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THE EFFECT OF METHYL SUBSTITUTION ON THE ELECTRONIC STRUCTURE OF BIS(DIMETHYL ETHER) PENTADIENYLLITHIUM

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Summary

The partially geometry-optimized structure of bis(dimethyl ether) pentadienyllithium has been calculated by the CNDO/2 method. The metal—anion interaction involves both σ and π bonding. The effect of methyl substitution on the electronic structure of the solvated species has been evaluated. In general, the electronic effect of a methyl group is substantially less for the solvated structure than for the isolated anion.

Introduction

We recently reported [1] a CNDO/2 MO evaluation of the effect of methyl substituents on the electron distribution in isolated charge delocalized acyclic anions possessing an odd number of carbon atoms in the chain. In general, the methyl group was found to be electron withdrawing, relative to hydrogen, when substituted on a delocalized anion and electron releasing when attached to a delocalized cation. The substituent effects were quite pronounced; for example, a 1-methyl group was calculated to withdraw, relative to hydrogen, a total of about 0.075 *e* from the pentadienyl anion. Libit and Hoffmann have recently analyzed the charge transfer and polarization effects of a methyl group interacting with a π-system [2].

The substantial withdrawing effect of the methyl group previously reported [1] was calculated for the isolated anion. It is entirely plausible, however, that the presence of a counter ion would reduce the electron density in the pentadienyl anion and thereby reduce or even reverse the electron accepting effects of a methyl substituent. While it is possible to test these hypotheses by carrying out detailed calculations which include the solvated counter ion, as we have done here, it is far more difficult to provide experimental verification of the results. However, recent reports of the CMR spectra of pentadienyl- and methylpentadienyl-lithium make it possible to compare the calculated charge densities on carbon with those inferred from the CMR chemical shifts [3—5]. Since the CMR spectra are determined in solution, carbon charge densities calculated for the solvated complex should correlate better with the densities inferred from the CMR shifts than would the corresponding densities calculated for the isolated anion.

The results of CNDO/2 calculations on bis(dimethyl ether) pentadienyllithium and the corresponding 1-methyl derivative and the comparisons of calculated and CMR inferred carbon charge densities are given below.

Method of calculation

The geometry and electronic structure of bis(dimethyl ether) pentadienyl ether were calculated by the CNDO/2 MO method [6]. This method was chosen because: *i* it provides for a direct comparison of the present results for the solvated species with those obtained earlier for the isolated anions [1]; *ii* the CNDO/2 and INDO methods have been applied with some success to other organolithium reagents [7-10] and *iii* preliminary ab initio calculations on pentadienyllithium have convinced us that the expense of such calculations on the solvated species is prohibitive.

The structure shown in Fig. 1 was arrived at in the following manner. The most reasonable sites of interaction of the lithium cation with the pentadienyl anion were first determined by systematically varying the unsolvated lithium

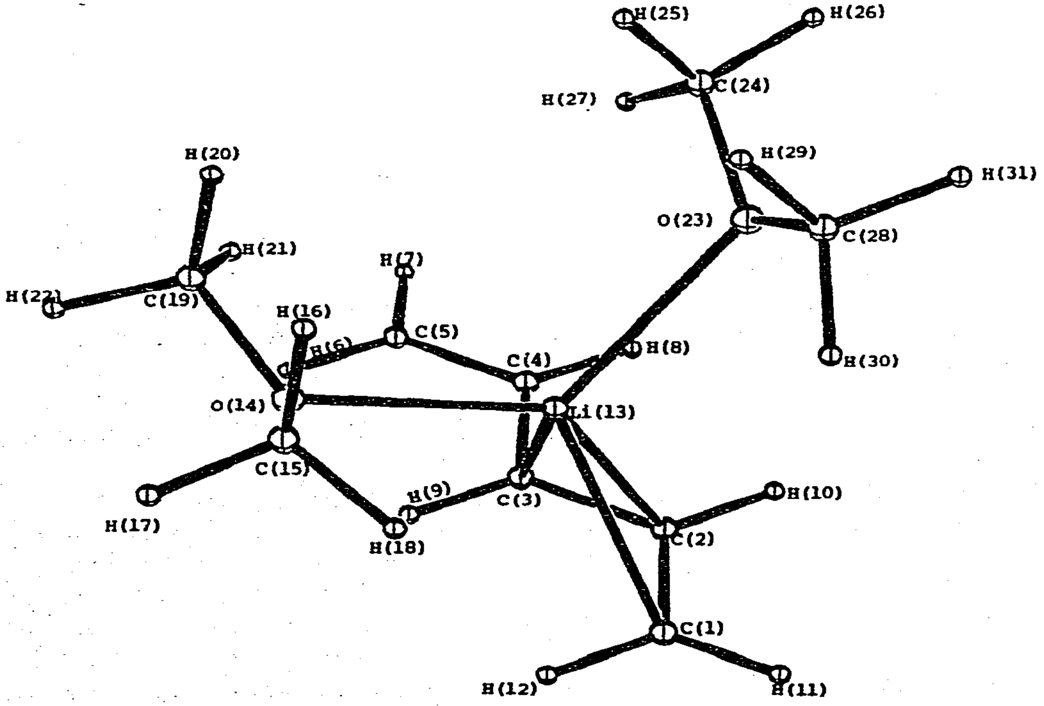


Fig. 1. The calculated geometry of bis(dimethyl ether) pentadienyllithium.

