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ORGANIC ANIONS

IV *. A THEORETICAL STUDY OF PENTADIENYLLITHIUM

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Summary

CNDO II calculations suggest that, for all three conformations of the pentadienyl anion and of pentadienyllithium, the central carbon atom should be more reactive than either of the two terminal carbon atoms. They also reveal that, for the sickle- and W-shaped conformations there is more than one potential bonding site for the lithium. Bonding is discussed both in terms of FMO theory and in terms of possible Möbius aromatic character.

Introduction

SCF-MO calculations suggest that in either "charge" controlled reactions [1—3] or in "orbital" controlled reactions [3] the central carbon atom (C(3)) of the pentadienyl anion ** should be more reactive than either of the terminal carbon atoms (C(1) and C(5)). Practical experience, however, shows that attack at C(3) only predominates in the reactions with ethylene oxide [5], some carbonyl compounds ***, and some alkyl halides [7]. In reactions with other carbonyl compounds [6] and alkyl halides [7,8], the reaction with water [8], autoxydation [9], and polymerisation [10], attack at the terminal carbon atom is preferred. It is possible that, in this second group of reactions, steric [6,7] and product stability [1] factors play a part. However, a possible alternative is that

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* For part III see ref. 1.

** In CNDO II calculations this is only true after geometry optimisation. If it is assumed that C(1)—C(2) equals C(2)—C(3) [4a] the charge distribution is reversed (see also comments in ref. 8). For example, using the optimised geometry for the W-shaped anion and assuming the sum C(1)—C(2)) + C(2)—C(3) to be constant, but varying the ratio gives the following results: (ratio C(1)—C(2)/C(2)—C(3); charge at C(1); charge at C(3)), (0.95, —0.24, —0.28), (0.96, —0.24, —0.28), (0.97, —0.25, —0.27), (0.98, —0.25, —0.26), (0.99, —0.26, —0.25), and (1.00, —0.26, —0.25).

*** As these reactions are reversible, and in spite of our efforts to check, it is difficult to be sure whether the reported product ratios are the kinetic or the thermodynamic ratios, or something between the two [6].

these reactions proceed via an ion pair rather than a free anion and that, in the ion pair, the relevant charge and orbital terms for C(1) and C(3) are reversed. Indeed, similar ion-pairing arguments [11] have been advanced a number of times in order to explain the dependence of organic anion ambident reactivity on solvent and counter ion. In order to test this suggestion we have performed a series of CNDO II calculations on pentadienyllithium. Calculations on other organolithium compounds had shown that the charges and orbital coefficients for the carbon atoms can be very dependent on geometry, but that relative values are not greatly affected by solvation of the lithium. For this reason, unlike previous workers, we have not attempted to simulate the effect of added solvent molecules [12,13] but have concentrated on a more complete geometry optimisation.

Method

The method of calculation can best be illustrated by consideration of the U-shaped conformer (Fig. 1). For the free anion the following assumptions were made: (1) That the anion is planar. (2) That it is symmetrical about the plane shown in Fig. 1. (3) That the C(1)—C(2) bond bisects the H—C(1)—H angle. (4) That the hydrogen attached to C(2) bisects the C(1)—C(2)—C(3) angle. (5) That all C—H bond lengths are equal. This leaves six independent variables; the bond lengths C(1)—C(2), C(2)—C(3), and C—H and the angles C(1)—C(2)—C(3), C(2)—C(3)—C(4), and H—C(1)—H. Calculations were performed on the Leeds 1906A computer [14] using standard Pople—Segal parameters [15]. Variables were normally treated in pairs. For example the energy of the anion was calculated for a range of C(1)—C(2) and C(2)—C(3) bond lengths and a simple program was then used to find the minimum in the resultant energy surface. After this minimisation had been completed for all six variables it was repeated (two or three additional "cycles" usually required) until bond lengths were consistent to the nearest 0.005 Å and angles to the nearest 1° *. Results for all three conformations of the anion are given in Table 1. After optimisation of the geometry of the free anion the calculations were repeated for the ion pair; scanning all possible positions of the Li^+ **. For each energy minimum the bond lengths, angles and lithium position were optimised to the same degree of consistency as above. For the U-shaped conformation only one energy minimum was found. In this the lithium was centrally placed ca. 1.42 Å above the plane of the anion (Fig. 2) (indeed, in all cases, it was found that the preferred lithium position was 1.4—1.6 Å above the plane of the anion). For the sickle conformation (Fig. 3) two local minima were found; one with the lithium in position A, bridging C(1) and C(3), and one with the lithium in position B, bridging C(3) and C(5). Similarly for the W-shaped conformation (Fig. 4) two local minima were discovered; one with the

