STUDY OF THE GROWTH CENTRES OF THE ANIONIC POLYMERIZATION OF (METH)ACRYLATES. VI. MO LCAO SCF STUDY OF THE MODEL DIMER, ITS SOLVATION AND AGGREGATION STATES

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Dedicated to Dr Blahoslav Sedlacek on the occasion of his 70th birthday.

The nature of the intramolecular coordination in dimethyl 2-lithio-2,4,4-trimethylglutarate (*I*) as the model of living dimer of methyl methacrylate was studied by comparison with the specific solvation of methyl 2-lithioisobutyrate, using *ab initio* SCF calculations with the 3-21G basis set. In both cases, electron-density donation from the incident oxygen leads to a weak coordination bond (20 to 30% of full covalency) accompanied by polarization and weakening of the original O–Li bond. The directionality of any O–Li or C–Li bond in all the systems under study is poor and the position of Li results from a complex interplay of covalent and electrostatic interactions with its molecular environment. The covalent part of the bond system can be characterized as a system of polycentric electron-defficient bonds. Possible conformational geometries of *I* were examined by *ab initio* calculations and the results were compared to those of the semiempirical MNDO method. The inclination of MNDO to create artificial local energy minima in previously unsuspected cases was detected and shown to be avoidable if the valence sphere of Li is saturated by electron donors. The formation of aggregation dimers of *I* was studied by MNDO and the most stable conformers were found. The study was paralleled for the di-*tert*-butyl ester analogue of *I*. The tendency of *I* to intramolecular coordination and self-aggregation is discussed in view of the known kinetics of the first steps of anionic propagation.

The renewed interest in the model studies of the growth centres in the anionic polymerization of (meth)acrylates[1–9] reflects both the still unexploited potentialities of this polymerization and the new possibilities offered by modern methods of spectroscopy and computational analysis. In addition to this, such studies give an opportunity to scrutinize the limitations of the conventionally used methods of molecular orbital calculations and the state of the theory of chemical bond.

In our previous studies[4,7] of model 2-lithioesters, their aggregation[4] and coordination with lithium alkoxides[7], we have shown that (i) the bonding of Li is weak in covalency and rich in electrostatic interactions but by no means really ionic; (ii) the structure of

the Li-carrying group is nearer to the esterenolate structure but not really identical with it; (iii) lithium is able and apt to form up to four electron-deficient bonds, i.e. up to three coordination bonds of a strength comparable to its original bonding; (iv) the bonding of the complexes or supramolecules formed by self-aggregation or coordination with Li alkoxides is enacted by a system of polycentric electron-deficient bonds and electron interactions. From the point of view of methodology, we have shown that (a) *ab initio* MO LCAO SCF calculations are able to describe the most important properties of Li esterenolates starting with the basis set 3-21G whereas no significant gain in precision can be achieved by upgrading the level even up to 6-31G** or 6-31+G*; (b) the semiempirical MNDO method, when used in molecular geometry optimization, tends to produce artificial local minima on the energy hypersurface, corresponding to an overestimation of e.g. C–Li covalent bonding; however, in the cases, where the coordination ability of Li is saturated, e.g. by specific solvation, MNDO produces results semiquantitatively similar to those of medium-level *ab initio* SCF calculations. By specific solvation, we mean the inner-sphere solvation by an electron-donating solvent with a definite geometry and interaction strength comparable with a coordination bond.

METHODS OF CALCULATION

All *ab initio* and MNDO calculations were performed using the GAMESS set of programs[10,11] running on a Silicon Graphics Indy 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_1 symmetry unless otherwise explicitly stated. Bond orders were calculated according to Mayer[12].

Molecular parameters 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, we cannot be quite certain that no local minima exist although meticulous search through this space was performed in all the discussed cases. The qualitative or semiquantitative agreement of our calculations with our experimental results[9] is the proof of their reasonability.

