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The Physical Properties and Structure of *t*-Butyllithium¹

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t-Butyllithium has been isolated and characterized; it is a colorless crystalline solid, tetrameric over a range of concentrations both in benzene and hexane. The vibrational spectrum of the compound has been studied employing Li⁶ substitution. From Raman spectral evidence, a tetrahedral structure for the molecules of *t*-butyllithium is suggested, in which the lithium and α -carbon atoms occupy the vertices of concentric interpenetrating tetrahedra.

Alkyl lithium compounds are known to be associated in solution from measurements of their molecular weights by the freezing point and boiling point methods in various solvents.²⁻⁶ Recent studies of the mass spectrum⁷ and infrared spectrum⁸ of ethyllithium vapor have indicated that this compound is polymeric even in the gaseous state. The association of alkyl lithium compounds is thought to take place by the formation of Li-C-Li bridge bonds involving multi-center molecular orbitals, similar to those formed in polymeric dimethylberyllium⁹ and the dimeric aluminum trialkyls.^{10,11} Polymerization in such electron-deficient systems is sterically inhibited by alkyl substitution at the alpha carbon atom,^{10,11} which must assume a coordination number greater than four. In addition, Coates¹² has discussed this inhibition of polymerization in terms of decreased electronegative character of the branched alkyl groups. It therefore seemed possible that *t*-alkyllithium compounds would exist as low polymers or even as monomeric molecules. Accordingly, this study of *t*-butyllithium was undertaken.

t-Butyllithium has been known for some time

as a reagent prepared and used in solution,¹³⁻¹⁵ but apparently it has not previously been isolated as a pure substance. The compound can be prepared from *t*-butyl chloride and lithium in refluxing pentane. Recently it has been found that 1-2% sodium alloyed with the lithium is necessary in order for this reaction to take place.¹⁶

Experimental

Materials.—A dispersion in mineral oil of lithium metal (99.7% Li⁷) containing 2% sodium was obtained from the Lithium Corporation of America. Metallic lithium-6 (99.3% isotopic purity) was obtained from the Union Carbide Nuclear Corporation. To this lithium-6 was added 2% sodium and the mixture converted into a similar mineral oil dispersion in the laboratory. The finely divided lithium was filtered from the mineral oil under an argon atmosphere before use. Commercial pentane was purified by treatment with concentrated sulfuric acid, washed, dried, and finally distilled from lithium aluminum hydride. *t*-Butyl chloride was obtained from the Eastman Kodak Company and was redistilled immediately before use.

Preparation of *t*-Butyllithium.—The preparations were carried out under a nitrogen atmosphere. To 150 cc. of purified pentane was added 2.1 g. (0.3 mole) of the lithium-7 dispersion. While refluxing and rapidly stirring this mixture, 10 g. (0.11 mole) of *t*-butyl chloride in 150 cc. of pentane was added very slowly over 10-15 hr. After the reaction mixture had cooled, it was transferred to an argon filled drybox where the solids were removed by filtration. The solvent then was evaporated at reduced pressure and the solid residue was sublimed at 70-80° (0.1 mm.). The yield of *t*-butyllithium-7 was 4.4 g. (63%). The compound was analyzed by titration with standard hydrochloric acid. Equivalent weight: Calcd. for C₄H₉-

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Li: 64.1. Found: 65.9. Flame photometric analysis indicated the presence of about 0.04% sodium in the compound.

The preparation of *t*-butyllithium-6 was accomplished in the same manner.

Infrared Spectra.—The spectra of samples in Nujol or in benzene solution were measured in the 650–3500-cm.⁻¹ region using a Baird Model 4-55 double-beam spectrometer with a sodium chloride prism. The 350–650-cm.⁻¹ region of the spectrum was studied using a Perkin-Elmer Model 112 single-beam spectrometer with a cesium bromide prism. An attempt was made to obtain the spectrum of a sample in perfluorokerosene, which contains no C–H bonds. However, the *t*-butyllithium reacted with this mulling agent to form a carbonaceous mass.