(continued on p. 168)

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* It was found that the energy of the anion was much more sensitive to bond lengths than to angular distortions, particularly angular distortion within the plane.

** It was still assumed that the organic moiety is planar. This is in contrast to the work described in ref. 19 and 16, but in agreement with calculations on allyllithium [17a,12] and with most X-ray results for related systems [17b]. It was also assumed for the work on methylpentadienyl anions described in ref. 13.

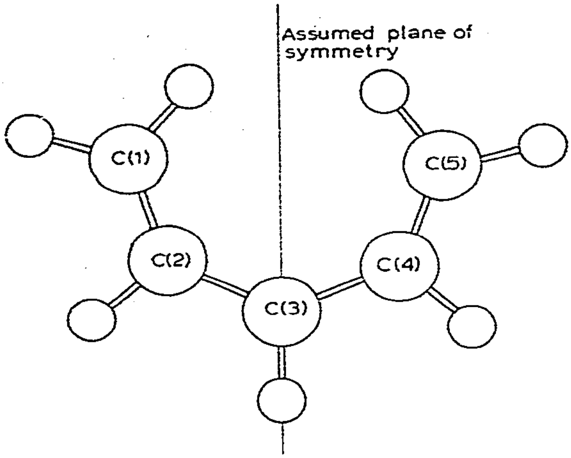


Fig. 1. U-Shaped conformation of the pentadienyl anion (I). Optimised bond lengths and angles.

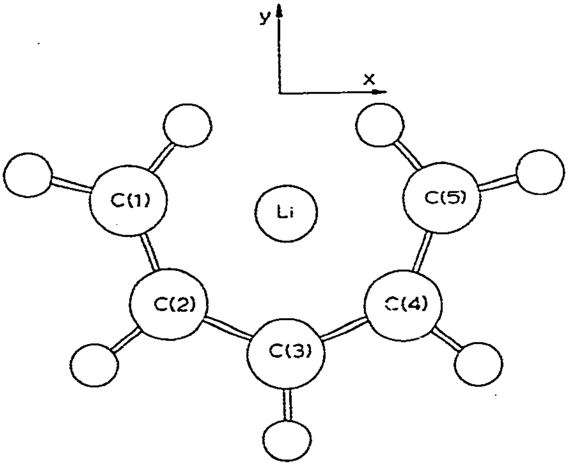


Fig. 2. U-Shaped conformation of pentadienyllithium (II) and coordinate system (Origin at C(3)). The lithium is 1.42 Å above the plane of the other atoms.

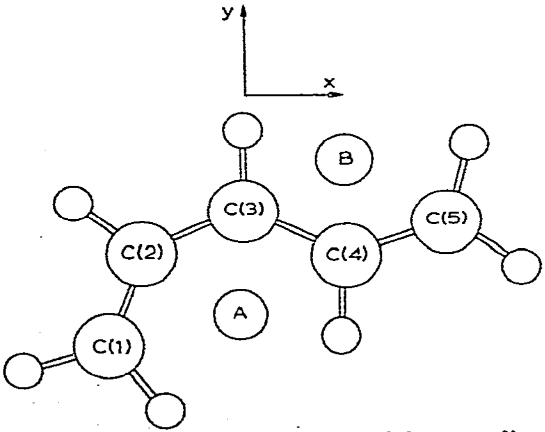
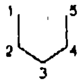
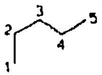
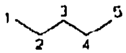
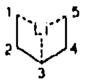
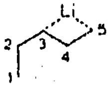
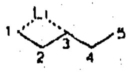
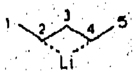


Fig. 3. Sickle-shaped conformation of the pentadienyl system (III) showing the two potential bonding sites. A (1.58 Å above the plane) and B (1.60 Å above the plane), for the lithium and also the coordinate system (Origin at C(3)).

