Journal of Organometallic Chemistry, 110 (1976) 1–6

A THEORETICAL STUDY OF THE ALLYLLITHIUM ION-PAIR

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(Received October 28th, 1975)

Summary

Ab initio SCF computations have been performed on allyllithium using STO/3G atomic orbitals. Both the covalent and the ion-pair structures have been investigated and their energies minimized with respect to most of the geometrical parameters. The ion-pair structure is found to be more stable by 8 kcal/mol and a simple bonding scheme leads to the interpretation of its stability.

The allyllithium molecule coordinated to two water molecules has also been studied to determine the effect of the solvent on the allyllithium bond.

Introduction

It is well known that the nature of the carbon—lithium bond in organolithium compounds R—Li varies considerably with the nature of the organic moiety R and is strongly affected by interaction with solvent molecules. In alkyllithiums the C—Li bond is thought to have a prevalent covalent character. SCF computations on methyllithium support this conclusion [1,2]. The tendency of the lithium atom to form covalent bonds, where its vacant p orbitals are also involved, provides an explanation of the formation of molecular aggregates both in solution and in the vapour phase. Geometries and stabilities of the polymeric species have also been explained within the framework of the SCF-MO theory [2,3].

If the organic moiety contains a delocalized π electron system, the organolithium compound is supposed to exist either as an undissociated ion-pair or as a dissociated ionic salt [4].

We show that, in this case also, SCF computations on simple molecular models can provide useful information about structure and electron distribution of organolithium derivatives. In this study, non-empirical ab initio SCF calculations of various geometries of the allyllithium ion-pair are reported. While this work was in progress the results of a similar investigation appeared [5], in which

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the geometry of the allyllithium ion-pair coordinated to two solvent molecules of dimethyl ether was theoretically determined by the CNDO method. In our computations, the role played by the solvent in the formation of the ion-pair was simulated by considering the lithium atom coordinated to two water molecules.

Allyllithium

Evidence of the essentially delocalized nature of the allyllithium bond is afforded by UV, IR and NMR spectroscopy [6]. To explain the AX_4 shape of the proton NMR spectrum at room temperature, the following equilibrium was proposed:

(I)

(II)

In this the ion-pair concentration dominates; accordingly, we have considered the two limiting models I and II and determined their energies and geometries through an energy-minimizing process with respect to most of the geometrical parameters. The computations were carried out using the Gaussian-70 program [7].

We first optimized the geometry of the unsymmetrical covalent structure I and of the symmetrical ion-pair form II in the absence of any interaction with solvent molecules. The geometrical parameters for both cases are reported in Table 1.

The ion-pair structure was found by computation to be more stable by 8.4 kcal/mol *. Since the model does not include any interaction with the

TABLE I

COMPUTED GEOMETRIES FOR THE COVALENT AND THE ION-PAIR FORMS OF ALLYLLITHIUM

Bond distances (A)		Bond angles (°)		Dihedral angle (°)	
Structure I					
C(1)—C(2)	1.32	C(1)—C(2)—C(3)	127	C(1)—C(2)—C(3)—Li	90
C(2)—C(3)	1.51	H—C(1)—H	116		
C(1)—H, C(2)—H	1.08	C(1)—C(2)—H	119		
C(3)—H	1.09	Li—C(2)—C(3)	110		
C(3)—Li	2.02				
Structure II					
C(1)—C(2)	1.39	C(1)—C(2)—C(3)	127		
C(1)—H, C(2)—H, C(3)—H	1.08	H—C(1)—H	116		
		C(1)—C(2)—H	117		
C(2)—Li [a]	1.89				
C(3)—Li, C(1)—Li	2.12				

[a] Li is located 1.71 Å above C(1)C(2)C(3) plane.

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* The total molecular energies of the covalent and the ion-pair forms computed with STO/3G atomic orbitals are −122.3607 and −122.3741 a.u., respectively.

