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A THEORETICAL STUDY OF THE BONDING IN METHYLLITHIUM, TRIMETHYLBORANE AND DIMETHYLZINC

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SUMMARY

The bonding in the methyl compounds of lithium, boron and zinc is studied by semi-empirical and *ab initio* molecular orbital calculations. The delocalized molecular orbitals are transformed to localized orbitals, revealing in greater detail the nature of the bonding, particularly the multicentre bonding in the tetrameric methyllithium.

INTRODUCTION

The methyl compounds of the Group I, II, and III elements display some interesting variations in electronic structure. Some of these compounds are electron deficient and form polymeric species, such as the trimethylaluminium dimer, the dimethylberyllium polymer and the methyllithium tetramer. By contrast, other methyl compounds, such as trimethylborane and dimethylzinc are monomers, showing no tendency towards association.

To investigate the bonding in such molecules we present the results of *ab initio* and semi-empirical molecular orbital calculations on the molecules $ZnMe_2$, BMe_3, LiMe and $(LiMe)_4$. To aid the understanding of the bonding in these molecules in chemical terms we also describe the results of transforming the calculated molecular orbitals to localized orbitals (LMO's). Such orbitals are generated by a unitary transformation of the canonical molecular orbitals (CMO's, which diagonalize the Fock operator). The most-used transforms have been those first suggested by Lennard-Jones and Pople[1] and implemented by Edmiston and Ruedenberg[2], which generate the energy LMO's, and secondly that suggested by Foster and Boys[3], yielding the exclusive LMO's. The energy LMO's minimize inter-orbital repulsion and exchange energy, whilst the exclusive LMO's maximize the sum of the squares of the distances between the orbital centroids. This latter method, which involves only the $3n^2$ dipole moment integrals (when n is the number of basis functions) is for computational reasons more applicable to large molecular systems than the generation of the energy LMO's which requires repeated transformations of the two electron integrals, the number of which varies as n^4. However, this method may be more

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TABLE 1

BASIS FUNCTIONS

s(m) shows the number of Gaussian type functions (m) contracted to form Slater type orbitals.

	Lithium	*Boron*	*Carbon*	*Hydrogen*	*Zinc*
LiMe, $(LiMe)_4$	1*s*, $\zeta = 2.6906$, s(3) 2*s*, $\zeta = 0.6396$, s(3) 2*p*, $\zeta = 0.6396$, s(3)		1*s*, $\zeta = 5.6727$, s(3) 2*s*, $\zeta = 1.6083$, s(3) 2*p*, $\zeta = 1.5679$, s(3)	1*s*, $\zeta = 1.2$, s(3)	
BMe_3		1*s*, $\zeta = 4.7$, s(6) 2*s*, $\zeta = 0.88143$, s(3) $\zeta = 1.40704$, s(3) 2*p*, $\zeta = 1.00366$, s(3) $\zeta = 2.20855$, s(3)	1*s*, $\zeta = 5.7$, s(6) 2*s*, $\zeta = 1.16782$, s(3) $\zeta = 1.82031$, s(3) 2*p*, $\zeta = 1.25572$, s(3) $\zeta = 2.72625$, s(3)	1*s*, $\zeta = 1.2$, s(3)	
$ZnMe_2$			1*s*, $\zeta = 5.7$, s(6) 2*s*, $\zeta = 1.16782$, s(3) $\zeta = 1.82031$, s(3) 2*p*, $\zeta = 1.25572$, s(3) $\zeta = 2.72625$, s(3)	1*s*, $\zeta = 0.9$, s(3) $\zeta = 1.4$, s(3)	1*s*, $\zeta = 29.3245$, s(3) 2*s*, $\zeta = 10.9140$, s(3) 2*p*, $\zeta = 13.0490$, s(3) 3*s*, $\zeta = 5.4064$, s(3) 3*p*, $\zeta = 5.1231$, s(3) 3*d*, $\zeta = 4.0$, s(3) $\zeta = 5.2$, s(3) 4*s*, $\zeta = 1.2$, s(3) $\zeta = 1.8$, s(3) 4*p*, $\zeta = 1.2$, s(3) $\zeta = 2.0$, s(3)

readily applied within a semi-empirical molecular orbital framework where the number of two-electron integrals is usually drastically reduced. England and Gordon[4] suggested that LMO's generated from INDO wavefunctions are in better agreement with *ab initio* results than are those from CNDO/2 wavefunctions[5]. For this reason, we generate energy LMO's for LiMe, $(LiMe)_4$ and BMe_3 from INDO wavefunctions and compare these with the exclusive LMO's generated from our calculated *ab initio* wavefunctions.

