264. Tetrameric Cubic Structures of Two Solvated Lithium Enolates

by **René Amstutz**[1]), **W. Bernd Schweizer, Dieter Seebach** and **Jack D. Dunitz**

Organic Chemistry Laboratory, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich

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Summary

The structures of the crystalline lithium enolates derived from 3,3-dimethyl-2-butanone and from cyclopentanone have been determined by X-ray analysis. Both structures are tetrameric aggregates based on a Li_4O_4-cube, each Li^+-ion being additionally bonded to the O-atom of a tetrahydrofuran solvent molecule.

The recent resurgence of interest in diastereoselective reactions of alkali metal enolates has led to much discussion[2]) about the mechanisms of such reactions [2].

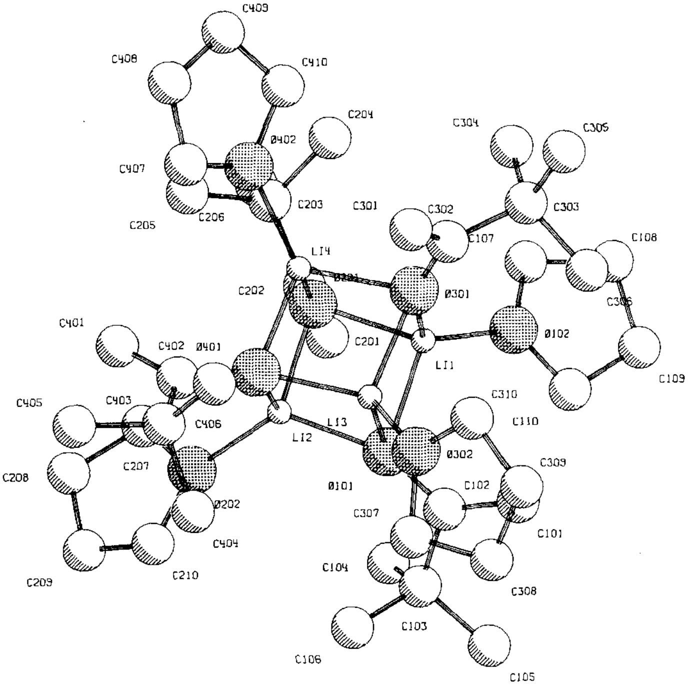

Fig. 1. *Structure of lithium 3,3-dimethyl-1-buten-2-olate: THF solvate* **1** (drawn by computer program PLUTO [7])

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[1]) Part of the projected Ph.D. thesis of *R.A.*

[2]) See the recent review articles [1].

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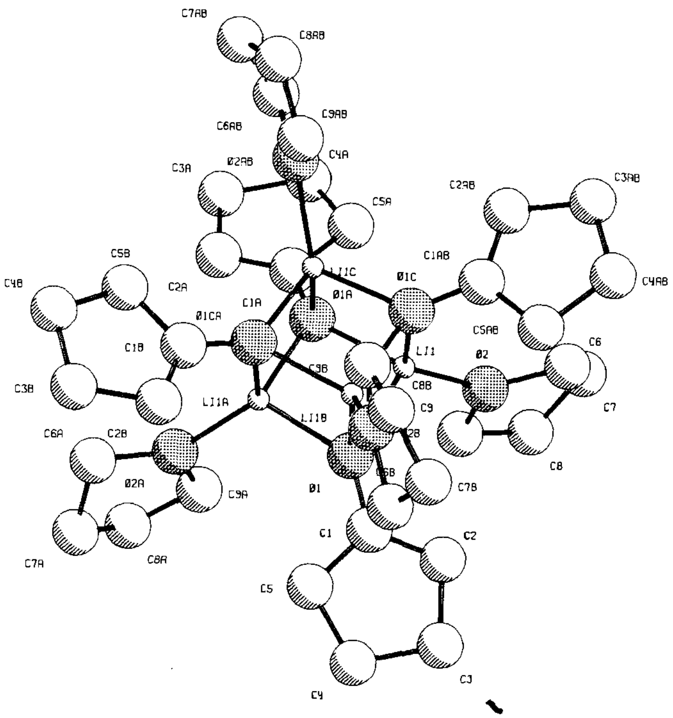

