

**MNDO AND *ab initio* CALCULATIONS OF METHYL  
2-LITHIOISOBUTYRATE AND ITS SOLVATES AND AGGREGATES**

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*Ab initio* and semiempirical (MNDO) molecular orbital calculations are reported of the energies, charge distributions, and geometries of methyl 2-lithioisobutyrate (LIMIB) used as a model of the propagation centre in the anionic polymerization of (meth)acrylates. Two stable forms energetically not very differing were found, one being near to the enolate, the other nearer to the keto form, both at the MNDO and 6-31G\*\* levels. Stabilization energies and geometries of the dimer, trimer, and tetramer aggregates of LIMIB and of its solvates with dimethyl ether molecules were calculated at the MNDO level. These results agree with our earlier experimental findings obtained with the tetrahydrofuran solutions of LIMIB.

Several problems concerning the nature of the propagation centre in the anionic polymerization of acrylates and methacrylates, especially in that initiated by organolithium compounds, remain open in spite of intensive studies done both on living polymers<sup>1</sup> and model compounds<sup>2-8</sup>. The most important questions are the following:

a) the multiplicity of forms of the propagation centre and its connection with the observed peculiarities of the polymerization kinetics and the distribution of molecular weights;

b) the ionicity of the bond between the centre and the lithium atom;

c) the structure of the centre itself, especially its possible keto-enolate and *E-Z* isomerism;

d) the ability of the centre to coordinate: (i) another centre in higher aggregates, (ii) solvent molecules, (iii) the monomer, (iv) other compounds, in particular alkoxides, formed by side reactions or added to the system, and the importance of such coordination in the polymerization mechanism.

The problems a) to d) are clearly connected which makes their experimental solution difficult. Thus the existence of two signals of  $\alpha$ -carbon in <sup>13</sup>C NMR spectrum of the living polymer was interpreted<sup>1</sup> as *E-Z* isomerism of the enolate form; a very similar but higher multiplicity of signals in the spectra of the model methyl 2-lithioisobutyrate (LIMIB)<sup>7,8</sup>, where no *E-Z* isomerism is possible, was proved to be caused by different aggregation states, namely dimer and tetramer<sup>7</sup> and even two kinds of trimer<sup>8</sup>. Further,

the frequencies of the carbonyl vibration in the infrared<sup>2</sup> and Raman<sup>8</sup> spectra as well as the chemical shift of both the carbonyl and  $\alpha$ -C signals<sup>7,8</sup> in <sup>13</sup>C NMR seem to indicate that the model LIMIB assumes an intermediary state between the keto and enolate form in all its aggregates which, however, appears to be shifted more to the keto form in the dimer<sup>8</sup>. At the same time, however, the early quantum-chemical calculations<sup>2</sup> persistently indicated the existence of two distinct, near-keto and enolate, forms of LIMIB. The reactivities of LIMIB and of the living polymers of (meth)acrylates seem to agree with the finding that the reaction of LIMIB and its analogues with chlorosilanes or phosphines gives exclusively enolate derivatives, whereas with acrylates the exclusive products correspond to the keto form although the addition of O-anions to the same compounds is quite easy<sup>9</sup>. Neither vibrational nor NMR spectra appear to be able to solve this puzzle, the resolution of the former being too low and the time scale of the latter being too large.

The problems listed above are sufficient motives for theoretical calculations, besides the need of a deeper insight into the bonding properties of the molecules in question. An additional motive is the non-existence or undetectability of the monomeric molecule of LIMIB in solution, which, however, has to be involved at some stage of the reactions with other compounds.

Some extensive quantum calculations of LIMIB are presented in this study. The calculations were made on different levels of theory, namely (i) in the semiempirical MNDO approximation which enables us to consider larger systems but has been suspected<sup>10,11</sup>, in its present form, to overestimate covalent C–Li bonding, and (ii) by *ab initio* SCF using various basis sets up to quite extended ones. In addition to this, we present optimized molecular parameters of oligomeric aggregates of LIMIB obtained by MNDO calculations.