When the single beam instrument was used, the spectrum of the solvent or mulling agent was obtained, with identical instrument settings, soon after the organolithium compound was studied. Values of I/I_0 were calculated by dividing the sample spectrum by that of the solvent or mulling agent point by point. The error in measurement of band positions obtained by this method was ± 1 cm.⁻¹ in most cases. In a few cases where the band maxima were broad, the error was ± 2 cm.⁻¹.

The vapor spectra were obtained using the single-beam instrument. A sample of *t*-butyllithium was placed into a cell of 9 cm. path length with cesium iodide windows, in the drybox. The cell then was evacuated to ca. 0.5 atm, and sealed off. For the determination of a spectrum the cell was heated to ca. 100° in an aluminum block thermostat. After the spectrum had been obtained, the cell was cooled to room temperature and the spectrum was remeasured to obtain values of I_0 . This was done in order to cancel out any effects due to volatile impurities. The room temperature spectrum also served to show that sublimation of the sample onto the cell windows had not taken place to any significant extent.

Raman Spectra.—The Raman spectra were obtained using a Cary Model 81 Raman spectrometer employing the mercury 4358 Å. line for excitation. The *t*-butyllithium samples were studied as 15% solutions in benzene, in Cary 7-mm. diameter cells.

N.m.r. Spectra.—N.m.r. spectra of solutions of *t*-butyllithium in benzene were determined on a Varian A-60 spectrometer. The benzene peak was taken as an internal reference. With the use of a spectrum of a sample of tetramethylsilane in benzene, the chemical shifts from the benzene reference peak were converted into τ values.¹⁷ Benzene solutions of ethyllithium and 2,2,4-trimethylpentane also were studied for comparative purposes.

X-Ray Powder Pattern Measurement.—A Pyrex capillary, 0.5 mm., was loaded with finely ground *t*-butyllithium-7 in the drybox. The capillary was sealed, loaded into an X-ray powder camera (57.3 mm. radius) and exposed for 6 hr. to CuK α radiation ($\lambda = 1.539$ Å.). The resulting pattern was analyzed using standard techniques. Lines were observed at the following d -spacings in Å.: 7.8 (m); 7.2 (s); 6.4 (w); 6.1 (m); 5.8 (w); 5.1 (m); 4.5 (m); 4.35 (s); 4.1 (m,d); 2.65 (m); 2.7–2.9 (m, broad diffuse band); 2.50 (w); 1.76 (w) (s = strong, m = medium, w = weak, d = diffuse).

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Boiling Point Measurements.—A differential ebulliometer¹⁸ was modified in such a way as to effect the rigorous exclusion of moisture and oxygen. The differential thermometer was a thermopile consisting of 41 copper-constantan thermocouples in series. The differential e.m.f. was measured on a Rubicon Type B high precision potentiometer with a Kiethley d.c. vacuum-tube voltmeter, Model 200B, as the null point detector. Temperatures were read to $\pm 0.002^\circ$. The thermopile was calibrated by measuring e.m.f. as a function of temperature differential, measured with two previously standardized Beckmann thermometers. The calibration was made at a number of temperatures in the range of interest.

Measurements were made at various concentrations in benzene and in hexane. No decomposition was observed after 10–15 min. of refluxing in either of these solvents. The average degree of association was calculated using 2.53 and 2.75 as the ebullioscopic constants for benzene¹⁹ and hexane,²⁰ respectively. The solutions were analyzed by titration with aqueous hydrochloric acid to a phenolphthalein end point, with isopropyl alcohol added for homogeneity.

