The Structures of Lithium and Magnesium Derivatives of Acetic Acid 'Dianions'

José Kaneti,*[a] Paul von Ragué Schleyer,*[b] and Alexander J. Kos[b]

[a] Institute of Organic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
[b] Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen, Federal Republic of Germany

Ab initio and semi-empirical MNDO calculations indicate that monomeric dilithiated and bis-magnesyl derivatives of carboxylic acids (Ivanoff reagents) favour the 1,3–1,3' doubly bridged structures generally found in metallated Y-conjugated dianion systems.

Metallation of carboxylate salts possessing α-hydrogens by alkylmagnesium derivatives was first observed at the beginning of the century by Grignard.[1] The bifunctional metal derivatives resulting from this reaction were shown by Ivanoff and coworkers to be quite versatile synthetically.[2,3] The highly stereospecific addition of Ivanoff reagents to carbonyl com-pounds is usually attributed to an early cyclic transition state involving the bis-enolate of the reagent (1)[3] and this form is usually considered to be the structure of the reagent itself.[3] Dilithiated carboxylic acids also are widely employed synthetic reagents;[4] these have been formulated as 'ate'[5] or as C-metallated derivatives, e.g., (2). Studies of bifunctional

(1) (2)

M = Li or MgX

(3) (4) (5)
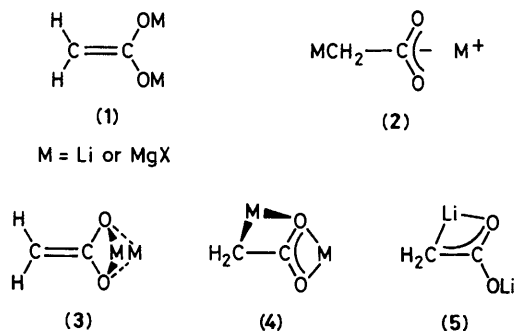
polar organometallic derivatives of carboxylic acids by physical methods such as i.r.[6] and n.m.r. spectroscopy,[7] indicate that there is only one isomer in solution, but have not established its nature. No X-ray structures are available yet.

We report a model theoretical study of dilithium and bis-magnesyl (MgH) derivatives of acetic acid. Our earlier work on the Y-conjugated dianions[8,9] has demonstrated the close correspondence between the results of such calculations and experimental structures.[10]

Ab initio MO calculations for $C_2H_2Li_2O_2$ and $C_2H_4Mg_2O_2$ isomers were carried out with the GAUSSIAN series of computer programs.[11] All geometries were completely optimized with the 3-21G basis set.[12] In addition, single point 6-31G[13] and MP2/6-31G[14] calculations were performed on the most stable forms of $C_2H_2Li_2O_2$, but no qualitative differences in the energy orderings were found. Semi-empirical MNDO theory[15] was used to study the association of dilithioacetate bis-enolate and carboxylate forms and to model solvation by water, simulating ether solvents.

Several symmetrically 1,4- and 1,5-doubly bridged organolithium compounds are now known;[9,10,16] this suggests (3) as a candidate for the most stable structure. However, 1,3-double bridging is less favourable energetically[16] and lithiated Y-conjugated dianion systems are known to favour less symmetrical metal placements as in (4).[8,9] Indeed, the 3-21G//3-21G results on $C_2H_2Li_2O_2$ indicate (4) (M = Li, $-240.285\,34$ a.u.)† to be the most stable isomer and (3) (M = Li, $-240.272\,66$ a.u.) to be the best alternative, 33.3 kJ mol⁻¹ higher in energy. The singly bridged (5) ($-240.257\,26$ a.u.) and the classical (1) (M = Li, $-240.249\,24$ a.u.) are not competitive; even less so at the higher theoretical levels. In the 3-21G structure of (4) (M = Li, Figure 1), one lithium is roughly in the carboxylate plane while the second is involved in π-enolate anion bridging.[8] The electrostatic ion triplet interactions are more important than π-delocalization; the C_s form of (4) (M = Li), with both lithiums in the same plane and the CH_2 group twisted to 'shut off' the enolate resonance, is only 50 kJ mol⁻¹ higher in energy.

