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Preliminary communication

AB INITIO SCF COMPUTATIONS ON PENTADIENYLLITHIUM

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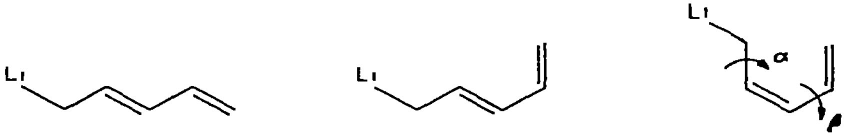
Summary

SCF energies have been obtained for various geometries of pentadienyllithium using STO/3G atomic orbitals. In agreement with experiment, the "W"-form of the pentadienyl anion is shown to be the most stable. For the covalent molecule, the strong chelating ability of the lithium atom favours a non planar structure.

The geometry of pentadienyllithium has been investigated in relation to the problem of base-catalyzed olefin isomerization [1]. The pentadienyl anion is the intermediate in such reactions and the stabilities of its various stereoisomeric forms are thought to determine the stereochemistry of the isomerization. Consideration of the symmetry of the π molecular orbitals led Hoffmann [2] to conclude that the U-form (c) of the pentadienyl anion is more stable than the sickle (b) and W-forms (a) (Fig.1).



(a) (b) (c)

Fig. 1. Conformations of the pentadienyl ion.

In contrast PMR [3] and CMR [4] spectroscopic investigations on pentadienyllithium derivatives showed conclusively that the W-form of these molecules is favoured in THF. For these reasons, we felt it worthwhile to reinvestigate the problem theoretically.

We report below the results of SCF computations on this molecule performed with STO/3G atomic orbitals [5]. Since the nature and polarity of C—Li bonds may be strongly affected by interaction with solvent molecules, we have considered two limiting models of pentadienyllithium; (i) the ionic model with lithium ion infinitely separated from the molecule; (ii) the "covalent model" with the C—Li bond length determined variationally. A limited number of dihedral angles have been also determined by variational treatment. All bond distances and angles were assumed fixed at their standard values [6].

The ionic model

The W-form is computed to be more stable than the sickle and U-forms by 5 and 160 kcal/mol respectively. Thus the SCF energies agree with the results of the experimental analysis in refs. 3 and 4, in contrast to the results of the previous semi-empirical treatment [2].

Among the internal coordinates of the U ion, the gradual helical folding of the molecular skeleton around each carbon—carbon bond was determined variationally, since this coordinate may reduce the steric effects, and this could in principle, have a moderate effect on the delocalization of the π electrons. The variational treatment leads to a torsional angle as high as 20° with an energy of the U ion 30 kcal/mol higher than the W ion. The latter result indicates that the arguments presented in ref. 2 based on Π orbital energies cannot be applied to the acyclic pentadienyl anion in the U-form because of the large steric interaction between the two terminal methylene groups.

The covalent model

For the planar forms in Fig.1 the relative stability of the W isomer with respect to the sickle and U-forms is 5 and 80 kcal/mol, respectively. The energy of the U isomer is especially sensitive to rotation around the C_1—C_2 (α angle) and C_3—C_4 (β angle) bonds. In particular, the lowering of the molecular energy with decrease in α may be interpreted in terms of the chelating properties of the Li atom. When the C—Li bond is in the plane of carbon atoms, the highest occupied molecular orbitals in the molecule may be approximately written in terms of localized molecular orbitals:

$\Pi_1 = \pi_1 - \pi_2 + \pi_{CH_2}$ $\Sigma = \sigma_{C-Li}$

where π_1 and π_2 are the bonding orbitals for the two π bonds of the molecule, σ_{C-Li} is the σ-bonding orbital for the C—Li bond and π_{CH_2} is a combination of the π orbital on C_1 and 1s orbitals of the methylene hydrogen atoms [2].

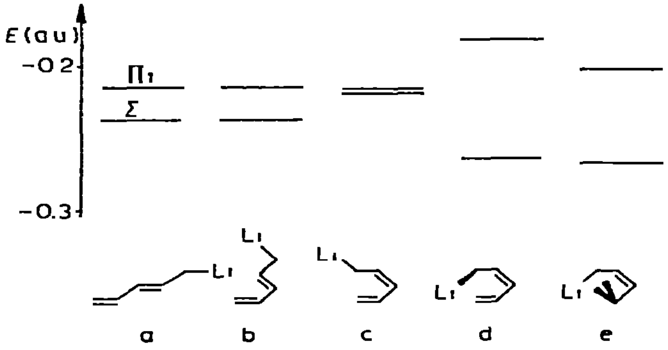


Fig. 2. Conformational energies.

In Fig.2 the corresponding orbital energies are represented for different values of the internal coordinates of the molecules. Deviation from planarity leads to interaction between the Σ and Π orbitals, which is important since the Li *p*-orbitals may accept small amount of π charge. Consequently, the separation of the two MO's of highest energy is an indication of the chelating properties of the metal atom.

The splitting is therefore higher in the U-form when the Li is in the region between the two terminal atoms (Fig.2d) and for β = 90° (Fig.2e) where the Li approaches one double bond of the molecule. In this form the reduction of the steric effects and the strong chelating properties of the metal compensate for the rupture of the π conjugation of the diene. The resulting molecular energy for the geometrical model in Fig.3 is 12 kcal/mol lower than that of the W isomer and is the lowest of the computed energies.

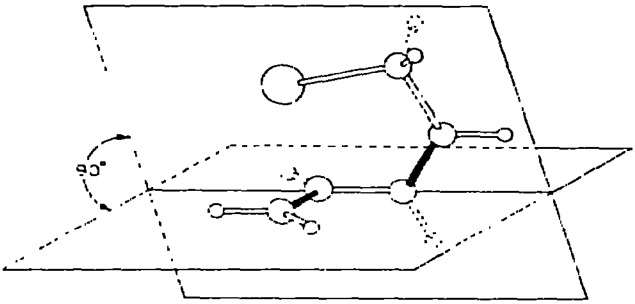


Fig.3 Geometry of conformation 2e

From our SCF computations we conclude (a) the pentadienyl anion is more stable in the W-form and (b) in the covalent form of the lithium salt the large bonding interaction between the Li atom and the π electron system and the steric effect between the two terminal methylene groups favour a non-planar structure. In terms of the stereochemistry, the latter form could be very similar to the U-form, and could be invoked to explain the sigmatropic hydrogen shifts observed in certain alkylpentadienyllithium derivatives [7] and the hydrolysis of these derivatives to *cis*-1,3-pentadienes [8].

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