COMPUTATIONAL DETAILS

The assumed molecular geometries were taken from the literature[6] except for the methyllithium monomer, where Li–C and C–H bond lengths of 2.30 and 0.96 Å were taken. All electron *ab initio* self-consistent field molecular orbital (SCF–MO) calculations were performed in bases of Slater type orbitals (STO) each STO being expanded in Gaussian type functions (GTF). The size of the Slater basis was dictated by computer time limitations. For this reason, a double zeta basis of valence orbitals was used for $ZnMe_2$ and BMe_3, but only a minimal basis could be used for the methyllithium tetramer. The orbital exponents and size of Gaussian expansion are summarized in Table 1. The exclusive LMO's were generated from the set of all CMO's for BMe_3, LiMe and $(LiMe)_4$, and from the valence set of CMO's for $ZnMe_2$ using the criterion of Foster and Boys. The INDO calculations were performed using the parameters of Pople *et al.*[7], and the semi-empirical energy LMO's generated using the method of Edmiston and Ruedenberg[2].

ANALYSIS OF RESULTS

The CMO's are described in terms of their symmetry, orbital energy, and atomic components obtained by a Mulliken analysis. The quantities[8] characteristic of the localized orbitals allow estimates of the polarity, atomic components, transferibility and degree of localization of each LMO to be made. The distribution of the total orbital population over the component atoms and the separation of the bond centroid from these atoms provide information on the polarity of each LMO. The degree of transferibility of each exclusive LMO may be inferred from the orbital kinetic energy, and that of the energy LMO's from values of the orbital self-repulsion energy. The atomic hybridization is evaluated from the definition of Switkes *et al.*[9], and the deviation of a LMO from a pure bonding, or one-centre non-bonding orbital is provided by the localization degree, defined as the overlap between the LMO and this orbital renormalized after removal of contaminating components. Finally, a pictorial representation of the electron density distribution is provided by contour plots of the density associated with the LMO. The bonding in each of the three molecules studied here is now discussed.

The methyllithium monomer and tetramer

The calculated molecular energies [-185.4886 a.u. for $(CH_3Li)_4$ and -46.3268 a.u. for CH_3Li] predict the tetramer to be more stable than four isolated molecules of CH_3Li by 1.2 eV/CH_3Li unit, whereas the INDO calculation is found to overestimate the stability of the tetramer (16.1 eV/CH_3Li unit).

A Mulliken analysis of the CMO's (Table 2) of the tetramer reveals an excess

TABLE 2

LiMe AND $(LiMe)_4$ ORBITAL AND BOND OVERLAP POPULATIONS

Orbital populations		$(LiMe)_4$	*LiMe*
Carbon Orbital	1*s*	1.994	1.994
	2*s*	1.280	1.274
	2*p*	3.696	3.531
Atomic charge		−0.970	−0.800
Lithium orbital 1*s*		1.991	1.994
2*s*		0.130	0.471
2*p*		0.273	0.182
Atomic charge		+0.606	+0.353
Hydrogen orbital 1*s*		0.879	0.851
Atomic charge		+0.121	+0.149
Bond overlap populations			
Carbon orbital 2*s*	Lithium orbital 2*s*	0.017	0.073
2*s*	2*p*	0.030	0.041
2*p*	2*s*	0.031	0.193
2*p*	2*p*	0.086	0.153
Carbon orbital 2*s*	Carbon orbital 2*s*	0.000	
2*s*	2*p*	−0.001	
2*p*	2*p*	−0.004	
Lithium orbital 2*s*	Lithium orbital 2*s*	−0.015	
2*s*	2*p*	0.021	
2*p*	2*p*	0.024	

TABLE 3

VALENCE MOLECULAR ORBITALS OF $(LiMe)_4$ AND LiMe

Symmetry	*Energy (a.u.)*	*Atomic composition (%)*				
		Lithium orbital		*Carbon orbital*		*Hydrogen orbital*
		2*s*	2*p*	2*s*	2*p*	1*s*
$(LiMe)_4$						
$5t_2$	−0.2574	2.7	11.8	4.8	78.7	1.8
$4a_1$	−0.3441	12.2	17.6	2.2	65.5	2.0
$1t_1$	−0.5111		0.8		54.3	44.9
$4t_2$	−0.5213	1.0	0.7		53.7	44.5
1*e*	−0.5268		3.4		52.6	43.9
$3t_2$	−0.8949	0.4	−2.9	58.7	2.1	41.3
$3a_1$	−0.8998	−2.6	0.7	58.9	1.6	40.9
LiMe						
$4a_1$	−0.2503	23.5	9.3	3.2	62.9	1.0
1*e*	−0.4977		0.4		55.5	44.0
$3a_1$	−0.8749	−0.3	−1.0	59.5	2.5	38.8