RESULTS AND DISCUSSION

Ab initio SCF and MNDO Calculations on I *and Its Specific Solvates*

The three forms of *I* obtained by *ab initio* SCF 3-21G calculation as local minima of the energy hypersurface of an unrestricted vector space of molecular inner coordinates are shown in appropriate projections in Fig. 1. The most important parameters of their structure are in the last three columns of Table I except the total energies which are –691.71587, –691.70418, and –691.66914 hartree for the forms *Ia*, *Ib* and *Ic*, respectively. The stabilization energies of *Ia* relative to *Ib* and *Ic* are thus predicted to be 30.7

and 122.5 kJ/mol, respectively. The latter quantity can be considered as the energy gained by intramolecular coordination in the bare, i.e. unsolvated molecule of *I*. Relevant atoms to which the structure parameters are related are numbered according to Scheme 1 where *I* is shown in the intramolecularly coordinated disolvated form.

I . 2 DME

SCHEME 1

Table II and Fig. 2 show the results of the parallel MNDO calculations. Here, six local minima were found for the bare *I*. To each of the obtained structures, one molecule of dimethyl ether (DME) was added so that the ether oxygen–lithium distance was

Ia

Ib

Ic

FIG. 1

Ab initio optimized geometries of three stable forms *Ia*, *Ib* and *Ic* of dimethyl 2-lithio-2,4,4-trimethylglutarate obtained with the 3-21G basis set

200 pm and the calculation with unconstrained energy optimization was run again until a new local minimum of *I* . DME was found. Then the same procedure was repeated with an additional molecule of DME giving five locally stable forms *I* . 2 DME.

The MNDO method is known[4,7] to produce some artefacts if used with bare Li esters but to behave reasonably if the affinity of Li to coordination is saturated by soft electron donors such as DME. The sense of the just described calculations is to check its behaviour with a more complex molecule such as *I* which itself contains a group with coordinating ability. At the same time, these calculations should give an indication of the ability of *I* to bind DME and analogous ethers into specific solvates in analogous manner as the simple Li esters and their dimeric aggregates do[4].

TABLE I
Ab initio 3-21G molecular parameters for bare 2-lithioisobutyrate (*II*), its solvates with dimethyl ether and the stable forms of dimethyl 2-lithio-2,4,4-trimethylglutarate (*I*)

Site[a]	*II*	*II* . DME	*II* . 2 DME	*Ia*	*Ib*	*Ic*
			Charge[b]			
C1	–0.27	–0.23	–0.24	–0.25	–0.27	–0.27
C2	0.89	0.86	0.84	0.90	0.74	0.86
O1	–0.87	–0.86	–0.86	–0.85	–0.75	–0.87
Li	0.63	0.51	0.47	0.52	0.53	0.62
O_{lig}	–	–0.69	–0.67	–0.72	–0.73	–0.64
C_{lig}	–	–0.28	–0.31	1.10	1.13	1.02
			Bond order			
C1–C2	1.63	1.64	1.62	1.55	1.55	1.64
C2–O1	1.00	1.02	1.06	1.07	1.19	1.00
O1–Li	0.62	0.58	0.42	0.49	0.45	0.61
Li–O_{lig}	–	0.25	0.23	0.31	0.31	0.00
C_{lig}–O_{lig}	–	0.77	0.76	1.43	1.41	1.73
			Bond length (pm)			
C1–C2	133	133	133	134	134	133
C2–O1	132	131	131	130	131	132
O1–Li	159	162	169	169	180	159
Li–O_{lig}	–	182	187	180	182	186
C_{lig}–O_{lig}	–	145	145	124	124	121