TABLE II

NET ATOMIC AND OVERLAP CHARGES IN THE COVALENT AND ION-PAIR FORMS OF ALLYLLITHIUM

Net atomic charges		Overlap charges	
Structure I			
C(1)	—0.182	C(1)—C(2)	1.200
C(2)	—0.035	C(2)—C(3)	0.779
C(3)	—0.172	C(3)—Li	0.579
Li	0.200		
Structure II			
C(1)	—0.197	C(1)—C(2)	1.012
C(2)	—0.063	C(3)—Li	0.189
C(3)	—0.197	C(2)—Li	0.028
Li	0.159		

solvent molecules, it appears that the delocalized nature of the allyllithium bond is due to the intrinsic bonding properties of the lithium atom. It is therefore interesting to discuss the nature of the electron interactions responsible for bonding in the two cases. Essential data concerning the charge distribution in the two structures, expressed in terms of net atomic charges and overlap populations, are reported in Table 2. In structure I the C—Li bond is essentially covalent involving an sp^3 hybrid of the terminal carbon atom and a σ hybrid of the lithium with a prevalent *s* character; the population of the lithium 2*s* orbital is 0.519 and of the 2*p* orbitals 0.293. With respect to methyllithium, for which results of similar computations are available [8], the polar character of the carbon—lithium bond is slightly increased. The most stable rotamer is represented in Fig. 1. Along the coordinate of the internal rotation of the CH_2Li group two

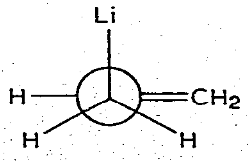


Fig. 1. Computed geometry of the CH_2Li group in the covalent form of allyllithium.

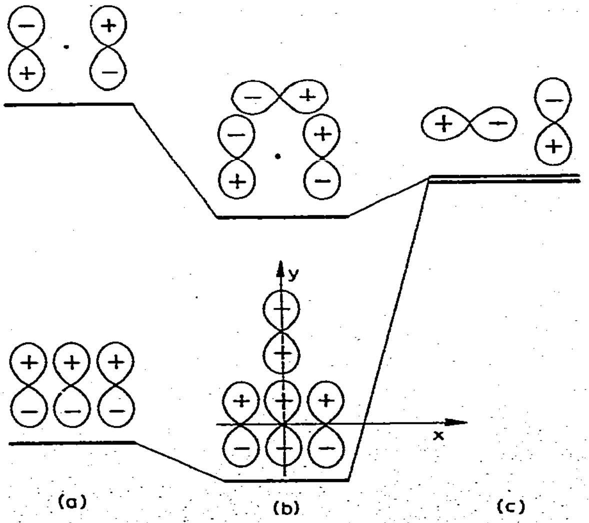


Fig. 2. Bonding interactions in allyllithium ion-pair. π-Molecular orbitals: (a) Allyl group, (b) allyllithium ion-pair, (c) lithium atom.

barriers of 5.2 and 7.3 kcal/mol were obtained when the C—Li bond is eclipsed to the C=C double bond and to the C—H bond, respectively. These values may be considered as indirect evidence of the absence of large interactions between the Li p orbitals and the π-electron system.

In the ion-pair form II the lithium valence orbital has prevalent p character; the orbital populations of 2s and 2p orbitals of the metal are now 0.183 and 0.674 electrons, respectively. The overlap charge between lithium and the central atom is indicative of the presence of only a small σ interaction between the allyl and lithium ions. Moreover, 99% of the overlap charges between the terminal carbon atoms and the metal comes from the $2p_x$(Li)—$2p_y$(C) charge densities. The stability of allyllithium may be explained, therefore, using the orbital scheme represented in Fig. 2.

