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ORGANIC ANIONS

VIII *. A SIMPLE ELECTROSTATIC MODEL FOR BENZYL- AND RELATED ALKYL-LITHIUMS

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Summary

Often the structures of 1 : 1 organolithium "contact ion pairs", in which the organic portion consists of a delocalised π system, have been interpreted in terms of FMO theory or in terms of Möbius/Hückel aromaticity. We have now shown that some of these structures including those of benzyl-, allyl-, indenyl- and trityl-lithium can be explained on the basis of a simple electrostatic model.

Results and discussion

In recent years a combination of spectroscopic methods, MO calculations and X-ray crystallographic studies [2] has done much to improve our understanding of the structure of Group I organometallic compounds. In those cases where simple 1 : 1 "contact ion pairs" are formed and where the organic portion consists of a delocalised π system (allyl, pentadienyl, etc.) Stucky [2] has proposed that the structure is determined by Frontier Molecular Orbital (FMO) factors. Hence both in the case of allyllithium (I) and in that of $Li^+/acac^-$ (II) the lithium adopts a position in which there is favourable overlap between the highest occupied π molecular orbital (HOMO) of the organic ligand and a vacant p orbital (lowest unoccupied molecular orbital, LUMO) of the lithium. In a previous paper in the series [3] we suggested an alternative explanation for these structures using the concept of Hückel/Möbius aromaticity. Hence in allyllithium the p orbitals complete an aromatic four electron Möbius array (III) and in $Li^+/acac^-$ an aromatic six electron Hückel array (IV). An interesting extension of this Hückel/Möbius aromaticity treatment has since been proposed by Schleyer [4] and Day has shown

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* For Part VII see ref. 1.

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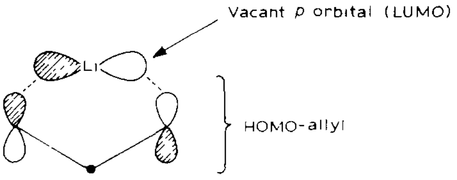
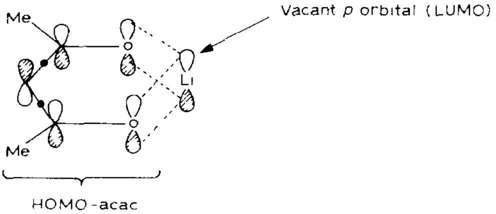


(I)



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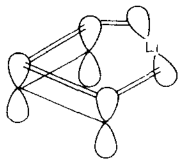

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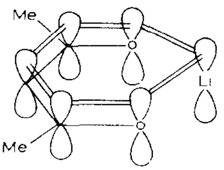

(IV)

that the FMO and Hückel/Möbius aromaticity treatments are in fact topologically equivalent [5]. Both the FMO and Hückel/Möbius treatments rest on the assumption that the bonding is predominantly or at least significantly covalent. However, bonding in these compounds also has ionic character and it is interesting to enquire whether, in some cases, the observed structure is the result of electrostatic factors. Indeed for a few organolithium compounds of the type considered in this paper (e.g. pyrazenyl [6] and allyl [7]) and in rather more cases of aggregated lithium salts [8] it has been shown that a reasonably good account of structure and bonding can be given by electrostatic models. Despite this, for three of the compounds considered in this paper (benzyl-, trityl- and fluorenyl-lithiums) Stucky has argued that electrostatic factors are unimportant [2]. In the case of benzyllithium, for example, he points out that the electrostatic potential for the interaction between a point positive charge and the benzyl anion taken in a plane 2.0 Å above the ring has a minimum above the C–CH_2 bond (ref. 2 Fig. 19) whereas an X-ray study of benzyllithium [7] shows the lithium bridging between the CH_2 position and an *ortho*-carbon (Fig. 1a). He then uses this apparent failure of the electrostatic method to support his FMO model for bonding. What we wish to point out is that this discrepancy does not imply a general failure of electrostatic models, nor does it necessarily point to predominantly covalent bonding, but rather it reflects a failure of the particular approximate electrostatic model Stucky used. In particular his model makes the unrealistic assumption that the metal ion is constrained to move in one plane. We have employed a simple alternative model; the HSE (Hard Sphere Electrostatic) model which gives results that are generally closer to those obtained experimentally. In the HSE treatment the following assumptions are made: (i) That the organic ligand is composed of hard sphere atoms; Pauling radius for carbon 0.77 and for hydrogen 0.28 Å. (ii) That the net charge on each atom can be approximated as a point charge located at its nucleus. (iii) That the solvated cation can be treated as a hard sphere with unit positive charge. In the case of lithium the radius of this sphere was chosen as 1.79 Å, to match the C–Li distance of 2.56 Å [9,10] found in most of these compounds. (iv) That, except for the hard sphere/hard sphere repulsive interaction, the only interaction between the organic ligand and the solvated lithium