Fig. 2. *Structure of lithium cyclopentenolate: THF solvate* **2**. The C,C-double bonds are labelled C1-C2, C1A-C2A, *etc.*

Up till now, however, definitive structural information about enolates is lacking, although it has been recognized for some time that for lithium enolates ion-pair aggregates [3] of various kinds, especially tetramers [4], must be involved. In this paper we provide some of the hitherto missing information; we describe the structures of the crystalline lithium enolates **1** and **2** derived from 3,3-dimethyl-2-butanone (pinacolone) and from cyclopentanone respectively, both crystallized from tetrahydrofuran (THF). In an accompanying paper [5] we show how this new structural information can be used to interpret several facets of enolate chemistry.

The two structures, depicted in *Figures 1* and *2*, are built on a common plan. Both exist in the crystal as solvated tetramers of the kind postulated to occur in solution by *Jackman & Szeverenyi* from their NMR. studies [4]. Four Li-atoms and four enolate O-atoms form a nearly regular cube of edge about 1.97 Å[3]); each Li-atom achieves its usual 4-coordination by making an additional Li,O-bond (also *ca.* 1.97 Å) to a THF molecule situated along the extension of the body-diagonal of the cube. The entire aggregate retains S_4 symmetry, exact for **2**, and approximate for **1**.

There appears to be a quite definite preferred orientation of the enolate double bond with respect to the Li_4O_4-cube; this is shown in *Figure 3* for **1**. The C,C-double

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[3]) Interatomic distances are based mainly on the analysis of the enolate from **1** *(Fig. 1)* because it is more accurate (see *Experimental Part*).

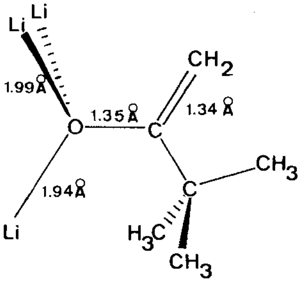

Fig. 3. *Orientation of the 3,3-dimethyl-1-buten-2-olate anion with respect to its three coordinated counter-ions on the Li_4O_4-cube*

bond (length *ca.* 1.34 Å) is antiperiplanar *(app)* to one of the Li,O-bonds and synperiplanar to a C,C-single bond[4]). The difference between the two kinds of Li,O-edges is even detectable by the small but systematic difference in interatomic distance, the *app* edge being distinctly shorter. The O–C=C fragment shows almost the same interatomic distances as an enol ether (C=C, 1.32 Å; C–O, 1.36 Å; averages of 10 structures from the *Cambridge Crystal Structure Database* [7]).

The Li_4O_4-cube presumably owes its stability to electrostatic interactions. On a simple point-charge model, its potential energy is $(-12+12/\sqrt{2}-4/\sqrt{3})\cdot e^2/r = -5.82\ e^2/r$, a gain of $1.82\ e^2/r \sim 300$ kcal mol^{-1} compared with the energy of four isolated monomers with the same distance $r \sim 2$ Å. Even though the model is crude this stabilization energy is so large that allowance for solvation and entropic effects or covalent character of the bonds is unlikely to change its sign. The dimensions of the cube may be compared, with due account for the differences in coordination, with those in crystalline Li_2O (antifluorite structure; $a = 4.619$ Å [8]): Li-O, 1.97 Å *vs.* 2.00 Å; Li···Li, 2.79 Å *vs.* 2.31 Å (3.04 Å in metallic Li); O···O, 2.79 Å *vs.* 3.27 Å. In the related structure[5])[6]) of $(TlOCH_3)_4$ only the dimensions of the Tl_4-tetrahedron (Tl···Tl 3.81–3.86 Å) are known [9 a].

In addition to the two compounds whose structures are described here, we have also prepared the following lithium enolates (and related species) in the solid state (mostly crystalline): from pinacolone, solvated with dioxane, tetramethylethylenediamine (TMEDA), hexamethylphosphoric acid triamide (HMPT), and dimethylpropylene urea (DMPU); from cyclohexanone, solvated with THF, dioxane, and diethylether; from 2,4,6-trimethylacetophenone, solvated with pinacolone (!); from diisopropylamine (LDA), solvated with THF. In all cases the molar ratio ketone (amine)/solvent is 1:1 as determined by ^{1}H-NMR. spectroscopy of solutions in CD_3OD. If we assume that the Li-atoms in these complexes have their usual

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[4]) Compare with the analogous situation in enamines [6].