Results and Discussion

Pure *t*-butyllithium is a colorless crystalline solid. It is pyrophoric in air and is readily soluble in hydrocarbon solvents. The compound sublimes readily at about 70° and 0.1 mm. pressure.

t-Butyllithium does not melt when heated in a sealed tube, but slowly decomposes at temperatures above 140°. A solution of the compound in refluxing *n*-heptane turned brown and deposited a precipitate after about an hour, indicating that noticeable decomposition had occurred during this time. The evolved gases were found to consist of 94% isobutylene and 6% isobutane. This parallels the results of Ziegler and Gellert,²¹ who obtained 95% 1-butene and 5% *n*-butane from the decomposition of *n*-butyllithium in boiling octane (126°). The decomposition of *t*-butyllithium in *n*-heptane probably occurs principally in the manner indicated by the equation



The small amount of isobutane may indicate that some hydride abstraction takes place at the temperature of the experiment.²¹

Measurements of the molecular weight in benzene and hexane solution (Table I) show that the average degree of association of *t*-butyllithium is very nearly four over a considerable range of concentrations in both solvents. These results

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(21) K. Ziegler and H. Gellert, *Ann.*, **567**, 179 (1950).

indicate preferential polymerization to a tetrameric form. If equilibrium exists between several species in solution this equilibrium must be greatly displaced in favor of the tetramer. It is interesting to compare these results with those for ethyllithium, which exhibits a degree of association of about six in benzene solution.^{2,3} Recently, ethyllithium vapor has been shown to consist exclusively of tetrameric and hexameric molecules.⁷

The infrared and Raman spectral data for *t*-butyllithium-6 and -7 are given in Table II. In the C-H stretching region, a pair of bands are observed at unusually low frequencies. The presence of these bands in the spectra of methyl- and ethyllithium has been noted previously^{2,8} and attributed to the influence of electron deficient bonding on the character of the alpha carbon-hydrogen bond. However, in the case of *t*-butyllithium, the carbon atoms involved in the electron deficient bonding have no attached hydrogen atoms. Thus the exact nature of these low frequency bands remains in doubt.

By analogy with the spectra of other compounds containing *t*-butyl groups,²²⁻²⁵ the remaining infrared bands in the sodium chloride region (near 1450, 1375, 1210, 1130, 1000, 925, and 780 cm.⁻¹) can be assigned to various vibrations of the *t*-butyl moiety.²⁶ None of these bands shift upon substitution of Li⁶ for Li⁷, and so they cannot represent vibrations involving the lithium atom to any significant extent.

As was observed previously for the infrared spectra of other alkyl lithium compounds,⁸ bands which shift upon lithium isotopic substitution occur only below 625 cm.⁻¹. Bands are found at 480 and 420 cm.⁻¹ in the infrared spectrum of *t*-butyllithium-7 dissolved in benzene. These bands shift to 496 and 429 cm.⁻¹ upon substitution of Li⁶ for Li⁷. The band at 525 cm.⁻¹ (shifting to 533 cm.⁻¹) can be attributed to an impurity, because it exhibited widely variable intensity in various determinations and disappeared altogether

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(25) R. S. Rasmussen, *ibid.*, **16**, 712 (1948).

(26) There is some disagreement as to the exact assignment of several of these bands. The bands near 1450 and 1375 cm.⁻¹ are probably C-H bending vibrations. Although the band around 925 cm.⁻¹ is very weak in the spectrum of *t*-butyl iodide,²² it is much stronger in the spectra of isobutane and neopentane.^{24,25} This band is thought to be characteristic of the *t*-butyl group, but it is not clear whether it is due to a C-C stretching or a methyl rocking mode. The band near 1000 cm.⁻¹ is much more intense in the spectrum of *t*-butyllithium than in the spectra of isobutane or neopentane. It has been assigned by Rasmussen²⁵ to a skeletal vibration.