negative charge on each carbon atom of nearly one electron, each lithium atom having a charge of +0.6, while analysis of the monomer reveals a less ionic system, the carbon having a charge of −0.8 and the lithium a charge of +0.4. The bond overlap populations show that there are a number of contributions to the carbon–lithium bonds. The dominant interactions in the monomer involve the lithium valence orbitals with the carbon 2*p* orbitals. Although the components of the lithium–carbon bond overlap population are decreased on formation of the tetramer, such a decrease appears to be compensated by the three-fold increase in the number of carbon–lithium bonds and the lithium–lithium bonding interactions (Table 2). There are no significant bond overlap populations involving two carbon atoms in this molecule.

The valence molecular orbitals of both monomer and tetramer (Table 3) fall into two groups. The highest filled orbitals, the $5t_2$ and $4a_1$ of the tetramer, and $4a_1$ of the monomer, involve the carbon 2*p* and lithium valence atomic orbitals, and contribute to the bonds other than the C–H bonds. The remaining valence orbitals, the $1t_1-3a_1$ of the tetramer and $1e$ and $3a_1$ of the monomer have mainly hydrogen 1*s* and carbon 2*s* and 2*p* components, and are involved in the C–H bonds in the molecules.

A more convenient description of the bonding is obtained by construction of the LMO's. Both the semi-empirical energy LMO's and the *ab initio* exclusive orbitals provide a very similar description of the bonding (Tables 4, 5). In both the monomer and tetramer each carbon atom is involved in three equivalent two-centre C–H bond orbitals. The bonding of each carbon to lithium is described by a single C–Li bond orbital in the monomer polarised towards the carbon, and by a four-centre $C-Li_3$ bond orbital with the three equidistant lithium atoms in the tetramer. Both the semi-empirical and *ab initio* calculations yield a strong polarization of the four-centre bonds towards the carbon atom. Figure 1 shows maps of the density of the four-centre CLi_3 exclusive orbital. The electron density in the Li_3 plane (Fig. 1a) illustrates

(*continued on p.* 66)

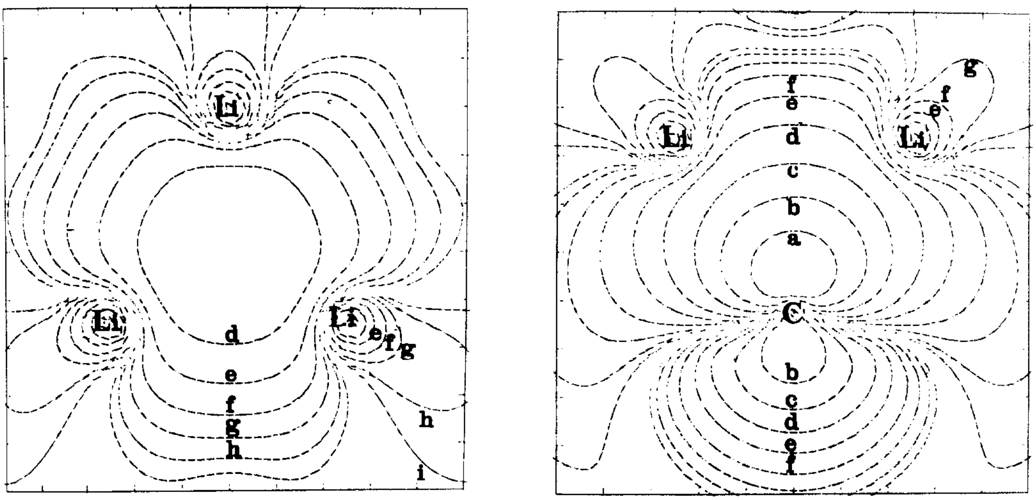

Fig. 1. Contour plot of the four-centre exclusive Li_3C bond orbital density in $(LiMe)_4$, (a) in the Li_3 plane and, (b) in the Li_2C plane. Contours are keyed to Table 8.

TABLE 4

ANALYSIS OF VALENCE LMO's

THE C–H BOND ORBITALS

Exclusive orbitals from the *ab initio* calculations and energy localized orbitals from the INDO calculations.

