molecule. A large calculated dipole moment and large localized charges on the atoms suggest that allyllithium is appreciably ionic and will interact strongly with donating solvents. The predicted geometry for the dimer, using the results for the monomer, is a "stacked" structure which is capable of being extended to higher degrees of aggregation.

The interactions of ammonia as the donor solvent with allyllithium have been considered. The solvated species is predicted to be more stable than the neat compound in agreement with experimental observations. The geometry of the solvated species is predicted to be slightly altered, compared to the unsolvated species the separation of the allyllithium fragment increased by +0.10 Å. The calculated electron density changes are as expected with the donor solvent decreasing the positive charge on the lithium atom. Mulliken overlap populations predict a decrease in the bonding between the lithium and allyl fragment with the greatest change for the central carbon of the allyl fragment.

It would be most informative to make X-ray crystallographic studies on allyllithium, or donor solvent complexes thereof, to determine its structure and possible bonding mechanisms. ^{13}C NMR chemical shift data would also aid in the establishment of allyllithium's ionic character.

Acknowledgements

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