TABLE I
DEGREE OF ASSOCIATION OF *t*-BUTYLLITHIUM IN BENZENE
AND *n*-HEXANE

Solvent	Concn., <i>m</i>	Degree of assoc. ^a
Benzene	0.049	3.5 ± 0.3
	.052	3.7 ± 0.3
	.087	3.5 ± 0.2
	.104	3.7 ± 0.2
	.117	4.2 ± 0.2
	.182	3.9 ± 0.2
	Av.	3.8 ± 0.2
<i>n</i> -Hexane	.052	3.7 ± 0.3
	.106	3.9 ± 0.2
	.164	4.3 ± 0.2
	.226	3.9 ± 0.2
	Av.	4.0 ± 0.2

^a Limits of error to 90% confidence.

in one spectrum.²⁷ The low frequencies of the bands which shift upon lithium isotopic substitution are consistent with their assignment to complex modes of vibration of the tetrameric molecules. The volatility of *t*-butyllithium was so low at 100° that bands below 625 cm.⁻¹ could not be observed in the vapor spectra. Bands were observed in the sodium chloride region, although the absorption was weak. These bands occurred at the same frequencies as those in the benzene solution spectra.

In the Raman spectra of *t*-butyllithium only a single band was found which shifts upon lithium isotopic substitution. This strongly polarized band occurs at 521 cm.⁻¹ in the Li⁷ compound and shifts markedly to 563 cm.⁻¹ with substitution of Li⁶ (Fig. 1).

The proton magnetic resonance spectrum of a 15% solution of *t*-butyllithium in benzene showed only a single narrow line at $\tau = 9.01$, indicating that the environment of all nine protons is identical, at least on a time-average basis. There was no change of resonance position upon lithium isotopic substitution. The resonance occurs at appreciably higher field than that for the methyl protons of ethyllithium dissolved in benzene ($\tau = 8.73$). The magnetic environment of the protons of the *t*-butyl group is not greatly different in *t*-butyllithium and in 2,2,4-trimethylpentane. In the latter compound the *t*-butyl protons come into resonance at $\tau = 9.11$ in benzene solution.

The Structure of the *t*-Butyllithium Tetramer.—

(27) Since there appears to be a correspondence between the bands in the benzene and Nujol spectra, the band at 522 cm.⁻¹ (shifting to 538 cm.⁻¹) in the latter possibly also is due to an impurity. The spectrum of lithium *t*-butoxide was determined and none of the bands in the spectrum of *t*-butyllithium were found to be due to this likely impurity.

TABLE II
 LIST OF FREQUENCY (CM.⁻¹) MAXIMA FOR *t*-BUTYLLITHIUM SPECTRA

<i>t</i> -C ₄ H ₉ Li ⁶				<i>t</i> -C ₄ H ₉ Li ⁷			
Raman ^{a,b}	Nujol	Infrared Benzene	Vapor	Raman ^{a,b}	Nujol	Infrared Benzene	Vapor
2833	2810	2805		2835	2810	2805	
2781 (dp)			2780	2782 (dp)			2780
2755	2730	2725		2757	2730	2725	
2692 (p)				2692 (p)			
2603 (p)				2603 (p)			
1474 (dp)		1455		1475 (dp)		1455	
1436 (dp)				1433 (dp)			
1385 (dp)		1375		1385 (dp)		1375	
1360 (dp)	1350	1355		1360 (dp)	1350	1355	
	1210	1215	1210		1210	1215	1210
1129 (p)	1130	1130	1130	1130 (p)	1130	1130	1130
	995	990	980		995	990	980
929 (a)	930	930	925	933 (a)	930	930	925
773 (dp)	775	780		774 (dp)	775	780	
	608				580		
563 (p)				521 (p)			
	538	(533)			522	(525)	
	500	496			480	480	
463 (p)				467 (p)			
	429	429			415	420	
383 (dp)	386	384		388 (dp)	385	384	

^a Raman spectra taken on solutions in benzene. ^b p, polarized; dp, depolarized; a, possibly due to a benzene vibration.

