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Crystal Structure of Isopropyllithium

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Organolithium reagents are of paramount importance in modern preparative chemistry, and our empirical knowledge concerning their chemical behavior is rather well-developed.¹ Since their fascinating, and notoriously complex, structural chemistry can provide a key to a deeper understanding of the factors governing their reactivities, structural investigations are of great current interest.² However, owing to the sensitivity of these compounds toward oxygen and moisture, X-ray structural investigations are often fraught with problems. This is especially true for the extremely reactive organolithium compounds RLi that are not stabilized by a Lewis base. There is thus a lack of information concerning the solid-state structures of these simple molecules.

To date, the only X-ray structure determinations available for such "naked" organolithium compounds are those for R = Me,³ Et,⁴ *n*-Bu,^{2c} *t*-Bu,^{2c} CH₂(*c*-CHCMe₂CMe₂),⁵ *c*-C₆H₁₁,⁶ and CH₂(SiMe₃)_{3-n} (*n* = 0, 7, 1, 8, 29). [Bis(trimethylsilyl)methyl]lithium forms a polymeric chain structure; [tris(trimethylsilyl)methyl]lithium is dimeric in the solid state; methyl-, ethyl-, and *tert*-butyllithium crystallize as tetramers; [(trimethylsilyl)methyl]lithium, *n*-butyllithium, [(tetramethylcyclopropyl)methyl]lithium, and cyclohexyllithium are hexameric. Cyclohexyllithium represents a borderline case in this series of "naked" organolithium compounds since the crystals contain two molecules of benzene per hexamer; although benzene is not normally considered to be a Lewis basic solvent, there is evidence for weak donor interactions between benzene and organolithium compounds (*vide infra*).

We report the crystal structure of isopropyllithium,¹⁰ which is among the first examples of structurally characterized secondary alkyl lithium reagents.¹¹

Isopropyllithium is tetrameric in dilute (<10⁻² M) cyclohexane solutions, but is predominantly hexameric in more concentrated solutions as demonstrated by cryoscopic measurements; benzene as the more Lewis basic solvent favors the existence of tetrameric units.¹² The hexamer–tetramer equilibrium is shifted toward the hexamer upon lowering of the temperature as shown by NMR spectroscopic investigations of 2 M solutions of *i*-PrLi in

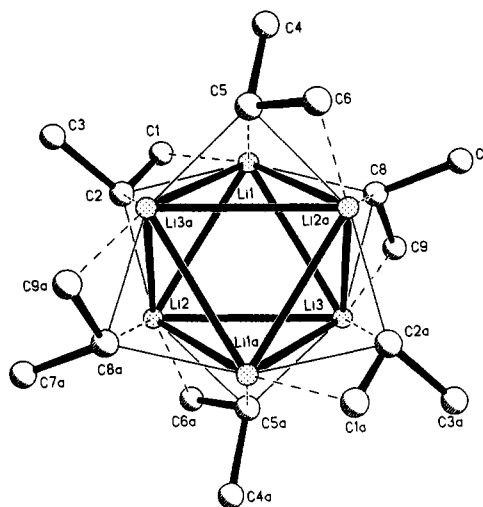


Figure 1. Molecular structure of (*i*-PrLi)₆. Hydrogen atoms are omitted for clarity. Solid lines signify short and dashed lines signify long Li–C distances. Selected bond lengths (Å) and angles (deg): C1–C2 1.531(2), C2–C3 1.533(2), C4–C5 1.528(2), C5–C6 1.541(2), C7–C8 1.533(2), C8–C9 1.541(2); C1–C2–C3 109.2(2), C4–C5–C6 107.99(13), C7–C8–C9 108.00(13).

cyclopentane.¹³ When a 1.86 M solution of isopropyllithium in *n*-hexane¹⁴ is allowed to stand at –35 °C for several days, the hexamer is obtained as colorless platelets.

In contrast to methyl- and ethyllithium there are no interactions between the oligomeric units in the crystal (the shortest Li–C distance between two aggregates is 4.13 Å for *i*-PrLi and 2.52 Å for both MeLi and EtLi).

The crystal structure of isopropyllithium resembles those of *n*-butyllithium^{2c} and benzene-solvated cyclohexyllithium.⁶ The six lithium atoms form a distorted octahedron with six short [2.388(3)–2.404(3), average 2.395 Å] and six long [2.926(3)–3.014(3), average 2.959 Å] Li–Li distances (Figure 1).

Six of the eight faces of the octahedron are each capped by a single *i*-Pr unit. Two almost equilateral (and opposite) triangular faces remain uncapped; it is noteworthy that in (C₆H₁₁Li)₆·2C₆H₆ the two benzene molecules are positioned parallel above the two uncapped faces. The secondary carbon atom (C_α) of an *i*-Pr unit coordinates the two lithium atoms that form the longest side of a capped triangular face [distances: 2.160(3)–2.197(3), average 2.180 Å]. The distance between C_α and the third lithium atom of a capped triangular face is significantly longer [2.297(3)–2.316(3), average 2.308 Å]; at an almost identical distance from this lithium atom is a methyl carbon atom (C_β) of a neighboring

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(2) Recent references: (a) Nichols, M. A.; Williard, P. G. *J. Am. Chem. Soc.* **1993**, *115*, 1568. (b) Barnett, N. D. R.; Mulvey, R. E.; Clegg, W.; O'Neil, P. A. *J. Am. Chem. Soc.* **1993**, *115*, 1573. (c) Kottke, T.; Stalke, D. *Angew. Chem.* **1993**, *105*, 619; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 580. Reviews: (d) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353. (e) Weiss, E. *Angew. Chem.* **1993**, *105*, 1565; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501.