TABLE 1

CHARGE DISTRIBUTION IN THE BENZYL ANION AS CALCULATED BY HMO, CNDO II, AND STO-3G AB INITIO MO METHODS AND RELATIVE ENERGIES[a]

Atom	HMO		CNDO II		STO-3G	
	Charge/ electrons	Relative electrostatic binding energy (kcal mol^{-1})	Charge/ electrons	Relative electrostatic binding energy (kcal mol^{-1})	Charge/ electrons	Relative electrostatic binding energy (kcal mol^{-1})
C(1)	−0.5714	−0.02	−0.3637	−0.91	−0.3246	−5.46
C(2)	0.0000	0.00	0.1268	−0.04	0.0189	−0.92
C(3)	−0.1428	−0.16	−0.1373	0.00	−0.1399	−0.06
C(4)	0.0000	−10.30	0.0413	−3.73	−0.0605	−2.12
C(5)	−0.1428	−11.30	−0.1329	−5.92	−0.1912	−2.72
C(6)	0.0000	−8.46	0.0304	−3.96	−0.0872	−0.28
C(7)	−0.1428	−0.83	−0.1704	−1.11	−0.2018	0.00
H(1)	0.0000		−0.0680		−0.0415	
H(2)	0.0000		−0.0672		−0.0457	
H(3)	0.0000		−0.0520		0.0002	
H(4)	0.0000		−0.0819		−0.0010	
H(5)	0.0000		−0.0514		0.0117	
H(6)	0.0000		−0.0539		0.0277	
H(7)	0.0000		−0.0191		0.0348	

[a] For the CNDO II and STO-3G calculations the geometry of the anion was based on that given in ref. 7. The numbering system is given in Fig. 1a. This Table also gives values for the electrostatic binding energy for the "best" position associated with each carbon atom. These "best" positions are displayed in Fig. 1b (HMO), Fig. 2a (CNDO II) and Fig. 2b (STO-3G). The electrostatic interaction was determined according to the formula

$$-(Z_c/D)\,\Sigma_i(Z_i/d_{ci})$$

where Z_i is the charge on the ith atom of the ligand and d_{ci} the distance from the nucleus of the ith atom to that of the cation. Since Z_c, the charge on the cation and D the dielectric constant of the medium are constant the "ranking order" of binding sites will be independent of both factors. The bonding energies given in the Table were calculated with a dielectric constant of 1.000 and are expressed in kcal mol^{-1} relative to the best site = 0.000.

The results given in this Table represent a self-consistent set in which the surface of each atom was scanned in steps of 0.5° arc. In a few cases we have carried out other calculations in which the position of the cation has been further refined. Whilst these more accurate calculations resulted in a very similar overall picture some of the bonding energies obtained were up to 0.5 kcal mol^{-1} lower. This suggests that maybe only energy differences between sites > 0.5 kcal mol^{-1} should be treated as significant.

is electrostatic. (v) That the minimum energy for the system will be obtained when atom and carbon are in contact. A simple computer program was then written to determine the position of this energy minimum. This program effectively "rolls" the cation over the "available" surface area for each atom in the organic ligand in turn (consistent with there being no interpenetration of spheres between the anion and the cation) and at each point on its surface works out the sum of the electrostatic interactions between the nucleus of the cation and the nuclei of the anion. The program then determines and stores the coordinates and electrostatic potential for the best position in contact with each atom and after scanning each atom in turn the coordinates and electrostatic potential for the best overall "binding site".

One system which we have investigated by this method is benzyllithium. The geometry of the benzyl group was taken from an X-ray crystallographic study of $C_6H_5CH_2Li$ $\{N(CH_2CH_2)_3N\}_2$ [10]. The charge associated with each atom in the isolated anion was calculated by HMO, CNDO II and ab initio STO-3G methods.

