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Preliminary communication

ELECTRONIC STRUCTURE AND GEOMETRY OF BIS(DIMETHYL ETHER)-ALLYLLITHIUM*

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Summary

The geometry-optimized structure of bis(dimethyl ether)allyllithium has been calculated by the INDO method. The metal—carbanion interaction involves both σ and π bonding. Approximately 0.82 electrons are transferred from the allyl anion to the solvated lithium moiety upon formation of the lithium—carbanion bond.

There is virtually no information regarding the geometry and detailed electronic structure of solvated allyllithium, although there have been many and various studies of allyllithium and its derivatives [1]. We have now calculated the geometry-optimized structure of bis(dimethyl ether)allyllithium employing the INDO approximation [2]. The structure is shown in Fig. 1. Bond angles and bond distances are given in Table 1 and charge densities listed in Table 2. The total energy was minimized with respect to each bond distance and bond angle

TABLE 1

SELECTED BOND DISTANCES AND ANGLES

Atoms	Distance (Å)	Atoms	Angles (°)
C(1)—C(2)	1.40	C(1)—C(2)—C(3)	128
C(2)—C(3)	1.40	O(10)—Li(9)—O(19)	110
Li(9)—C(1) [a]	2.29	O(10)—Li(9)—C(2)	134
Li(9)—C(2)	2.11	C(11)—O(10)—C(15)	117
Li(9)—C(3)	2.29	C(11)—O(10)—Li(9)	114
Li(9)—O(10)	2.34	H(4)—C(3)—H(5)	120
Li(9)—O(19)	2.34	Li(9)—C(2)—C(3)	78.5
C(11)—O(10)	1.40		

[a] Li is located 1.88 Å above the C(1)—C(2)—C(3) plane.

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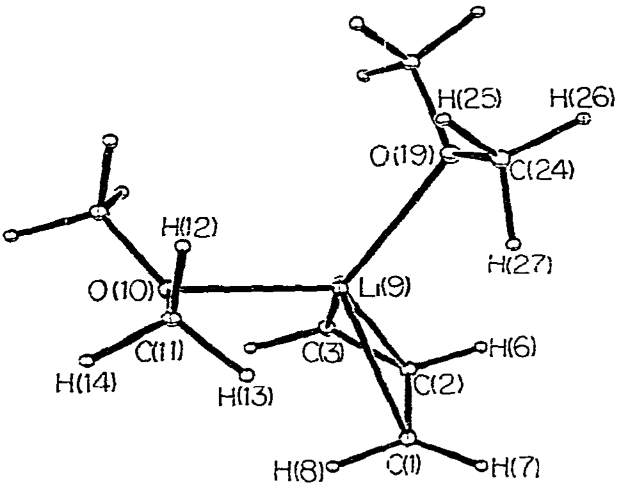

Fig. 1. The calculated geometry of bis(dimethyl ether)allyllithium.

TABLE 2

INDO TOTAL CHARGE DENSITIES

Atom	Charge density	Atom	Charge density
C(1) [a]	−0.184	H(12)	−0.037
C(2)	+0.197	H(13)	−0.035
H(6)	−0.039	H(14)	−0.004
H(7)	−0.012	O(19)	−0.196
H(8)	+0.022	C(24)	+0.266
Li(9)	−0.179	H(25)	−0.036
O(10)	−0.195	H(26)	−0.004
C(11)	+0.266	H(27)	−0.035

[a] The positions indicated correspond to those shown in Fig. 1; C(1) = C(3) by symmetry.

with two exceptions; Pople's "standard bond lengths" were assumed for the C—H bonds [3], and the carbon atoms of the dimethyl ether moiety were chosen to be tetrahedral.

The nature of the allyl anion—bis(dimethyl ether)lithium bond may be inferred by an analysis of the INDO wave functions. Both lithium and allyl orbitals contribute significantly to the INDO highest occupied molecular orbital (HOMO). These orbitals are, specifically, the p_x and p_y orbitals of lithium and the allyl p_z orbitals of carbons 1 and 3. The coefficients are zero for the p_z orbital of allyl carbon 2 and the s and p_z orbitals of lithium.

$$\psi_1(\text{HOMO}) = 0.646\, p_z^{C(1)} + 0.000\, p_z^{C(2)} - 0.646\, p_z^{C(3)} - 0.336\, p_x^{Li} - 0.164\, p_y^{Li} + 0.000\, p_z^{Li} + 0.000\, s^{Li}$$

This analysis suggests a substantial π-type three-center bond between the metal and the carbanion.

σ-type bonding is inferred from examination of the INDO MO which contains substantial contributions from the carbon s orbitals and the lithium s and p_z orbitals.

$$\psi_2 = 0.249\, p_z^{\mathrm{Li}} - 0.226\, s^{\mathrm{Li}} - 0.414\, s^{\mathrm{C(1)}} - 0.572\, s^{\mathrm{C(2)}} - 0.414\, s^{\mathrm{C(3)}}$$

Additional σ bonding results from an MO with symmetry properties appropriate for σ overlap between the lithium s and p_z orbitals and the allyl p_z orbitals, and containing sizeable coefficients for these orbitals.

$$\psi_3 = 0.079\, p_z^{\mathrm{Li}} + 0.096\, p_y^{\mathrm{Li}} - 0.045\, p_x^{\mathrm{Li}} - 0.160\, s^{\mathrm{Li}} - 0.494\, p_z^{\mathrm{C(1)}} - 0.651\, p_z^{\mathrm{C(2)}} - 0.494\, p_z^{\mathrm{C(3)}}$$

A simplified picture of the lithium—allyl anion bonding suggested by these INDO results is shown in Fig. 2. Both σ and π bonding are important.

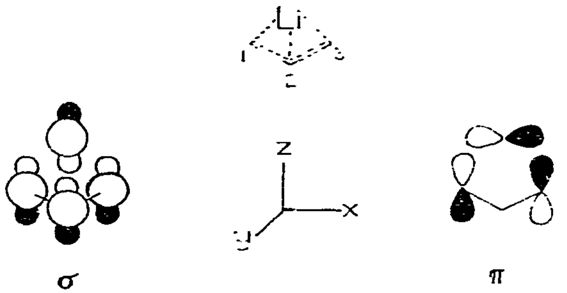

Fig. 2. A simplified picture of σ and π bonding between lithium and allyl anion.

Approximately 0.82 electrons are transferred from the allyl anion to the solvated lithium upon formation of the allyllithium complex: 0.43 electrons from the allyl π system and 0.39 electrons from the allyl σ bonds. This charge transfer results in negative charge densities on lithium and ether oxygens (Table 2).

The bonding scheme described here for allyllithium is very similar to the one proposed by Stucky and co-workers for benzyllithium and fluorenyllithium [4]. The present results corroborate the suggestion that both σ and π bonding are important in delocalized carbanion—lithium complexes [4, 5].

For purposes of comparison we have completed an INDO study of $[\mathrm{N(CH_3)_4}]^+[\mathrm{C_3H_5}]^-$ and find that this salt is essentially complete ionic. This is in marked contrast to the results obtained for bis(dimethyl ether)allyllithium.

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