[a] O_{lig} means O2 in *I* and O4 in solvated *II*; C_{lig} means C3 in *I* and C4 in solvated *II*; [b] Mullikan population.
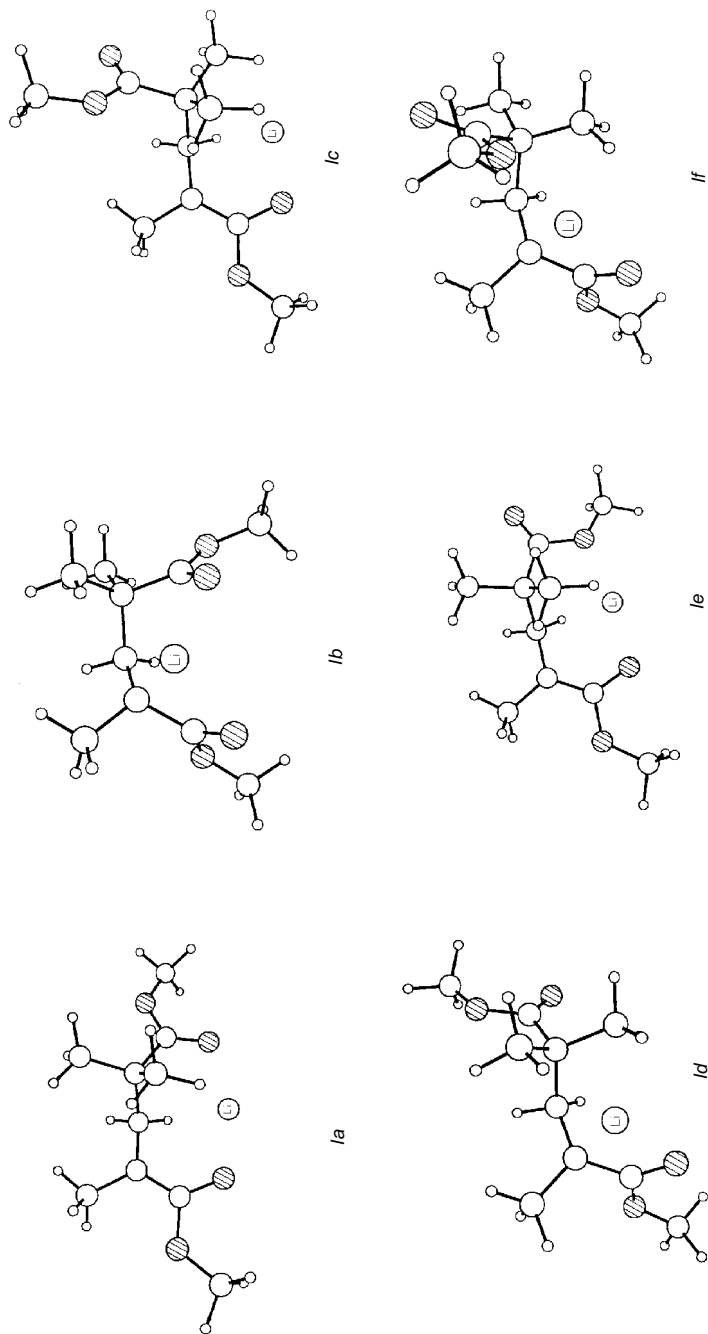
Fig. 2
MNDO optimized geometries of six stable forms *Ia*, *Ib*, *Ic*, *Id*, *Ie* and *If* of dimethyl 2-lithio-2,4,4-trimethylglutarate

As one can see in Fig. 2 and Table II, MNDO finds for the bare *I* three forms *Ia*, *Ib* and *Ic* which are roughly analogous to those found by *ab initio* SCF. Along with them, however, other forms are found, among which *Id* and *If* have their Li-carrying groups close to the "keto" form already known[4] to be an artefact of overestimation of the C–Li

TABLE II
MNDO molecular parameters of stable forms of dimethyl 2-lithio-2,4,4-trimethylglutarate (*I*) and their mono- and disolvates with dimethyl ether