TABLE 1

CNDO II CALCULATIONS ON PENTADIENYL ANION AND PENTADIENYLLITHIUM

	Free anion			Ion pair				
	U-shaped	sickle-shaped ^{c}	W-shaped	U-shaped	sickle-shaped ^{c} Li$^+$ position "A"	sickle-shaped ^{c} Li$^+$ position "B"	W-shaped ^{c} Li$^+$ position "A"	W-shaped Li$^+$ position "B"
								
Optimum bond lengths								
C(1)—C(2) (Å)	1.345	1.345	1.345	1.380	1.360	1.360	1.360	1.350
C(2)—C(3) (Å)	1.400	1.400	1.405	1.440	1.440	1.430	1.435	1.405
C—H (Å)	1.120	1.120	1.120	1.130	1.130	1.120	1.130	1.120
Optimum angles								
C(1)—C(2)—C(3) (°)	135	134	134	134	131	131	130	133
C(2)—C(3)—C(4) (°)	130	128	127	130	129	125	125	127
H—C(1)—H (°)	111	111	111	111	111	111	112	111

Lithium ion coordinates [a]								
x (Å)	—	—	—	0.00	−0.05	1.27	−1.26	0.00
y (Å)	—	—	—	1.73	−1.48	+0.70	+0.80	−1.35
z (Å)	—	—	—	1.42	1.58	1.60	1.53	1.60
Energy (a.u.) [b]	−40.5734	−40.5734	−40.5731	−41.3623 [b]	−41.2850 [b]	−41.2278 [b]	−41.2273 [b]	−41.2063 [b]
Charges								
C(1)	−0.24	−0.24	−0.24	−0.15	−0.16	−0.15	−0.16	−0.15
C(2)	+0.12	+0.12	+0.11	+0.17	+0.16	+0.09	+0.16	+0.14
C(3)	−0.27	−0.27	−0.28	−0.16	−0.19	−0.17	−0.17	−0.23
C(4)	+0.12	+0.12	+0.11	+0.17	+0.13	+0.15	+0.09	+0.14
C(5)	−0.24	−0.24	−0.24	−0.15	−0.13	−0.16	−0.14	−0.15
Coefficients (HOMO)								
C(1)	−0.53	−0.54	−0.53	−0.52	−0.57	−0.53	−0.49	−0.51
C(2)	−0.01	−0.01	−0.01	−0.01	+0.03	−0.17	+0.06	−0.07
C(3)	+0.66	+0.66	+0.66	+0.62	+0.63	+0.61	+0.62	+0.66
C(4)	−0.01	−0.01	−0.01	−0.01	−0.12	+0.06	−0.17	−0.07
C(5)	−0.53	−0.53	−0.53	−0.52	−0.52	−0.48	−0.53	−0.51

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[a] Optimised to the nearest 0.01 Å. Coordinate systems defined in II, III and IV. Origin at C3. [b] As no attempt has been made to simulate the effect of solvation of the relative energies of the ion pairs have no relevance to their relative stabilities in solution. [c] No attempt was made to take into account the lack of symmetry of bond lengths and angles about C(3).

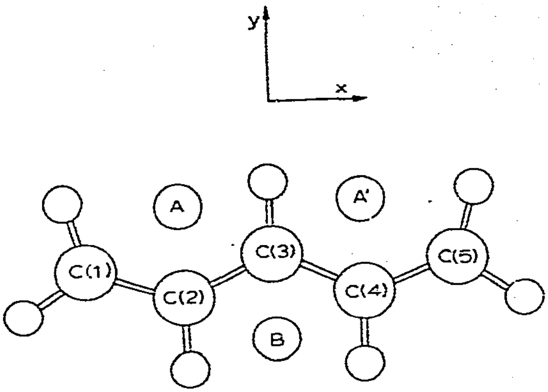

Fig. 4. W-Shaped conformation of the pentadienyl system (IV) showing the potential bonding sites, A, A' (1.53 Å above the plane), and B (1.60 Å above the plane), for the lithium and also the coordinate system (Origin at C(3)).

lithium bridging C(1) and C(3) (position A [13], which is clearly equivalent to position A') and one with the lithium bridging C(2) and C(4) (position B).