[5]) For other cubic M_4X_4 structures *e.g.*, $(CrOCp)_4$, $(C_6H_5AlNC_6H_5)_4$, $Co_4(NO)_4(\mu_3\text{-N-CMe}_3)_4$, $[Et_3MeN]_3[Fe_4S_4(SC_6H_5)_4]$ s. [9b–c].

[6]) The Li_4O_4-cube also stands comparison with the $Li_4(alkyl)_4$ tetramers [10] where the Li-atoms form an inner tetrahedron (Li···Li 2.4–2.6 Å), the alkyl C-atoms (situated outside the triangular faces) a second, outer one (C···C, about 3.7 Å). Thus the Li_4-tetrahedron has shrunk slightly, while the C_4-tetrahedron is greatly expanded, as compared with the Li_4O_4-cube.

tetrahedral coordination, this is strong evidence that the tetrameric cubic type of structure shown in *Figures 1* and *2* may be the rule for highly polar complexes of lithium with electronegative ligands and may be safely used for discussing the chemistry of such species [5].

Experimental Part

Preparation of lithium 3,3-dimethyl-1-buten-2-olate: THF solvate. - To a solution of 10 mmol of LDA in 20 ml hexane/THF 3:1 in an Ar atmosphere at $-20°$, 1 g of freshly distilled ketone was added dropwise. The colourless precipitate was dissolved in 4 ml THF at RT. by stirring (1 h). Crystals were obtained by slowly cooling the solution to $-20°$ and dried i.HV. after removing the supernatant with a syringe.

Crystal structure analysis. - $C_6H_{11}OLi + C_4H_8O$, $M = 178.20$. A single crystal approximately 0.3 mm in edge was mounted in a quartz capillary under Ar with tetradecane as adhesive. Monoclinic, space group $C2/c$, $a = 17.520$, $b = 13.178$, $c = 39.191$ Å, $\beta = 85.79°$ at $-70°$, $Z = 32$, d(calc) = 1.10 gml^{-3}. Intensity measurements were made at $-70°$ with an *Enraf-Nonius* CAD-4 diffractometer equipped with graphite monochromator and cooling device (Mo$K\alpha$ radiation, $\lambda = 0.7107$ Å, 7056 independent reflexions with $\theta \leq 24°$, 2563 with $I > 3\sigma(I)$). The structure was solved by direct methods using the program-system SHELX [11] and refined by full-matrix least-squares analysis with experimental weights using SHELX and XRAY 72 [12] programs. H-atoms were located at an intermediate stage and included in the refinement with isotropic vibrational parameters (other atoms anisotropic); final R was 0.046.

Preparation of lithium cyclopentenolate: THF solvate. - Trimethylsiloxycyclopentene (0.78 g, 5 mmol) in 4 ml THF was added to 2.95 ml (5.02 mmol) MeLi 1.7N in ether in an Ar atmosphere at $-30°$. The reaction mixture was stirred for 30 min at 0° and cooled to $-78°$. After standing for several hours at $-78°$ the supernatant was removed and the colourless crystals were dried i.HV.

Crystal structure analysis. - $C_5H_7OLi + C_4H_8O$, $M = 162.16$, tetragonal, space group $I4_1/a$, $a = b = 19.84$, $c = 10.026$ Å (at $-90°$), $Z = 16$, d(calc) = 1.09 gml^{-3}. Crystal mounting, intensity measurements, structure solution and refinement were as in the other analysis except for the following: 1732 reflections, 446 with $I > 3\sigma(I)$, $T = -90°$, structure solved by MULTAN 80 [13], H-atoms located from stereochemical considerations and not refined, final R was 0.105. Some anomalous bond lengths and large vibrational parameters, especially in the THF moiety, point to a certain amount of orientational disorder in the crystal structure.

Atomic coordinates for both crystal structures have been deposited [7].

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