Compound	Bond	*Ia*	*Ib*	*Ic*	*Id*[a]	*Ie*[a]	*If*
				Heat of formation (kJ/mol)			
I		–826.90	–845.11	–785.96	–811.92	–812.46	–828.99
I . DME		–1 084.05	–1 099.75	–1 074.09	–1 074.09	–1 063.50	–1 076.35
I . 2 DME		–1 311.68	–1 289.66	–1 274.14	–1 277.02	–1 277.02	–1 276.69
				Bond length[b] (pm)			
I	C1–C2	142	152	142	152	142	152
I . DME		141	151	141	152	141	152
I . 2 DME		141	147	140	152	152	148
I	C1–O1	129	125	129	126	129	126
I . DME		128	125	129	125	129	125
I . 2 DME		128	126	129	125	125	127
I	O1–Li	192	224	191	221	192	223
I . DME		195	229	195	228	197	236
I . 2 DME		195	233	185	232	232	221
I	C3–O2	125	125	123	123	122	123
I . DME		125	124	123	123	122	123
I . 2 DME		124	124	123	123	123	123
I	O2–Li	214	211	–	–	215[c]	216[c]
I . DME		215	216	–	–	226[c]	225[c]
I . 2 DME		221	234	–	–	–	–
I . DME	O4–Li	215	217	215	216	218	219
I . 2 DME		221	234	214	224	224	225
I . 2 DME	O5–Li	222	235	229	229	229	228

[a] The forms found for disolvates *Id* and *Ie* are identical. [b] Only relevant bonds <250 pm are given. [c] O3–Li.

covalency by the method. Additionally, *Ie* and *If* have Li coordinated to O3 which is probably another artefact as one can see from the results of simulated solvation where *Ie* eventually merges with *Id* and both result in a conformer of the "open", i.e. intra-molecularly noncoordinated form similar to *Ic*, as also does *If*. As the calculation of the disolvated *I* by *ab initio* SCF is beyond our computational means, we are unable to say whether these conformers can be expected to exist as distinct species. In view of the small differences in their stabilization energy we are inclined to take disolvated forms *Ic* to *If* as one "open" form of *I*.

Apart from the recognition of the artefacts produced by MNDO method in this type of structure which opens its use for still more complicated systems, the important result of these calculations is the unequivocal prediction that the Li coordination to the carbo-nyl of the γ-ester group is energetically advantageous even in the disolvate. The stabili-zation energy due to this coordination is predicted to be at least 34.7 kJ/mol in the disolvated state. This value is high enough to assure that intramolecular coordination and specific solvation of Li in *I* do not exclude each other but do cooperate in the stabilization of the non-aggregated form of *I*. Further, the stabilization energy gain by intramolecular coordination predicted by both *ab initio* SCF and MNDO calculations ensures that the monomeric form of *I* is almost exclusively intramolecularly coordi-nated. This prediction is in full accord with our experimental observations[9].

The Effect of Specific Solvation and Intramolecular Coordination on the Li Bonding to the Esterenolate Group: ab initio SCF Results

As explained in the introduction, specific solvation by donor molecules such as di-methyl ether, tetrahydrofuran (THF) and the like is different from the usual random or partly organized solvation. There is some evidence (cf. e.g. ref.[13]) that one or two mole-cules of the solvent in the inner solvation sphere adopt definite positions and that they take part in the system of cooperative coordination bonds. *I*n some cases, such as the model dimer *I* and THF, a definite number of solvent molecules is bound so strongly that it accompanies the esterenolate in the crystal lattice from which it cannot be easily removed. This is why we compare here specific solvation with intramolecular coordi-nation.

Table I shows some molecular characteristics predicted by *ab initio* SCF at the 3-21G level for methyl 2-lithioisobutyrate (*II*), its specific monosolvate and disolvate with dimethyl ether, and three different stable conformers of *I*. Although two stable forms slightly differing in geometry were found[4] for bare *II* (the more stable one is shown in Table I), for both the specific monosolvate and disolvate of *II* with DME only one stable form is predicted by *ab initio* calculations. This finding supports the idea[4,7,8] that higher coordination of the lithium atom in the lithioester molecules leads to a less complicated energy hypersurface with less and deeper energy minima. In the following,

we assume the basic similarity of the lithium-carrying groups in *II* and in the linear or uncoordinated form of *I*.