## METHODS OF CALCULATION

All *ab initio* and MNDO calculations were performed using the GAMESS set of programs<sup>12,13</sup> running on a Silicon Graphics Indigo 4000 workstation. A full optimization of all degrees of freedom was carried out using the gradient optimization routine in the program. The calculations were performed in C<sub>1</sub> symmetry. In order to test the effect of the basis set selection on the equilibrium geometry, the *ab initio* optimizations at the Hartree–Fock (HF) level were performed with the 3-21G, 6-31G, 6-31+G\* and 6-31G\*\* basis sets. Optimized geometries obtained at the lower level were always re-optimized with the more extended basis set.

Molecular characteristics of the stable structures discussed below correspond to the local energy minima obtained by geometry optimization. As the energy surface of the multi-dimensional coordinate space has a very complicated shape, especially in the case of higher aggregates, we cannot be quite certain that no other local minima exist. We are sure, however, that no such minima exist in the near surroundings of the geome-

tries discussed here. The qualitative or semiquantitative agreement of our calculations with our experimental results<sup>8</sup> is the proof of their reasonability.

## RESULTS AND DISCUSSION

### Monomer LIMIB Molecule

The results of the *ab initio* calculations at the HF level with four kinds of progressively extended bases are shown in Table I. The extension of the orbital basis set expectedly leads to a lower energy, but shows a tendency to converge. In all the basis sets, we persistently find two distinct forms of the molecule with similar energies. Of them, form B with planar symmetry (Fig. 1) can be considered to be near to the chemist's idea of enolate, whereas form A can be considered to be somewhat nearer to the keto form.

At the HF/6-31G level the stationary structures discussed above were characterized by vibrational frequency calculations. For both A and B, all frequencies were found real proving that they correspond to true minima on the energy surface. Electron correlation effects were accounted for by the energy correction calculated by the second-order Moller–Plesset perturbation method<sup>14,15</sup>. The single-point computations were performed on the geometries obtained at the HF/6-31G level. Using these corrections the relative energy of B compared to A was changed from  $-17.3$  kJ/mol to  $-6.1$  kJ/mol. This result together with the preference of form A at the HF/6-31+G\* and HF/6-31G\*\* levels indicates that this is the most stable form in the bare LIMIB molecule. On the other hand, the small energy gap between B and A indicates that a dynamic equilibrium

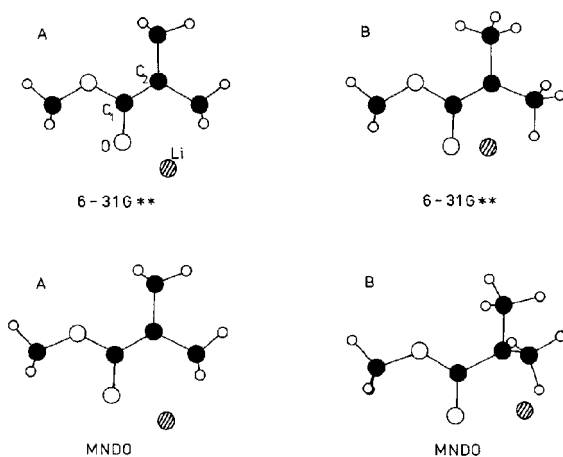


FIG. 1

Optimized geometries of methyl 2-lithioisobutyrate obtained at the 6-31G\*\* and MNDO level