Two general types of structures can be considered for the tetrameric molecules of *t*-butyllithium: I. Some type of an eight-membered cyclic structure, in which ordinary three-center electron-deficient bonds are present, involving two lithiums and one carbon atom. Such a ring might have the crown, tub, chair, or other conformations, but the highest possible symmetry would be that for the regular puckered crown form, in which the eight atoms in the ring would constitute a

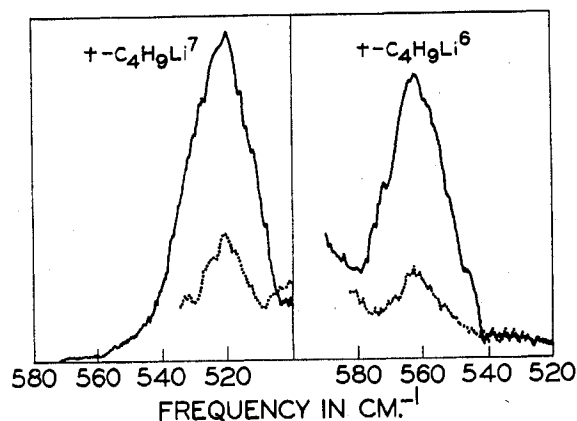


Fig. 1.—Raman spectra of *t*-butyllithium-6 and -7 in the region 500–600 cm.⁻¹: —, parallel polarization; ·····, perpendicular polarization.

C_{4v} point group. II. A structure in which the lithium and α -carbon atoms occupy the vertices of two concentric interpenetrating tetrahedra.²⁸ The structure is that of a cube, in which lithium atoms at alternate corners have been pushed in along the threefold axes (Fig. 2). The lithium and α -carbon atoms make up the framework of a structure which would have T_d symmetry.

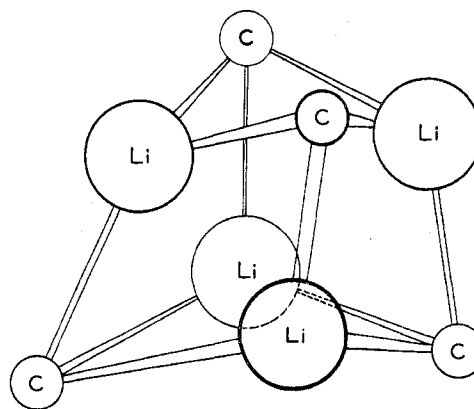


Fig. 2.—Proposed model for the C–Li framework in *t*-butyllithium tetramer.

(28) This structure is essentially the same as that proposed by T. L. Brown and his co-workers for the tetramer of ethyllithium. T. L. Brown, D. W. Dickerhoof, and D. A. Bafus, *J. Am. Chem. Soc.*, **84**, 1371 (1962).

Both types of structures are equally consistent with the n.m.r. and infrared spectral evidence as well as with the molecular weight determinations. However, the Raman spectra of *t*-butyllithium-6 and -7 seem to provide a means for distinguishing between these models. Because of its strong polarization and large shift on isotopic substitution, the Raman line at 521 cm.^{-1} (563 cm.^{-1} in *t*-butyllithium-6) can be identified as a totally symmetric C-Li stretching frequency. This vibrational mode should be infrared-active in structures of C_{4v} or lower symmetry, but infrared-inactive in structures of symmetry class T_d .²⁹ No observed infrared band shows either the frequency or magnitude of shift upon isotopic substitution necessary for assignment to the totally symmetric mode. The tetrahedral structure (Fig. 2) therefore is favored.

In the proposed structure, bonding would be by means of four equivalent *four-center* electron-deficient bonds, each involving three lithium atoms

(29) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Princeton, N. J., 1945, chapter III.

and the sp^3 orbital of one α -carbon atom. Each lithium would be involved in three such four-center bonds, and so could use a larger number of orbitals for electron-deficient bonding than would be possible if only three-center bonds were formed. The structure is very similar to that found by Rundle and Sturdivant³⁰ for the tetramer of tetramethylplatinum. In this compound the platinum atoms and four of the carbons occupy the vertices of the two interpenetrating tetrahedra. A related structure involving electron-pair rather than electron-deficient bonding is that of the tetramer of thallium(I) methoxide.³¹

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