As one can see from Table I, both specific solvation by an ether and intramolecular coordination to the penultimate ester group have primarily the same effect on the Li-esterenolate group. It can be characterized by two main features: (i) by electron density donation from the coordinating oxygen atom (ether or carbonyl), a weak coordination O–Li bond (23–31% of the full covalent bonding strength) is formed; (ii) the original O–Li bond is somewhat weakened (relative decrease of the bond order by 6–32%) and, accordingly, lengthened and polarized.

The esterenolate nature prevailing in the case of bare 2-lithioester (*I* or *II*) could be expected to even deepen by specific solvation as well as by intramolecular coordination. However, slightly opposite tendency is predicted by the *ab initio* calculations. In order to quantify this feature, let us define somewhat arbitrarily the "enolate index" κ_e in the interval from 0 (pure keto form) to 1 (pure esterenolate form) by the relation

$$\kappa_e = (P_{C-C}/P_{C-O} - 0.5)/1.5 \qquad (1)$$

with the bond orders P_{C-C} and P_{C-O}. For noncoordinated *I*, bare *II*, monosolvated and disolvated *II* and the two stable forms of intramolecularly coordinated *I*, the κ_e values are 0.74, 0.75, 0.74, 0.69, 0.63 and 0.54, respectively. This fact can be explained in the following way. In the case of specific solvation, the system C=C–O becomes more polarized decreasing thus slightly the C=C bond order without promoting really the keto form. In the case of intramolecular coordination of *I*, conformational structure of the molecule is considerably changed and the lithium atom is forced into a position (Fig. 1) somewhat closer to that it would adopt in the keto form of 2-lithioester. The bonding orbitals adapt to this change and this is reflected in non-zero covalency of the Li bonding to the C=C–O system.

Polarization of the original Li bond does not lead to more ionic Li. Quite to the contrary, as one can see from Table I, the positive charge on Li is invariably less in the coordinated state. This is due to electron density donation from the ligand. Showing this effect in a pictorial extreme form, ionization due to interaction with ligand S takes the form
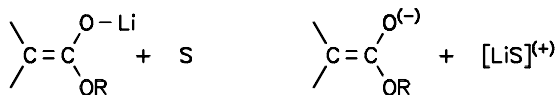
i.e. the relative positive charge is carried primarily by the ligand molecule. This should be taken into account in any consideration of the interactions of the polarized centre with the monomer.
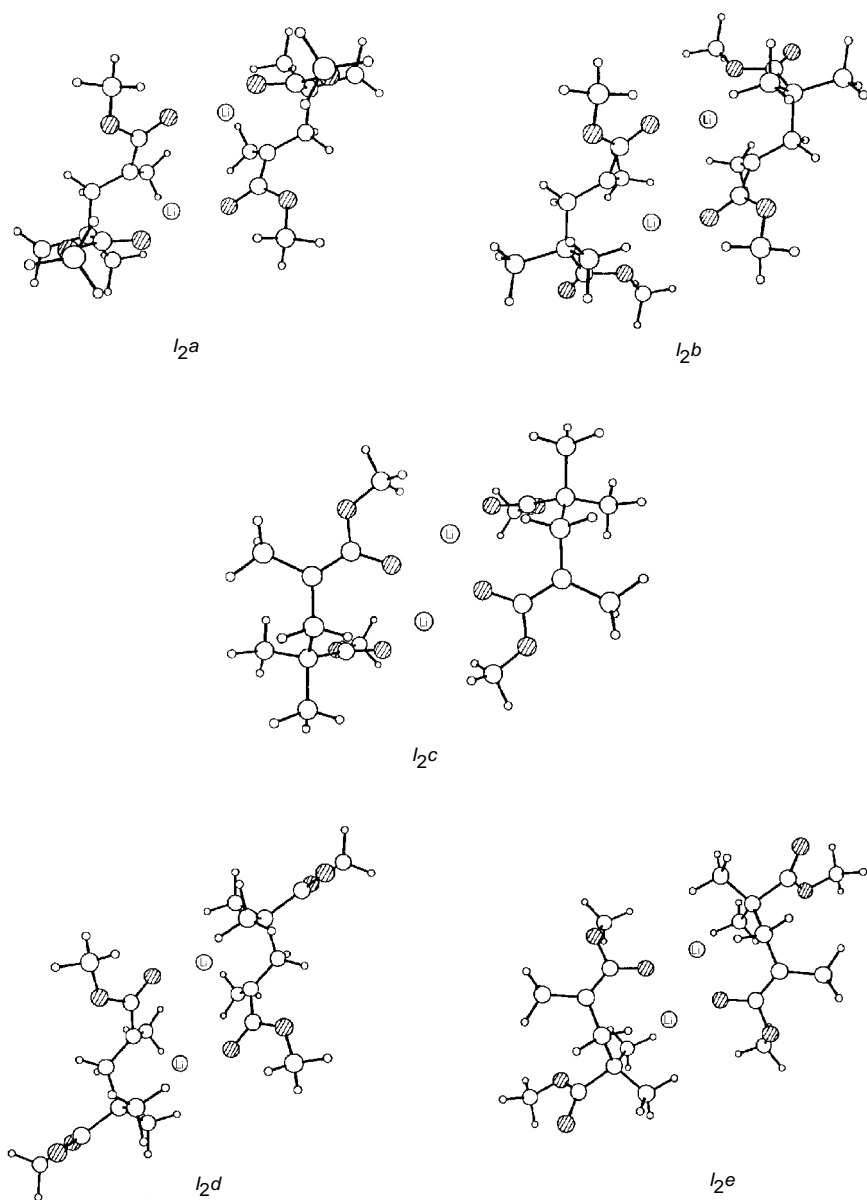
Fig. 3
MNDO optimized geometries of five stable forms I_2a, I_2b, I_2c, I_2d and I_2e of the aggregation dimer of dimethyl 2-lithio-2,4,4-trimethylglutarate