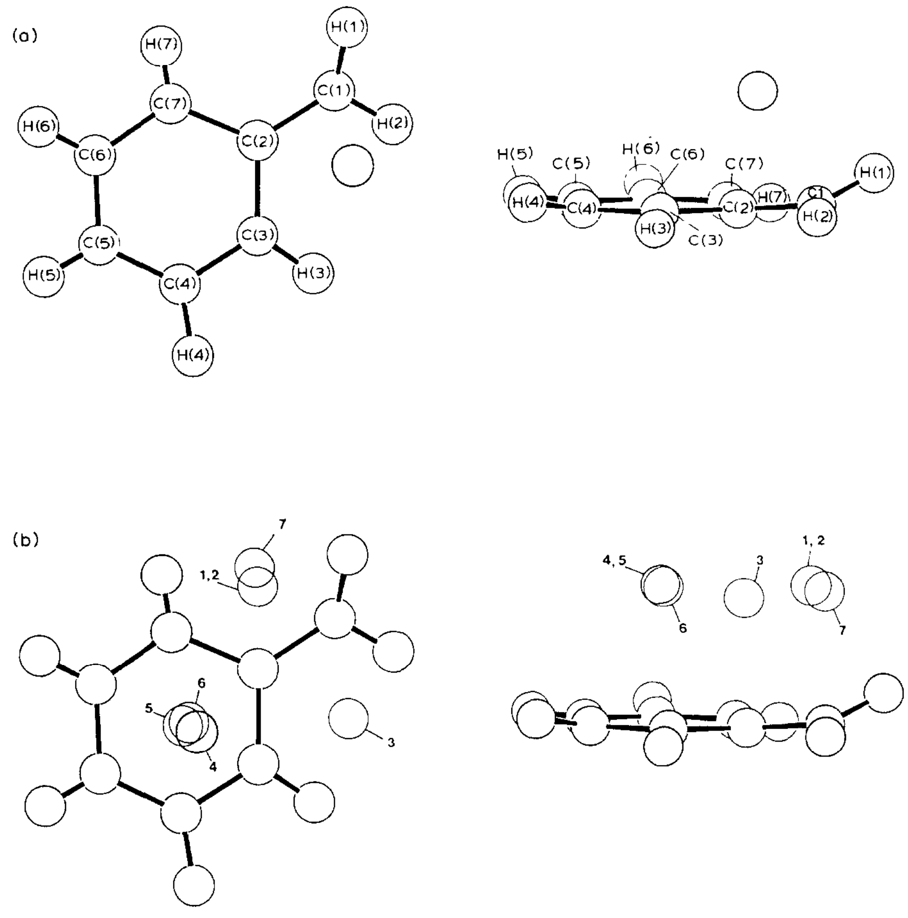

Fig. 1. Benzyllithium: (a) Geometry of benzyllithium taken from an X-ray crystallographic study of $C_6H_5CH_2Li$ $\{N(CH_2CH_2)_3N\}_2$ (ref. 7). View perpendicular to the benzene ring (left) and (right) view from the side. (b) Calculated "best" positions for counterion in contact with atoms C(1)–C(7) using HMO charges (see text and Table 1)

These calculated charges are summarised in Table 1. This Table also gives the relative energies for the "best" cation position associated with each carbon atom and these positions are displayed in Figs. 1b and 2. From these Figures it may be seen that the HSE method predicts two major types of bonding site, one over the benzene ring [1] and the other bridging between the *ortho*- and α-carbons (equivalent to the X-ray determined position). If HMO or CNDO derived charges are employed for the benzyl anion the *o*/α-bridging positions are favoured, in the case of STO-3G derived charges the position over the benzene ring. This is a consequence of the fact that STO-3G calculations place more charge on the ring and less on the α-carbon than other methods. (However, which MO method gives the best indication of charge distribution in these anions is open to debate).

Another system which was investigated by the HSE force field method was allyllithium [11]. Here the results agree with those of a range of MO methods which predict that in the 1 : 1 allyl anion/Li complex the lithium should occupy a position in which it bridges between C(1) and C(3) [7,12]. A similar HSE force field treatment of indenyllithium (using HMO charges) correctly predicts the favoured position of lithium as being above the five-membered ring [13] and for trityllithium (using HMO