TABLE I  
*Ab initio* molecular parameters of methyl 2-lithioisobutyrate

Parameter	Form	Level of theory			
		3-21G	6-31G	6-31+G*	6-31G**
Energy (hartree)	A	-349.822986	-351.615409	-351.776460	-351.782628
	B <sup>a</sup>	-9.3	-17.3	10.2	14.9
Bond length, pm					
C1-C2	A	136	136	138	138
	B	133	133	135	135
C1-O	A	131	132	127	127
	B	132	132	129	129
C2-Li	A	230	238	221	221
	B	373	375	292	291
O-Li	A	174	177	177	179
	B	159	163	170	171
Bond angle, °					
C1-O-Li	A	87.2	89.0	85.6	85.0
	B	167.8	165.4	119.1	118.4
Torsion angle, °					
C2-C1-O-Li	A	-40.7	-42.1	-38.9	-40.0
	B	0.0	0.0	0.0	0.0
O-C1-C2-Me <sup>1</sup>	A	173.8	173.9	175.2	175.5
	B	180.0	180.0	180.0	180.0
O-C1-C2-Me <sup>2</sup>	A	-29.6	-24.3	-29.9	-31.0
	B	0.0	0.0	0.0	0.0
Net atomic charge <sup>b</sup>					
O	A	-0.76	-0.87	-	-0.81
	B	-0.87	-1.01	-	-0.89
C1	A	0.83	0.76	-	0.88
	B	0.89	0.84	-	0.88
C2	A	-0.36	-0.22	-	-0.31
	B	-0.27	-0.15	-	-0.25
Li	A	0.59	0.67	-	0.52
	B	0.63	0.76	-	0.64

<sup>a</sup> Relative energy of B compared to A in kJ/mol. <sup>b</sup> Mullikan population; concept of atomic charges is not justified in the case of the basis set with diffuse functions 6-31+G\*.

of both forms – perhaps expressed as an apparently intermediate state between them – should be present at usual experimental temperatures.

The distribution of atomic charges shown in Table I indicates that the bond between lithium and the remaining part of the molecule is highly polarized but not fully ionic.

To check the accuracy and reliability of the MNDO method in describing our systems and to get an insight into the source of the differences using *ab initio* SCF, we have done MNDO calculations on the same bare LIMIB molecule. The results are given in Table II. The results show that MNDO prefers form A which, in this case, corresponds to the chemist's idea of the keto form. The analysis of the eigenvectors or the density matrix clearly shows that, in form A, the method predicts  $sp^3$  hybridization of the orbitals on C1 and thus a covalent, though polarized, bonding between C2 and Li. In form B, a  $\pi$  molecular orbital on C2 and C1, somewhat delocalized towards the carbonyl O atom, is predicted and a stronger bonding is found between O and Li. This comparison indicates that the MNDO method indeed tends to overestimate<sup>10,11</sup> the C–Li covalent bonding in the bare LIMIB molecule if the geometry roughly corresponds to  $sp^3$  hybridization of atomic orbitals on the C2 atom and the Li atom is not engaged in another bond. It is well known<sup>7,8</sup>, however, that organolithium compounds, LIMIB included, are apt to form various complexes in which the Li atom is involved in a coordination bond. As a monomer, this compound is imaginable in a tightly solvated form amounting to a defined complex with the solvent. Tetrahydrofuran molecule being rather big for extensive calculations, we chose dimethyl ether (DME) for this study. As it is shown in Table II, LIMIB accepts up to two DME molecules, with high stabilization energies according to MNDO (heat of formation of DME is  $-214.3$  kJ/mol). The complexes with two DME molecules are more stable than those with only one; no stable complex with more DME molecules was found. The coordination with DME clearly shifts the preference to the enolate form. The same pattern can be seen in the parallel *ab initio* calculations where, with the 3-21G set, the enolate form appears to be the stable one.

From this, two conclusions can be made: (i) the overestimation of C–Li bonding by MNDO in systems like LIMIB is reduced if the polarization of this bond is stabilized by partial electron-donating interactions; (ii) even under such conditions, the agreement of MNDO results with high-precision *ab initio* SCF is not full. MNDO can thus be used for semiquantitative predictions in the scope of our interest if Li is engaged in two electron-donating coordination bonds. High-precision results are unattainable using this method in the present standard form.