The first occupied π molecular orbital of the allyl group is almost unaltered in the ion-pair and contributes to the σ-bonding. The Li $2p_x$ orbital and the highest occupied allylic molecular orbitals interact strongly since they have closed orbital energies and generate in the complex a three-centre bonding molecular orbital. Also, it may be inferred that in allyl halides, where the Li atom is substituted with an electronegative atom (halogen), the lowering of the 2p orbital energy in the substituent makes such interaction considerably lower. In such a case the relative stability of the symmetrical ion-pair structure II with respect to the unsymmetrical covalent form I is expected either to decrease or to be reversed [6,9].

Interaction with solvent molecules

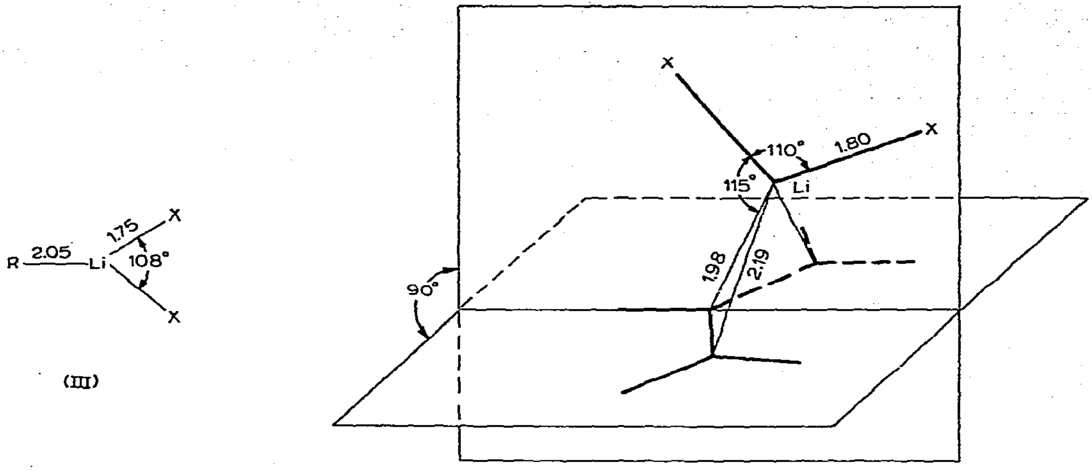
Next we examine the effect of coordination of H_2O with allyllithium both in the covalent form I and in the ion-pair structure II. The scheme of the computations has been to keep the internal coordinates of the allylic fragment fixed with respect to the previously determined values and to optimize the remaining internal coordinates of the composite system. In addition, a simplification was introduced to fix the internal coordinates of the solvent molecules to the experimental values of the isolated molecules, and to allow the C(2) axis of H_2O to coincide with the Li—O bond direction. In the second stage of the computation all allylic coordinates were subjected to optimization; no large deviations were observed from the values given in Table 1. The geometry of the solvated covalent and ion-pair forms are illustrated in Fig. 3.

In III the lithium has a distorted trigonal coordination, while in IV the bonds around the metal have an almost perfect tetrahedral arrangement. With respect to the CNDO results reported in ref. 5, the present computations on a simpler model seem to reproduce the essential features of the solvated ion-pair geometry. The main difference appears to be in the Li—O bond length, which in our computations is 0.5 Å lower, indicating that the solvent molecules are much more strongly coordinated to the lithium atom.

The solvation energy, as measured by the energy of reaction 1, is very

$$\mathrm{R{-}Li} + 2\,\mathrm{H_2O} \rightarrow \mathrm{RLi(H_2O)_2} \qquad (1)$$

similar for the two forms: 88.9 and 86.4 kcal/mol for III and IV respectively. Again, the ion-pair form is predicted to be more stable than the covalent structure, the



(III)

(R = allyl, X = H_2O)

(IV)

Fig. 3. Computed geometries of the allyllithium · 2 H_2O complex: (III) covalent structure; (IV) ion-pair.

energy difference being 6.2 kcal/mol*. It is interesting to compare the energy of reaction 1 with the dimerization energy of the organolithium derivatives.