Discussion

(1) Anions. For the free anion it is interesting to note that calculations using unoptimised, "standard" geometries predicted very large energy differences between the three conformers but that after optimisation these energy differences almost disappear. This is consistent with the spectroscopic observation [18] that, at least in some methyl substituted systems there are only a few kcal difference between the W- and sickle-shaped forms and also the observation of *cis* olefins in the reaction products of pentadienyl anions. The main difference between "standard" and our optimised geometries is the increase in the angles C(1)—C(2)—C(3) and C(2)—C(3)—C(4). This "opening out" of the anions presumably reduces both steric and coulombic repulsions [19]. In the case of the U-shaped conformer it is the opposite of what would be expected if the 1,5-homoaromatic interaction proposed by Hoffmann and Olofson [20] were, indeed, important. These authors based their arguments on the assumption that the total energy of each conformation would be determined principally by the energy of the π-electrons. In fact our calculations show that (after geometry optimisation) the energies of the three occupied π-orbitals are almost independent of conformation. It is energies of the σ-orbitals which are strongly conformation dependent.

(2) Organolithiums. Table 1 shows that, although the magnitudes of the charges and orbital coefficients are reduced on ion pairing, they are still greatest at the central carbon atom. Hence, in terms of the original objective of this work, it would seem that ion pairing is not the answer to the variable ambident reactivity of the pentadienyl anion *. Perhaps the most interesting finding,

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* Even with the degree of geometry optimisation we have employed this conclusion cannot be regarded as wholly secure, but total geometry optimisation would be prohibitively expensive in computer time.

however, was the discovery of the existence of more than one potential bonding site for the lithium in (III) and (IV). The occurrence of this phenomenon in lithium radical anions has been recognised for some time both from theoretical [21,22] and from experimental evidence [23]. However, whilst there is good spectroscopic evidence for a multiplicity of structures in "normal" organolithiums [24] this particular explanation seems to have been largely ignored. The bonding of the lithium in positions A and B of III and A and A′ of IV is very similar (V) to that in allyllithium (VI) (Fig. 5). Previous authors [12], like Stucky in his discussion [25] of benzyllithium (VII) (Fig. 5) have tended to stress the importance of overlap between the HOMO of the organic ion and a vacant *p*-orbital of the lithium. It is, however, interesting to note that the *p*-orbital of the lithium completes a cycle and hence an alternative approach is to discuss the bonding terms of Hückel and Möbius aromaticity [26]. From this standpoint allyllithium (VIII) can be seen as the Möbius, aromatic, 4-electron equivalent of the antiaromatic (Hückel) cyclobutadiene (IX) (Fig. 6). Similarly benzyllithium can be seen as the 8-electron (Möbius) equivalent of the antiaromatic benzocyclobuta-