### *Higher LIMIB Aggregates*

On the basis of the just discussed findings indicating the improvement of the MNDO results in the cases of lithium coordination, MNDO calculations of higher LIMIB aggregates – bare and solvated – are justified. We studied the optimal geometries and

TABLE II  
MNDO molecular parameters of methyl 2-lithioisobutyrate and its solvation complexes with dimethyl ether

Parameter	Form	LIMIB	LIMIB . DME	LIMIB . 2 DME
Heat of formation, kJ/mol	A	-472.8	-750.2	-983.2
	B	-461.2	-743.1	-985.6
Bond length, pm				
C1-C2	A	151	150	150
	B	141	141	141
C1-O	A	127	127	126
	B	130	129	129
C2-Li	A	199	204	208
	B	287	291	306
O-Li	A	215	218	224
	B	189	192	197
Bond angle, °				
C1-O-Li	A	82.4	81.9	81.6
	B	111.6	112.4	116.7
Torsion angle, °				
C2-C1-O-Li	A	-12.8	-17.5	-20.0
	B	0.0	0.0	0.0
O-C1-C2-Me <sup>1</sup>	A	147.6	153.0	149.9
	B	180.0	180.0	180.0
O-C1-C2-Me <sup>2</sup>	A	-70.8	-63.2	-68.2
	B	0.0	0.0	0.0
Net atomic charge				
O	A	-0.44	-0.45	-0.45
	B	-0.54	-0.53	-0.53
C1	A	0.48	0.48	0.48
	B	0.44	0.43	0.43
C2	A	-0.54	-0.53	-0.53
	B	-0.50	-0.51	-0.51
Li	A	0.46	0.30	0.22
	B	0.54	0.37	0.29

corresponding stabilization energies of the possible dimers, trimers, and tetramers of LIMIB. At all aggregation stages, several local minima were found depending on the starting geometry of the optimization process. Different starting geometries were constructed using combinations of keto and enolate forms of LIMIB and various spatial orientations of the LIMIB molecules. For the sake of brevity, we only show the most stable forms here. In Table III there are given the stabilization energies and the intuitively formulated geometry parameters characterizing the position between the extreme keto and enolate forms. The geometries of these stable forms are shown in Figs 2 to 4.

TABLE III  
MNDO molecular parameters of the most stable forms of methyl 2-lithioisobutyrate aggregates and their solvates with dimethyl ether

Parameter	Dimer	Dimer . 2 DME	Trimer 1	Trimer 2	Tetramer
Heat of formation, kJ/mol	-1 137.1	-1 607.9	-1 697.1	-1 730.4	-2 171.6
Stabilization energy <sup>a</sup> , kJ/mol	-95.8	-116.9	-92.9	-104.0	-70.1
Bond length, pm					
C1-C2	154	145	140	145	139
C1-O	125	127	131	127	132
C2-Li	215	210	301	206	312
O-Li	216	203	208	206	220
Bond angle, °					
C1-O-Li	89.2	143.0	109.4	102.5	113.0
Torsion angle, °					
C2-C1-O-Li	0.0	51.5	23.9	6.3	0.0
O-C1-C2-Me <sup>1</sup>	114.7	176.0	179.9	172.8	179.8
O-C1-C2-Me <sup>2</sup>	-114.7	27.9	0.5	21.9	0.6
Net atomic charge					
O	-0.39	-0.48	-0.47	-0.49	-0.46
C1	0.47	0.51	0.38	0.53	0.37
C2	-0.49	-0.51	-0.40	-0.52	-0.37
Li	0.33	0.30	0.37	0.40	0.38

<sup>a</sup> Stabilization energy per one LIMIB molecule; heat of formation of the most stable (A) form of LIMIB is taken as a reference value.

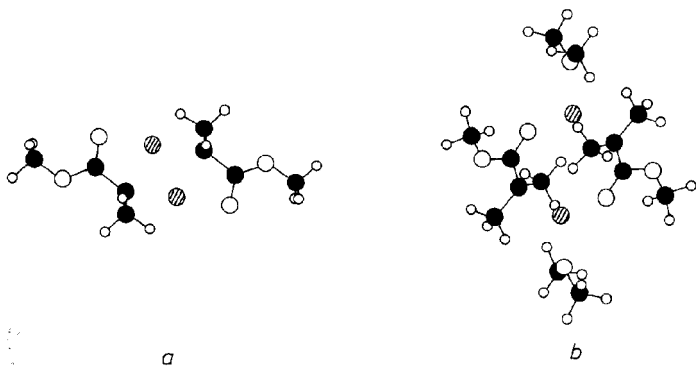


FIG. 2

MNDO optimized geometries of the methyl 2-lithioisobutyrate dimer (a) and its solvate with two dimethyl ether molecules (b)