		Total No. of equivalent orbitals	*Separation*[a]		*Population analysis*			*Kinetic energy (a.u.)*	*Orbital self-repulsion energy (eV)*	*Hybridisation C, sp*^{x}	*Localization degree (%)*
			C	*H*	*Atomic components*		*C–H overlap*				
					C	*H*					
BMe$_3$	Exclusive	9	1.35	0.64	1.15	0.91	0.89	0.938		2.9	99.2
	Energy	9	1.30	0.69	0.99	1.01	0.84		15.318	3.3	98.5
LiMe	Exclusive	3	1.29	0.53	1.16	0.90	0.93	0.913		2.2	99.0
	Energy	3	1.23	0.58	0.97	1.06	0.92		15.630	3.5	99.0
(LiMe)$_4$	Exclusive	12	1.29	0.52	1.12	0.92	0.92	0.907		2.4	99.0
	Energy	12	1.22	0.60	0.98	1.03	0.88		15.038	4.7	97.8
ZnMe$_2$	Exclusive	6	1.37	0.72	1.24	0.82	0.86	0.986		2.0	98.9

[a] Separation of orbital centroid from component atoms (a.u.).

TABLE 5

ANALYSIS OF VALENCE LMO's

THE C–X BOND ORBITALS

Exclusive orbitals for BMe_3, LiMe, $(LiMe)_4$ and $ZnMe_2$, and energy orbitals for BMe_3, LiMe and $(LiMe)_4$.

		Atom X	*Total number of equivalent orbitals*	*Separation (a.u.)*		*Population analysis*			*Kinetic energy (a.u.)*	*Orbital self-repulsion energy (e.v.)*	*Hybridisation* $sp^a d^b$			*Localization degree (%)*
						Atomic components		*C–X over-lap*			*C*	*X*		
				C	*X*	*C*	*X*				*a*	*a*	*b*	
BMe_3	Exclusive		3	1.20	1.75	1.33	0.74	0.84	1.159		3.3	2.4		98.6
	Energy	B	3	1.30	1.65	1.24	0.84	0.96		12.902	2.4	1.9		99.6
LiMe	Exclusive	Li	1	1.37	2.98	1.33	0.71	0.55	0.762		6.2	0.3		99.2
	Energy		1	1.21	3.13	1.49	0.64	0.75		11.872	2.6	0.9		99.9
$(LiMe)_4$	Exclusive		4	1.02	3.66	1.60	0.17	0.20	0.923		5.3	2.0		97.4
	Energy	Li_3	4	1.37	3.46	1.31	0.29	0.30		9.499	2.3	2.5		98.5
$ZnMe_2$		Zn	2	1.17	2.50	1.73	0.36	0.43	1.697		1.3	2.0	1.9	97.1

the bent Li–Li components of the bond, whilst Fig. 1b, the plot in the Li_2C plane, shows the strong polarity towards the carbon atom of the C–Li bond components. Both calculations predict a similar hybridisation (near sp^2) of the lithium atom in the four-centre bond orbital. However, that of the carbon atom differs in the two calculations, being near sp^5 in the exclusive LMO's, but having more *s* character (sp^2) in the energy LMO's.

Trimethylborane

The calculated orbital populations (Table 6) yield very polar boron–carbon bonds, with a charge of near +1 on the boron atom. The boron–carbon bonds are found to be almost entirely σ in character involving mainly the carbon 2*p* and the boron 2*p* and 2*s* orbitals. As in $(LiMe)_4$, the CMO's (Table 7) can be divided into those predominantly involved in the three boron–carbon bonds (5*e*, $4a_1$) and those involved in the nine carbon–hydrogen bonds ($1a_2$, 4*e*, $5a_1$, 3*e*, 2*e*, $3a_1$).

TABLE 6

BMe_3 ORBITAL AND BOND OVERLAP POPULATIONS

Carbon orbital		*Boron orbital*		*Hydrogen orbital*	
Orbital Populations					
1*s*	1.988	1*s*	1.990	1*s*	0.889
2*s*	1.240	2*s*	0.633		
2*p*	3.473	2*p*(σ)	1.239		
		2*p*(π)	0.081		
Atomic charge	−0.701		+1.057		+0.111
Overlap Populations					
2*s*		2*s*		−0.021	
2*s*		2*p*		0.135	
2*p*		2*s*		0.247	
2*p*(σ)		2*p*(σ)		0.242	
2*p*(π)		2*p*(π)		0.029	

TABLE 7

VALENCE MOLECULAR ORBITALS OF BMe_3

Symmetry	*Energy (a.u.)*	*Atomic composition (%)*				
		Boron orbital		*Carbon orbital*		*Hydrogen orbital*
		2*s*	2*p*	2*s*	2*p*	1*s*
5*e*	−0.4613		21.1		63.5	14.4
$1a_2$	−0.5419				55.1	44.9
4*e*	−0.5646				56.5	43.5
$5a_1$	−0.6002		6.4		56.5	36.9
3*e*	−0.6047		4.0		56.1	39.9
$4a_1$	−0.6325	26.0		1.1	56.2	16.4
2*e*	−0.9561		3.6	59.2		37.1
$3a_1$	−1.0210	4.2		62.3	2.8	30.2