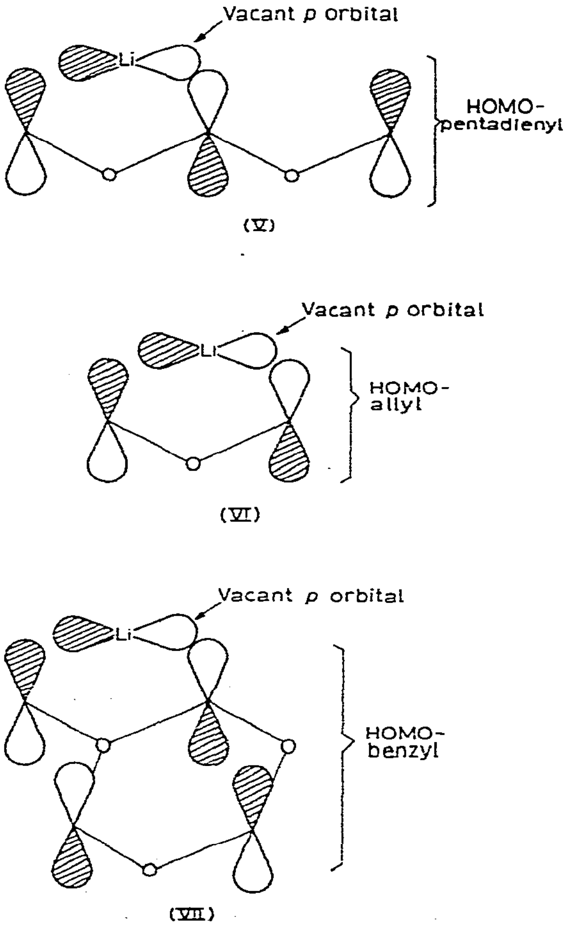

Fig. 5. Bonding systems in pentadienyllithium (V), allyllithium (VI) and benzyllithium (VII).

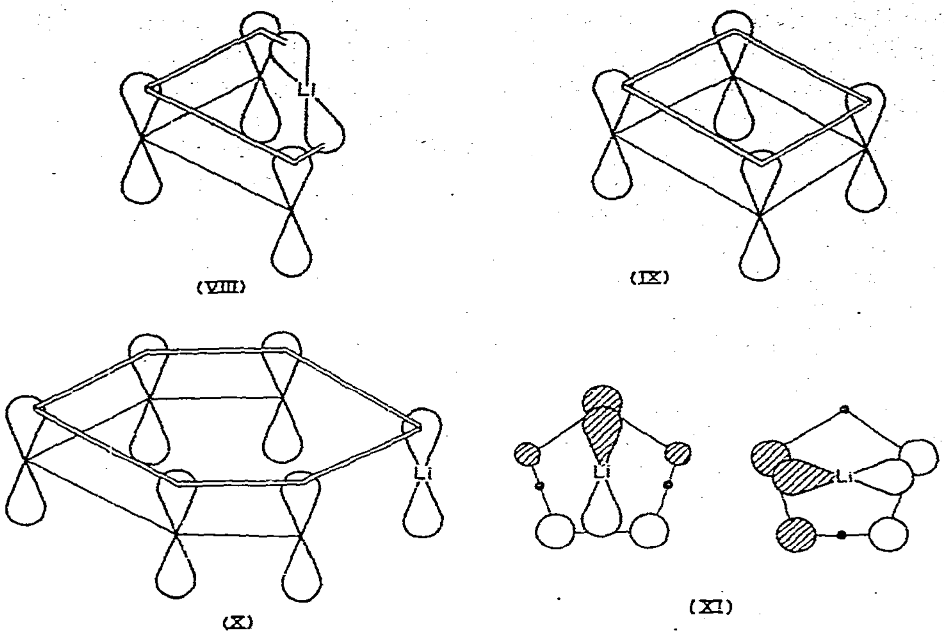

Fig. 6. Allyllithium basis set (VIII), cyclobutadiene basis set (IX), hypothetical "aromatic" pentadienyllithium basis set (X) and HOMO/LUMO interaction in cyclopentadienyllithium (XI).

diene, and pentadienyllithium (V) as the (Möbius) equivalent of vinylcyclobutadiene. A simple extension of this argument would suggest that addition of two more electrons to the cycle should convert it from the non-planar Möbius (VIII) to the planar Hückel form (X) (Fig. 6). This expectation is realised for the U-shaped conformer of Li/acac [27] * but not for the corresponding pentadienyllithium (II) [28]. This is possibly the result of the steric effect of the two terminal methylene groups which, even in the optimised geometry, make it difficult to "place" a counter ion between C(1) and C(5). The actual bonding pattern in (II) is strikingly similar to that which we have found for cyclopentadienyllithium, in which the lithium is centrally placed above the ring and the HOMO's are mainly combinations of ψ_2 and ψ_3 of the anion with the p_x and p_y orbitals of the Li^+ (XI).

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* Note, however, that in the solid state lithium adopts a bridging position between two ligands. For a discussion of aromaticity in organometallic systems compare ref. 28.

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