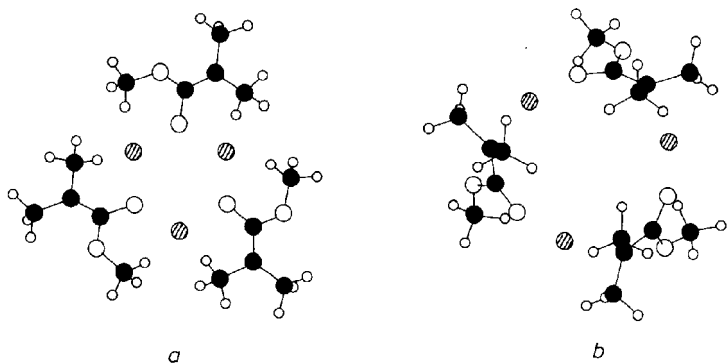


FIG. 3

MNDO optimized geometries of two low-energy structures of the methyl 2-lithioisobutyrate trimer: (a) trimer 1; (b) trimer 2

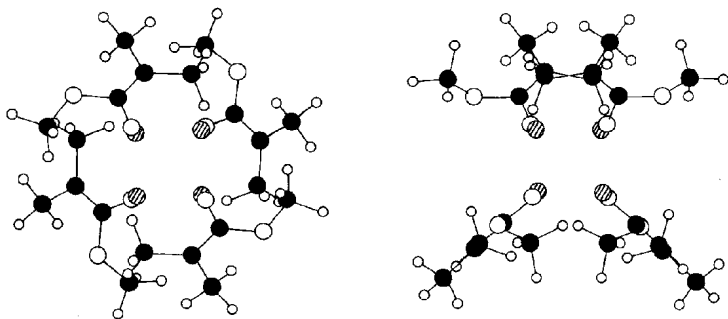


FIG. 4

MNDO optimized geometry of the methyl 2-lithioisobutyrate tetramer (two projections)



In a very good agreement with our experimental NMR results<sup>8</sup>, the dimer is most stable in a near-keto LIMIB form whereas the higher aggregation state shifts the geometry and bonding properties progressively to the enolate form. Compared to the keto form (Table III), stabilization energies of the LIMIB dimer in the enolate form and its solvate with two DME molecules are lower by 20.5 and 18.0 kJ/mol, respectively. It can be also seen from Table III that while for the most stable unsolvated dimer calculated MNDO parameters are very close to the keto form, its solvation with DME molecules shifts the MNDO parameters nearer to the enolate form.

Both dimerization and trimerization of LIMIB is energetically favourable which, again, agrees with the experiment<sup>8</sup>. Solvation by DME is energetically favourable in the case of the dimer, nearly neutral for the trimer and, again in agreement with the experiments<sup>7,8</sup>, unfavourable for the tetramer.

## CONCLUSIONS

Recalling now the problems listed under *a*) to *d*) in the first part of this paper, this study has shown that methyl 2-lithioisobutyrate as the simplest possible model of the living poly(methyl methacrylate) and also as the widely used initiator in the anionic polymerization of (meth)acrylates (i) can exist in at least three different, energetically not very differing aggregation states even in solvating media and (ii) has the lithium atom generally bonded in two, energetically not very different configurations; the more stable of these agrees with the intuitive idea of the enolate in all cases where the lithium atom effectively coordinates with an electron-donating group. These findings are in a very good agreement with experiment<sup>8</sup>.

As a by-product of this study, we have found the previously suggested<sup>10,11</sup> tendency of the MNDO method to overestimate the covalent C–Li bonding in the systems where the polarization of this bond is not stabilized by the interaction of Li with an electron donor. According to our calculations, at least semi-quantitative results can be obtained using this method if the examined system itself is realistic.

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