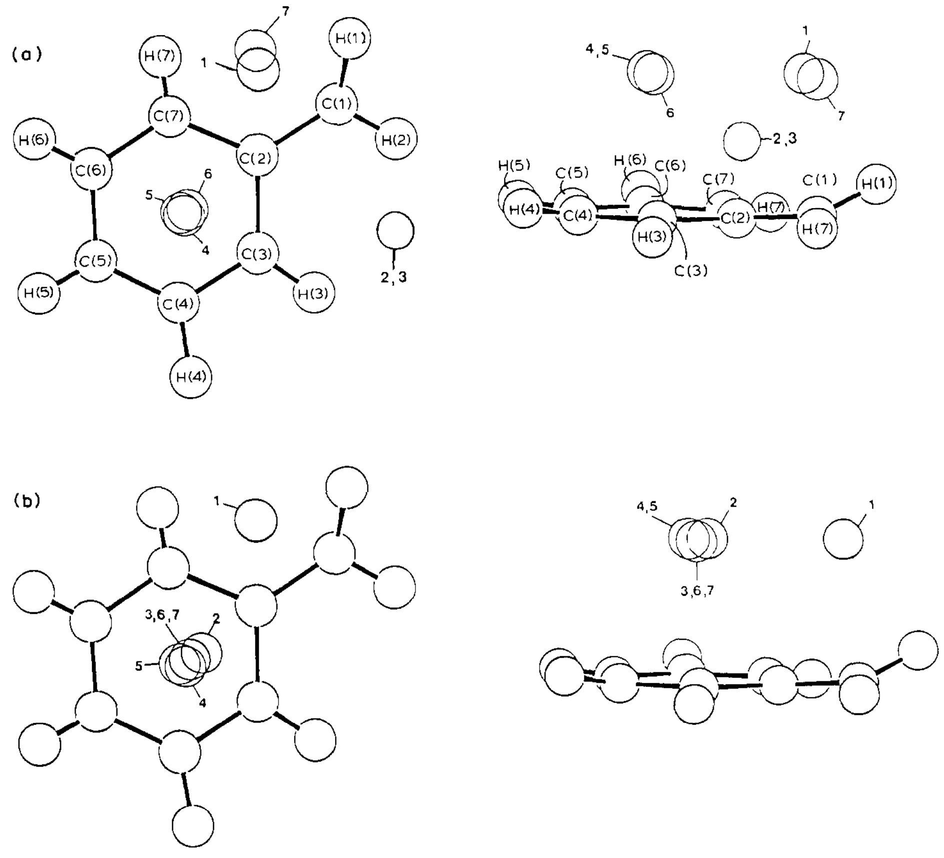

Fig. 2. Benzyllithium: (a) Calculated "best" position for the cation in contact with atoms C(1)–C(7) using CNDO II charges (see text and Table 1). (b) Similar but using STO-3G ab initio calculated charges.

charges) correctly as bridging between α- and *ortho*-carbons [14]. In the case of fluorenyllithium [9b] (HMO charges) the HSE force field method predicts that the X-ray observed position of the lithium (bridging between C(1) and C(9)) corresponds to a local minimum on the energy surface but the absolute minimum position predicted by this method is above the five-membered ring.

In conclusion, the results of these calculations are in line with those of other workers in suggesting that electrostatic factors are important in determining the structures of organolithium compounds. In the case of benzyl- and trityl-lithiums these results contrast with the claim made by Stucky [2] that electrostatic models are unable to predict the gross structural features.

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References

1 R.J. Bushby and A.S. Patterson, J. Chem. Res., (1980) (S) 306, (M) 3801.

2 G. Stucky, Advan. Chem. Ser., 130 (1974) 56.

3 R.J. Bushby and A.S. Patterson, J. Organomet. Chem., 132 (1977) 163.

4 A.J. Kos and P. von R. Schleyer, J. Amer. Chem Soc., 102 (1980) 2928.

5 A.C. Day, J. Amer. Chem. Soc., 97 (1975) 2431.

6 P. Cremaschi, A. Gamba and M. Simonetta, Theoret. Chim. Acta, 40 (1975) 303.

7 T. Clark, C. Rohde, and P. von R. Schleyer, Organometallics, 2 (1983) 1344.

8 A. Streitwieser, J. Organomet. Chem., 156 (1978) 1; A. Streitwieser and J.T. Swanson, J. Amer. Chem. Soc., 105 (1983) 2502; P. von R. Schleyer, A.J. Kos and E. Kaufmann, J. Amer. Chem. Soc., 105 (1983) 7617; P. von R. Schleyer, Pure Appl. Chem., 55 (1983) 355, T.P. Martin, J. Chem. Phys., 69 (1978) 2036.

9 (a) H. Dietrich, Acta Cryst., 16 (1963) 681; (b) J.J. Brooks, W. Rhine and G.D Stucky, J. Amer Chem. Soc., 94 (1972) 7339; (c) R. Zerger, W. Rhine and G.D. Stucky, J. Amer. Chem. Soc., 96 (1974) 6048; (d) H. Köster, D. Thoennes and W. Weiss, J. Organomet. Chem., 160 (1978) 1; (e) H. Dietrich, J. Organomet. Chem., 205 (1981) 291.

10 S.P. Patterman, I.L. Karle and G.D. Stucky, J Amer. Chem. Soc., 92 (1970) 1150.

11 H. Köster and E. Weiss, Chem. Ber., 115 (1982) 3422.

12 T. Clarke, E.D. Jemmis, P. von R. Schleyer, J.S. Binkley and J.A. Pople, J. Organomet. Chem., 150 (1978) 1; G. Decher and G. Boche, J. Organomet. Chem., 259 (1983) 31; E.R. Tidwell and B.R. Russell, J. Organomet. Chem., 80 (1974) 175; J.F. Sebastian, J.R. Grunwell and B. Hsu, J. Organomet. Chem., 78 (1974) Cl; A. Bongini, G. Cainelli, G Cardillo, P. Palmieri and A Umani-Ronchi, J. Organomet. Chem., 110 (1976) 1.

13 W.E. Rhine and G.D. Stucky, J. Amer. Chem. Soc., 97 (1975) 737.

14 J.J. Brooks and G.D. Stucky, J. Amer. Chem. Soc., 94 (1972) 7333