Calculations of structures similar to (1), (3), and (4) were also carried out for bis-magnesylacetate, $C_2H_4Mg_2O_2$. Organomagnesium derivatives are less polar than their lithium counterparts, C–Mg bonds are more covalent, and magnesium has a lowered bridging tendency.[17] However, in the present case magnesium does not show qualitative difference from lithium and the most stable form (4) is quite similar in geometry (M = MgH, Figure 2). The 3-21G//3-21G order of stability of bis-magnesyl isomers (4) (M = MgH, -623.56379 a.u.) > (3) (M = MgH, -623.54341 a.u.) > (1) (M = MgH, -623.52575 a.u.) is the same as that found for the corresponding dilithium derivatives. No minimum was found for a structure similar to (5).
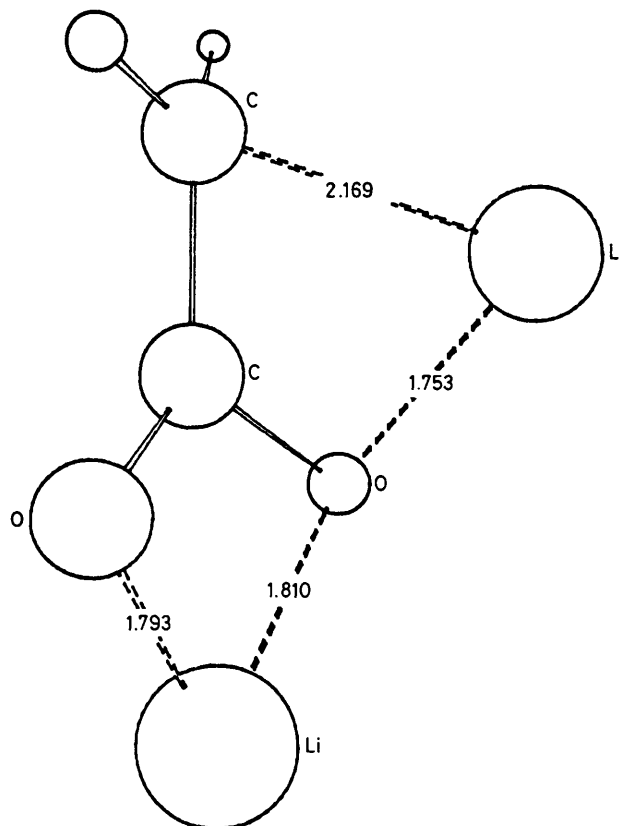
† 1 a.u. = 2625.46 kJ mol⁻¹.

Figure 1. Calculated (3-21G basis set) structure of (4) (M = Li), the most stable form of dilithiated acetic acid.
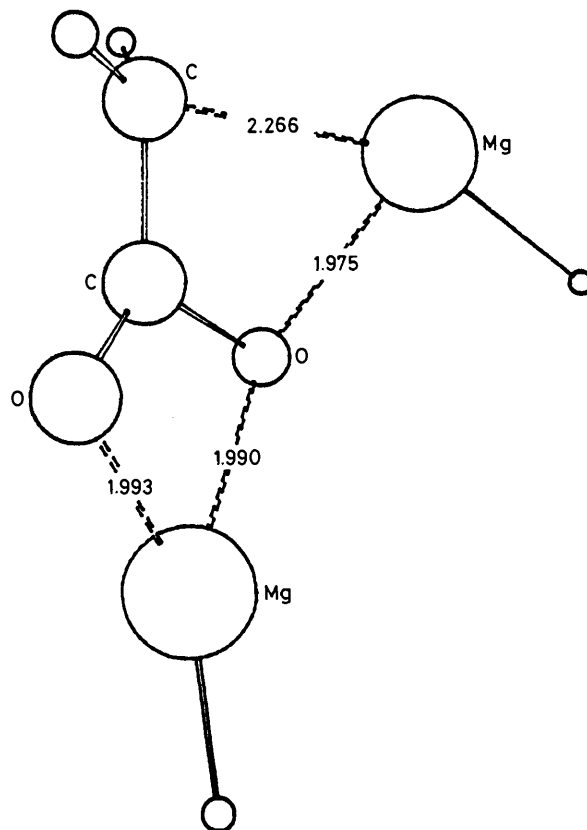

Figure 2. Calculated (3-21G basis set) structure of (4) (M = MgH), a model for the magnesium-based Ivanoff reagent. Note the similarity with Figure 1.

While these structures are calculated for isolated (gas phase) species, similar forms may be found in donor solvents. Our MNDO calculations of two possible dimers of dilithioacetate have not located structures with very favourable energies. Low association energies also are in line with the ^{13}C and [1]H n.m.r. studies of magnesium-based Ivanoff reagents, which indicate non-exchanging monomeric species to be present in tetrahydrofuran and hexamethylphosphoric triamide solutions.[18] MNDO calculations of solvation of dilithioacetate by water (to model ethers) show no changes of the stability order of bridged carboxylate (**4**) and bis-enolate (**1**) forms. While the first solvation step of dilithioacetate is favourable (an average of -16.0 kcal mol^{-1}‡ per complexation of a H_2O molecule with each lithium atom), further solvation of (**4**) is calculated to be endothermic. This is consistent with the experimentally known tendency of crystallosolvates of Ivanoff reagents to lose solvent ligands.[18] The bis-enolate form (**1**) is predicted to be better solvated than (**4**). While the average solvation energy for the first solvation of (**1**) is nearly the same (-16.2 kcal mol^{-1}‡), the energy of the second H_2O attachment also is favourable. Hence, solvation reduces the energy difference between (**4**) and (**1**), but the former is still more stable.

The present *ab initio* and MNDO calculations predict that monomeric Ivanoff reagents, dilithium and bis-magnesyl derivatives of carboxylic acids, probably have the bridged structures exhibited by other metallated Y-dianions in the presence of ether solvents.[8]

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‡ 1 kcal = 4.184 kJ.