$$R{-}Li + R{-}Li \rightarrow (R{-}Li)_2 \qquad (2)$$

Neither experimental nor theoretical values have been reported for allyllithium. For methyllithium the energy of reaction 2 has been theoretically determined to illuminate the stability of polymeric species of CH_3Li [2]. Using an orbital basis identical to that adopted in our computations and with full optimization of the geometries of both molecular species involved, the energy of reaction 2 was estimated to be 34.9 kcal/mol. The obvious comment is that the formation of polymeric species of organolithium derivatives may actually take place in hydrocarbon solvents; with donor solvents the interaction with solvent molecules is much greater.

Finally, assuming that the following equation represents the ionic dissociation reaction of the complex:

$$RLi(H_2O)_2 \rightarrow R^- + Li(H_2O)_2^+$$

both ion-pair and covalent structures are computed to be more stable than the free ions; the SCF computations predict for the ion-pair an ionic dissociation energy as large as 188.9 kcal/mol**.

The addition of solvent molecules does not alter the essential features of the allyl—lithium bond as described in the previous section. A considerable charge transfer (1/3 of the electronic charge) is observed from the inorganic

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* The total molecular energy of the solvated covalent and ion-pair models is −272.4337 and −272.4436 a.u., respectively.

** The geometry optimisation of the allyl anion and the $Li(H_2O)_2^+$ ion have been carried out with STO/3G orbitals. The computed values of the geometrical paramaters are: allyl anion C(1)—C(2) 1.38 Å, C—H (all assumed to be equal) 1.08 Å, C—C—C 130.4°, H—C—H 116.4° and the molecular energy is −114.8377 a.u.; $Li(H_2O)_2^+$ O—Li 1.71 Å, O—Li—O 120° (assumed value) and the molecular energy is −157.3049 a.u..

TABLE III

NET ATOMIC AND OVERLAP CHARGES IN THE SOLVATED COVALENT AND ION-PAIR MODEL OF ALLYLLITHIUM

Net atomic charge		Overlap charges	
Structure III			
C(1)	—0.202	C(1)—C(2)	1.197
C(2)	—0.034	C(2)—C(3)	0.787
C(3)	—0.189	C(3)—Li	0.557
$[Li(H_2O)_2]$	0.343		
Structure IV			
C(1)	—0.223	C(1)—C(2)	1.018
C(2)	—0.043	C(3)—Li	0.171
C(3)	—0.223	C(2)—Li	0.018
$[Li(H_2O)_2]$	0.323		

moiety of the molecule to the π orbitals of terminal carbon atoms in the allylic fragment, whose charge distribution resembles more that of the free anion (see Table 3). A large increase is also observed in the ionic character of the allyl—lithium bond. The essential π nature of the allyllithium ion-pair is confirmed in the solvated model and even increased, as σ orbitals of lithium are now mostly involved in bonding interactions with solvent molecules. In this respect our results differ from the CNDO results of ref. 5, where the allyl—lithium bond has a larger σ component. This may explain the large discrepancies in lithium—oxygen bond lengths. We have also shown that such discrepancies are not the result of the different models adopted in the two computations by repeating SCF computations on the solvated ion-pair model IV by the CNDO method and with full optimisation of the molecular geometry. The computed geometry was found in this case to be essentially similar to that reported in ref. 5*.

In conclusion, our results based on an ab initio SCF treatment predict the geometry and the stabilty of the allyllithium ion-pair, in harmony with the available experimental information, and in addition lead to a simple interpretation of the delocalized nature of the allyl—lithium bond. It is hoped that simple models, such as those adopted in the present study, will prove useful in investigations of the structure and electronic properties of organolithium derivatives in solution.

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[*] The geometrical parameters of Fig. 3 (IV) computed with the CNDO method are C(1)—Li 2.20, C(2)—Li 2.15, Li—X 2.52 Å; the total CNDO energy is —65.3433 a.u..