cation position with respect to the anion and comparing the total energies of the various configurations. This initial survey included bridged (π-interaction), covalent (lithium bonded to a tetrahedral carbon atom), and essentially ionic (a large carbon—lithium bond distance) species. Standard geometries were employed; the lithium—carbon bond distance was, however, partially optimized to 2.06 Å, which is in reasonable agreement with X-ray results [11]. These initial calculations showed a bridged molecule, similar to that shown in Fig. 1, to be the most stable structure. Previous molecular orbital calculations [12,13] and NMR studies [4,5] have shown that of the three conformations, *E*,*E*(W), *E*,*Z*(S), and *Z*,*Z*(U), the *E*,*E* form is the most stable.

As a check of the results described above, we compared partially optimized σ and bridged structures with ether solvated lithium cations with the unsolvated species and found the same relative order of stability; i.e., the bridged structure more stable than the σ covalent structure. Upon optimizing the lithium—carbon bond of the solvated structure shown in Fig. 1, it was revealed that the bridged structure was more stable than an ionic species. The lithium—pentadienyl bond distance, the carbon—oxygen bond distance, and the orientation of the bis(dimethyl ether) lithium moiety with respect to the pentadienyl group were optimized in the complex. Carbon—carbon bond distances and C—C—C bond angles, taken from the structure reported for bis(pentadienyl)dinickel [14], were found to yield a structure more stable than one based on "standard" bond lengths and angles [15]. Methyl groups were assumed to be tetrahedral and standard bond distances were employed for all C—H bonds. In calculations involving the 1-methylpentadienyl system, the conformation of the methyl group chosen was the one in which a C(methyl)—H bond was situated in the pentadienyl nuclear plane; previous calculations have established that charge distributions and substituent effects are not greatly dependent on methyl conformation in these systems [1].

Results and discussion

The calculated structure of bis(dimethyl ether) pentadienyllithium is shown in Fig. 1 and Tables 1 and 2. A novel feature of this structure and one which distinguishes it from the previously proposed species is a bridged lithium interacting via π- and σ-bonds with an allylic fragment of the pentadienyl anion. There is, in fact, precedent for this type of structure. Stucky's elegant X-ray studies on aromatic charge delocalized organolithium reagents have provided experimental evidence for the existence of covalent $\pi + \sigma$ interactions between the lithium cation and delocalized carbon ions [15]. The π-interaction of the lithium cation with the pentadienyl anion may be pictured as a lithium $2P_x$ orbital interacting with the HOMO of the pentadienyl anion. Electrons are donated from the anion to an empty p-orbital on lithium; a result similar to the

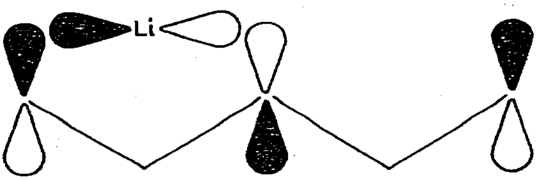


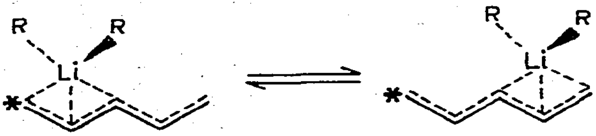
TABLE 1

SELECTED BOND DISTANCES AND ANGLES

Atoms	Distance (Å)	Atoms	Angles (°)
C(1)—C(2)	1.40	C(1)—C(2)—C(3)	121
C(2)—C(3)	1.44	C(2)—C(3)—C(4)	121
C(3)—C(4)	1.44	O(14)—Li(13)—O(23)	114
C(4)—C(5)	1.40	O(14)—Li(13)—C(2)	138
Li(13)—C(1)	2.29 [a]	C(15)—O(14)—Li(13)	114
Li(13)—C(2)	2.11	C(15)—O(14)—C(19)	117
Li(13)—C(3)	2.24	Li(13)—C(2)—C(3)	61.7
Li(13)—O(14)	2.32		
Li(13)—O(23)	2.32		
O(14)—C(15)	1.35		