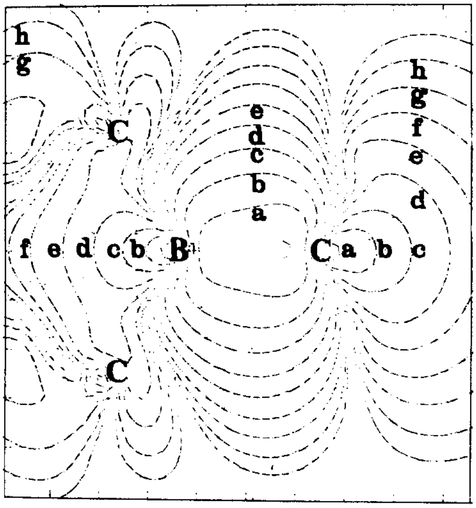

Fig. 2. Contour plot of the two-centre B–C exclusive bond orbital in the molecular plane in BMe_3. Contours are keyed to Table 8.

TABLE 8

CONTOUR KEY FOR THE LOCALISED ORBITAL DENSITY PLOTS
Figs. 1 and 2.

Letter	*Magnitude*[a]	*Letter*	*Magnitude*
a	0.1	f	0.0003
b	0.03	g	0.0001
c	0.01	h	0.00003
d	0.003	i	0.00001
e	0.001		

[a] Units are electrons/a.u.^{3}.

Localization of the INDO and *ab initio* CMO's yields essentially the same description of the bonding in this molecule. In both schemes each carbon–boron bond is described by a single bond orbital (Table 5) polarized towards the carbon atom. Such polarization is clearly shown by the plot of the electron density of this orbital (Fig. 2). In the localized orbital description, each C–H bond is represented by a single bond orbital, polarized towards the carbon atom. The exclusive LMO's predict each carbon atom to be involved in approximately sp^3 hybridization both in the localized C–H and B–C bonds, whilst the trigonal boron atom is approximately sp^2 hybridized (Table 5). The localized orbitals from the INDO calculation predict greater carbon *s* character in bonding to boron, and greater *p* character in bonding to the hydrogen atoms.

Dimethylzinc

We mention the results of the calculation on dimethylzinc only briefly, as the mode of bonding does not differ greatly from that in trimethylborane. We find six equivalent C–H bond orbitals (Table 4), with the carbon approximately sp^2 hybridized, polarized towards the carbon atom. Each carbon–zinc bond is described by a single bond orbital, involving the valence orbitals on both atoms. The bond overlap populations, calculated from the CMO's show that this bond has negligible π character, and that the zinc $3d$ orbitals are essentially non-bonding in character. This latter effect is reflected in the localized orbital calculation where a set of five non-bonding orbitals, localized on the zinc atom, and having a predominant $3d$ contribution, are found.

CONCLUSIONS

The *ab initio* SCF–MO calculations predict the methyllithium tetramer to be 1.2 eV/CH_3Li unit more stable than four isolated CH_3Li molecules, this stability being overestimated by the semi-empirical INDO calculations. With the aid of calculated overlap populations the increased stability of the tetramer is suggested to be associated with the lithium–lithium bonding in the Li_4 tetrahedron and the three-fold increase in the number of carbon–lithium bonds, which compensate for the decreased components of the lithium–carbon bond overlap on tetramer formation.

Carbon–boron π bonding in BMe_3 was first proposed by Mulliken[10] to account for its existence as a monomer in contrast to trimethylaluminium. Although this idea has found wide acceptance, both *ab initio* and semi-empirical calculations suggest that this π-type interaction contributes less than 10% of the bonding. The C–X bonds in all the monomeric species, LiMe, BMe_3 and $ZnMe_2$ are found to be highly polar and almost entirely σ in character.

Localization of the SCF–MO's described here yields a description of bonding in terms of bond pairs and non-bonding orbitals. Although the unitary transform used to generate the LMO's of the *ab initio* and semi-empirical wavefunctions are based on different criteria, we nevertheless find a similar description of bonding predicted in each molecule. In LiMe, $ZnMe_2$ and BMe_3 the C–X bonds are described by single bond orbitals polarized towards the carbon. In $(LiMe)_4$ each carbon is involved in a four-centre bond to the three equidistant lithium atoms. We find a high degree of transferibility of the two-centre C–H bond orbital throughout the methyl compounds, in agreement with results of previous localized orbital calculations[11].

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