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(10) Crystallographic data: data collection on a Syntex P2₁ four-circle diffractometer with graphite-monochromated Mo K α radiation; structure solution with direct methods, full-matrix least-squares refinement on *F*² (Siemens SHELXTL plus, SHELXL-93). *R* values: *R*₁ = $\sum ||F_o| - |F_c|| / \sum |F_o|$, *wR*₂ = $[\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^2]^{1/2}$. C₃H₇Li, space group *P*1, *Z* = 12, *a* = 9.272(3) Å, *b* = 10.049(3) Å, *c* = 13.734(4) Å, α = 85.12(2)°, β = 84.77(2)°, γ = 63.75(2)°, *V* = 1141.5(6) Å³, *d*_{calc} = 0.873 Mg m⁻³; 6984 reflections, 6617 unique observed, were measured at 173 K. The non-hydrogen atoms were refined anisotropically; all hydrogen atoms were located by difference Fourier synthesis and refined free isotropically. *R*₁ = 0.0584 calculated from 4039 reflections with *F*_o ≥ 4σ(*F*_o); *wR*₂ = 0.1394 for 385 parameters (no restraints). The asymmetric unit contains two crystallographically independent hexamers (each on a center of inversion); they are identical within the margin of error of the structure determination.

(11) Benzene-solvated cyclohexyllithium (C₆H₁₁Li)₆·2C₆H₆ is the only secondary alkyl lithium compound for which crystallographic data are available (ref 6). The structure of cyclopentyllithium has been reported to be isotopic with that of cyclohexyllithium (ref 2c); however, crystallographic data have not been published so far.

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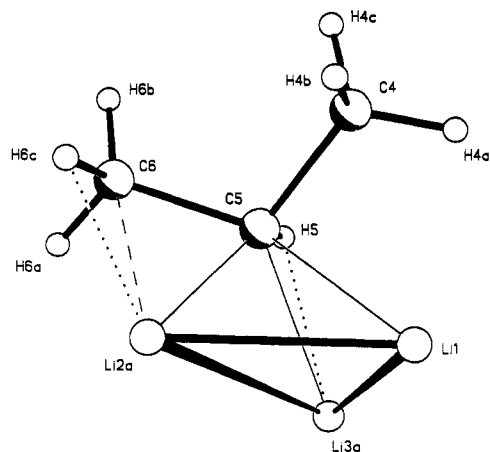


Figure 2. View of one of the Li triangles of the distorted octahedron with a coordinated *i*-Pr group. Selected bond lengths (Å) and angles (deg): C4–H4a 1.04(2), C5–H5 0.99(2), C6–H6a 0.97(2), C6–H6b 1.00(2), C6–H6c 1.04(2), C4–H4b 1.05(2), C4–H4c 0.99(2); C5–C4–H4a 113.2(11), C5–C4–H4b 111.4(11), C5–C4–H4c 116.5(10), C4–C5–H5 103.8(9), C6–C5–H5 103.0(9), C5–C6–H6a 114.8(13), C5–C6–H6b 112.9(10), C5–C6–H6c 111.8(10).

i-Pr unit [2.302(3)–2.314(3), average 2.308 Å]. Thus, each lithium atom is in contact with four carbon and four lithium atoms, respectively, and two short and two long distances are observed in each case. Additionally, the conformation has rather short Li–H distances (Figure 2), with the Li–H_a distances (1.908–1.965, average 1.936 Å) being significantly shorter than the Li–H_β distances (2.005–2.089, average 2.038 Å); strong Li–H_β interactions are discussed to be responsible for the thermal decomposition of alkyl lithium species *via* a β elimination pathway.¹⁵

Our structure determination of isopropyl lithium closes a gap between the structurally characterized primary and tertiary alkyl lithium reagents. As for *n*-BuLi,¹⁶ *t*-BuLi¹⁷ and (c-CHCMe₂-

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CMe₂)CH₂Li,¹⁸ Li–C_β interactions are an important structural feature for *i*-PrLi. Obviously, it is more favorable for all four compounds that a lithium atom interacts with four carbon atoms *via* two short and two long distances, rather than with only three carbon atoms *via* three short distances, which would correspond to a perfectly symmetric capping of a triangular face. The Li–C_β interactions within an oligomeric unit allow the existence of *isolated* aggregates in the crystal. For hexameric Me₃SiCH₂Li and dimeric (Me₃Si)₃CLi, which do not contain C_β atoms, Li–C_γ interactions are observed instead.¹⁹ In the case of (Me₃Si)₂CHLi, EtLi, and MeLi, respectively, the subunits are associated through Li–C_α interactions and form a one-, two-, and three-dimensional array, respectively.

It is remarkable that the basic structure of (C₆H₁₁Li)₆·2C₆H₆ is quite similar to that of (*i*-PrLi)₆. Obviously, the influence of the benzene molecules on the hexameric unit of cyclohexyllithium is almost negligible; this is in contrast to the well-documented depolymerizing effect of benzene on the aggregation of alkyl lithium compounds with a moderately bulky R group in solution.^{1a,12}

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Supplementary Material Available: Details of the X-ray analysis and tables of atomic coordinates, bond lengths and angles, and thermal parameters (14 pages); listing of observed and calculated structure factors (15 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(16) The average Li–C_β distance is 2.29 Å (ref 2c).

(17) The average Li–C_β distance is 2.37 Å (ref 2c).

(18) The average Li–C_β distance is 2.37 Å (calculated from the crystallographic data given in ref 5).

(19) The relevant Li–C_γ distances range from 2.47 to 2.54 Å for (Me₃-Si)₃CLi (ref 7) and from 2.59 to 2.85 Å for Me₃SiCH₂Li (calculated from the crystallographic data given in ref 9); these values are similar to the interaggregate Li–C distances in MeLi (refs 3) and EtLi (refs 4).