[a] Li is located 1.88 Å above the pentadienyl anion plane.

one which we obtained for allyllithium [17]. CMR studies have shown that C_1 is equivalent to C_5 on the NMR time scale [3,4]. Rapid equilibration between the asymmetric structures must obtain



$[R = O(CH_3)_2]$

if the calculated structure is to be consistent with this data. A symmetrical structure, such as one in which lithium bridges carbon atoms 2 and 4, is a pos-

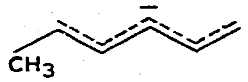
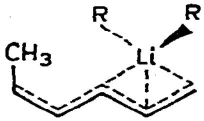
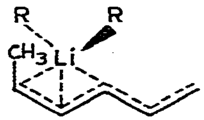
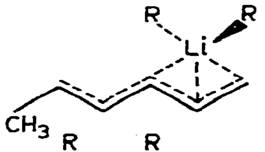
TABLE 2

CNDO/2 TOTAL CHARGE DENSITIES

Atom	Charge Density	Atom	Charge Density
C(1)	−0.187	H(17)	−0.006
C(2)	+0.142	H(18)	+0.023
C(3)	−0.172	C(19)	+0.165
C(4)	+0.083	H(20)	−0.011
C(5)	−0.187	H(21)	+0.017
H(6)	−0.007	H(22)	−0.007
H(7)	−0.016	O(23)	−0.157
H(8)	−0.021	C(24)	+0.165
H(9)	+0.034	H(25)	−0.010
H(10)	−0.001	H(26)	−0.007
H(11)	+0.003	H(27)	+0.017
H(12)	+0.039	C(28)	+0.164
Li(13)	−0.063	H(29)	−0.010
O(14)	−0.156	H(30)	+0.022
C(15)	+0.164	H(31)	−0.007
H(16)	−0.012		

TABLE 3

ELECTRONIC EFFECT OF THE METHYL GROUP

Compound [R = O(CH_3)$_2$]	Electrons withdrawn (donated) by methyl relative to hydrogen
	0.075
	0.076
	0.036
	(0.009)
	0.036
	0.039

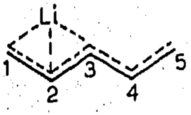
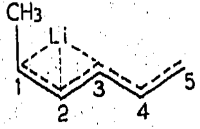
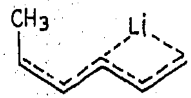
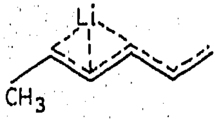
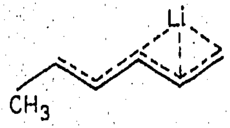
sible alternative which cannot be completely ruled out at the present time.

A comparison of the electron accepting or electron releasing effects of a methyl group in isolated anions with those of solvated complexes is shown in Table 3. As predicted, the methyl electron withdrawing effect is reduced in the complex as compared with the isolated anion and, in fact, in one structure *cis*-1-methylpentadienyllithium, lithium interacting with carbon atoms 1, 2, and 3, the methyl group is calculated to be slightly electron releasing (0.009 *e*) relative to hydrogen.

There is, in general, qualitative agreement between reported CMR shifts and total charge densities (Table 4). The order of and changes in chemical shifts upon methyl substitution are indeed reflected by the charge densities, although the calculations do not appear to account for the observed upfield shifts of the C_3 and C_5 resonances upon substitution of a methyl group at C_1. Qualitatively, the trends, in fact, do seem to be only slightly better than those determined by NMR shift comparisons with isolated anion calculations. However, the predicted downfield shift of the C_5 resonance calculated for the isolated 1-methylpenta-

TABLE 4

CNDO/2 TOTAL CHARGE DENSITIES AND CMR CHEMICAL SHIFTS

	Total charge densities[a]					CMR chemical shifts[b]				
	1	2	3	4	5	1	2	3	4	5
	−0.187	+0.112	−0.172			66.2	143.8	86.9		
	−0.187	+0.142	−0.172	+0.083	−0.187					
	−0.133	+0.118	−0.173	+0.083	−0.187					
	−0.138	+0.066	−0.168	+0.141	−0.183	85.7	137.3	81.4	143.6	56.7
	−0.144	+0.123	−0.177	+0.081	−0.187					
	−0.138	+0.067	−0.169	+0.140	−0.186	89.2	139.6	83.8	142.9	51.5

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[a] Calculated for solvated species. [b] See ref. 4.

dienyl anion is not supported either by the present calculations on the ether solvated lithium complex or, more importantly, by the observed CMR shifts.

In conclusion, these results suggest that lithium dietherate interacts with pentadienyl anion via σ- and π-bonds and that electron density is transferred from the pentadienyl anion to the solvated lithium moiety.

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