MNDO Calculations of the Aggregation Dimers of I

The tendency to form aggregates[3,4] cannot be expected with simple Li esterenolates only. Experimental evidence[9,14] suggests dimerization of I even in highly solvating media such as THF. MNDO results for five different local minima of the dimer I_2 are shown in Table III and Fig. 3.

In view of the computational evidence with I, the question of solvation has to be cleared up first before any consideration of individual forms. Specific solvation of I_2 was investigated by two complementary approaches in the MNDO method. In both of them, the DME molecule was initially placed into the vicinity of the Li-containing group in a position analogous to that found as stable for I . DME. In the subsequent geometry optimization, (i) no constrain of internal coordinates was applied or (ii) the interatomic distance between the DME oxygen and Li was first kept fixed and all other degrees of freedom were allowed to change. In both cases the solvent molecule was finally rejected, i.e. the distance between the DME molecule and I_2 increased to a non-bonding value at the end of the optimization. This leads to an unequivocal conclusion that the aggregation dimer I_2 rejects specific solvation, i.e. it only allows usual non-specific solvation.

TABLE III
MNDO molecular parameters of stable forms of the dimethyl 2-lithio-2,4,4-trimethylglutarate dimer (I_2)

Bond	I_2a	I_2b	I_2c	I_2d	I_2e
			Heat of formation (kJ/mol)		
–	–1 805.17	–1 792.45	–1 778.38	–1 771.85	–1 709.35
			Bond length[a] (pm)		
C1–C2	146	146	140	146	140
C1–O1	126	127	130	127	130
O1–Li	203	202	206	201	210
C3–O2	124	123	124	123	123
C2–Li	212	210	–	–	–
O2–Li	–	–	209	–	–
O1*–Li	–	–	211	–	203
O2*–Li	218	–	–	–	–
O3*–Li	–	217	–	–	–
C2*–Li	–	–	–	205	–

[a] Only relevant bonds <250 pm are considered; atoms of the other molecule are marked by asterisk.

On the basis of this conclusion, the dimerization of I in a solvating medium (S) is governed by the equilibrium

$$2\,I \cdot S_2 \;\rightleftharpoons\; I_2 + 4\,S\;.$$
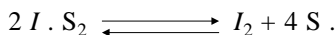
Taking all the heats of formation into account, the dimerization–desolvation process is endothermic; $\Delta H = 39.0$ kJ/mol for the most favourable forms, $I \cdot S_2$ and I_2. In contrast to simple esterenolates[2–4] where the deaggregation is driven chiefly by solvation entropy, a special case is encountered here where the main driving force of the same process is the enthalpy change. According to this, higher concentrations of I as well as higher temperatures should lead to an increasing content of the dimer, in agreement with NMR data[9].

Inspecting now the five different forms of I_2 (cf. Fig. 3 and Table III) and comparing them with those of I, we can almost certainly exclude the *b* form (with the ester oxygen of the second molecule used for coordination) as an artefact of the method. From the remaining four, there are two more advantageous (*a* and *c*) with the Li atoms of one molecule strongly coordinated to both the α- and γ-carbonyls (O1 and O2); the less probable structures *d* and *e* show only coordination to the α-carbonyl (O1). Out of all four forms, only *c* retains intramolecular coordination analogous to that found in I. In the remaining three forms, this coordination is eased or not present at all. Experimentally, the behaviour of the esterenolate group (i.e., carbons C1 and C2) in most of the dimer molecules should be markedly different from that in the cyclic intramolecular coordination whereas the behaviour of the γ-carbonyl (i.e., carbon C3), which is involved in Li coordination in both I and I_2, should be similar in the monomer and dimer. This is observed by NMR (ref.[9]).

MNDO Calculations on Cyclic Coordination, Solvation and Dimerization of the Di-tert-butyl Ester Analogue of I

All MNDO calculations presented here for dimethyl 2-lithio-2,4,4-trimethylglutarate (I) were also performed for the di-*tert*-butyl ester (III) which was chosen for experimental observations[9]. The results exhibit only minor differences in optimum geometries and bonding properties in comparison with the analogous instances of I showing thus that the steric requirements of the ester alkyl groups have no significant effect on the coordination, solvation and aggregation behaviour of the model dimer.

This conclusion seemingly contrasts with the common knowledge of significant differences in the course of anionic polymerization of various (meth)acrylates. The explanation probably has to be sought in a different relation between the propagation and termination rates of the monomers with different ester alkyl groups. This can be deduced from the fact that solvation, intramolecular coordination, aggregation and interaction with monomer (i.e. propagation) all involve C2, O1 and marginally O3 (in our

notation) whereas termination of any kind of condensation involves C1 which is much more influenced by steric requirements of the ester alkyl group.

CONCLUSIONS

By MNDO and partly *ab initio* SCF 3-21G calculations and their comparison with experimental NMR observations, we have shown that the model of living dimer of methyl methacrylate, dimethyl 2-lithio-2,4,4-trimethylglutarate (*I*), and its di-*tert*-butyl ester analogue (*III*) (i) have a strong tendency to intramolecular Li coordination to the carbonyl of the γ-ester group; (ii) bind up to two dimethyl ether or THF molecules into a specific solvate whereas (iii) such solvation does not interfere with the intramolecular coordination but cooperates with it in a complex coordination system. In addition to this, *I* and *III* have a tendency to dimerization by aggregation utilizing mainly the Li coordination to the γ-ester group of the mirror molecule in the dimer. In contrast to the monomeric *I* or *III*, the dimer is not stabilized by specific solvation. Therefore, both low concentrations of *I* and low temperatures prefer the monomeric form in solvating media (due to both solvation enthalpy and entropy).

The idea of the propagation centre in the first steps of the anionic polymerization of (meth)acrylates, based on the present and an experimental[9] study, is thus that of a monomeric, γ-carbonyl-coordinated and solvated esterenolate regardless of the steric requirements of the ester alkyl group.

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