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Spectra and Structure of Sterically Hindered Lithium Phenoxides*

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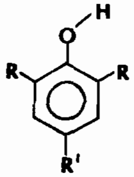
It has been shown from molecular weight determination and infrared spectra that lithium 2,6-di-tert-butyl-4-cresoxide-THF adduct is dimeric in benzene solution as well as in the crystalline state whereas lithium 2,6-dimethylphenoxide is dimeric in dioxane solution but polymeric in the crystalline state. Probable structures of the dimeric species have been discussed based on infrared and NMR spectra.

Introduction

Organic lithium compounds tend to form polymers in all physical states. Lithium alkyls and aryls form dimeric to hexameric aggregates in solution.[1-7] Lithium alkoxides are polymeric even in the gaseous state.[6] For example, lithium tert-butoxide is hexameric in benzene[6] and cyclohexane.[8,9] Even at 180°C in the vapor phase, it gives an infrared spectrum similar to that in the solid state (polymer).[10] The main purpose of this research was to obtain relatively simple lithium phenoxides by introducing steric hindrance around the O–Li–O bond,[11] and to obtain structural and bonding information from their molecular weights, infrared and NMR spectra. The lithium salts of the following 2,6-dialkyl-phenols have been studied in this paper.



R = t–Bu, R′ = CH_3, 2,6-Di-tert-butyl-4-cresol (abbreviated as DTBC)

R = CH_3, R′ = H, 2,6-Dimethylphenol (abbreviated as DMP)

Experimental Section

Preparation of Compounds. 1) Li–DTBC–THF. A solution of butyllithium in n-hexane (purchased from Alfa Inorganics) was added to a THF solution of DTBC from a hypodermic syringe in a 1:1 molar ratio using a minute amount of 1,10-phenanthroline as an indicator.[12]. After evaporating the solvent at reduced pressure, a white crystalline material was obtained. This solid was dried *in vacuo* at 110°C for four hours to remove excess THF. Lithium analysis: Calcd. for Li–DTBC–THF, 2.32%. Found, 2.32± 0.01%. This 1:1 adduct is soluble in benzene and can be recrystallized from it.

2) Li–DMP[13] . Lithium metal chunks were added to a toluene solution of DMP, and the mixture was refluxed under constant stirring in a nitrogen atmosphere for several days. After evaporation of toluene, a white crystalline solid was obtained. It was dricd *in vacuo* for several hours at 110°C. Lithium analysis: Calcd. for Li–DMP, 5.37%. Found, 5.32± 0.01%.

Lithium compounds containing ^{6}Li isotopes were prepared by using metallic ^{6}Li (isotope abundance, 99.32%) purchased from Oak Ridge National Laboratory. All the phenols used were purified by the conventional methods. THF and benzene were distilled twice over lithium aluminum hydride. Dioxane was distilled from melted sodium after refluxing it for three to five days. Carbon tetrachloride (Spectro grade) was purchased from Fisher Scientific Company.

All the rections were carried out in an oxygen- and moisture-free atmosphere since lithium phenoxides

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Table I. Molecular Weight Determination

Compound	Solvent	Concentration* Range (Mole/Kg solvent)	Molecular Weight	Degree of Polymerization
Li–DTBC–THF	Benzene	0.016-0.031	534 ± 16**	1.79 ± 0.06**
Li–DMP	Dioxane	0.015-0.081	242 ± 19**	1.89 ± 0.18**

* As monomer. ** Average deviation.

are easily oxidized by oxygen and readily react with moisture.

Molecular Weight Determination. The molecular weights of lithium phenoxides were determined by cryoscopic methods with a Beckman molecular weight apparatus which was modified to flush the whole system with dry nitrogen. The molecular weight of Li–DTBC–THF was measured in benzene while that of Li–DMP was determined in dioxane. Both compounds were not soluble in the same solvent. Table I gives the results of molecular weight determination.

Spectral Measurements. The infrared spectra (4000-200 cm^{-1}) of lithium phenoxides were measured on a Beckman IR 12 infrared spectrophotometer. All the sampling procedures were made in a dry bag to avoid contact with air. The spectra of solids were obtained as Nujol mulls sandwiched between CsI plates. The spectra of THF and benzene solutions were obtained by using 0.1 mm NaCl liquid cells (400-600 cm^{-1}) and 0.5 mm polyethylene cells (600-200 cm^{-1}). The NMR spectra of Li–DTBC–THF in various solvents were measured on a Varian A-60 NMR spectrometer. TMS was used as the internal standard.

Results and Discussion

Li–DTBC–THF. As is shown in Table I, Li–DTBC–THF is predominantly dimeric in benzene solution. Figure 1 illustrates the most probable structure of the dimer derived by constructing a molecular model. In order to minimize steric hindrance due to bulky tert-butyl groups, it was necessary to place the DTBC molecules perpendicular to and the THF molecules coplanar with the Li_2O_2 plane.

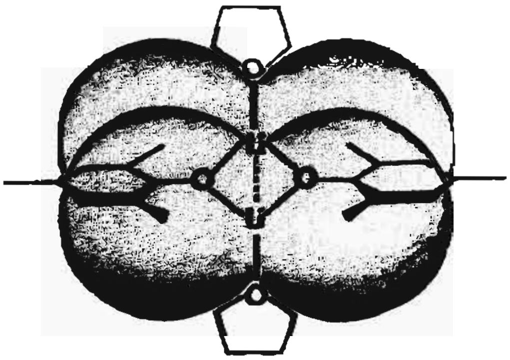

Figure 1. Proposed dimer structure of Li–DTBC–THF (Li–O = 1.95 A, Li–O(THF) = 2.00 A, O–C(DTBC) = 1.27 A, <OLiO = 90°. The sphere indicates the van der Waals radius of the tert-butyl group (3.00 A).

Table II. NMR Chemical Shifts of Li–DTBC–THF and Related Compounds*

		DTBC			THF	
		CH_3		CH	CH_2	
Compound	Solvent	t-Bu	4-CH_3	3,5	α	β
THF	benzene	—	—	—	3.57	1.46
	CCl_4	—	—	—	3.61	1.77
DTBC	benzene	1.39	2.29	—**	—	—
	CCl_4	1.39	2.22	6.82	—	—
Li–DTBC–THF	benzene	1.70	2.42	7.30	3.19	1.03
	CCl_4	1.40	2.15	6.73	3.48	1.68

* δ, ppm. ** Overlapped with solvent signal.

As Table II shows, the α- and β-methylene proton signals of THF in the dimer are 3.48 and 1.68 ppm while those of free THF in CCl_4 solution are 3.61 and 1.77 ppm down field from the TMS internal standard. Thus the methylene proton signals of THF are shifted to a higher field upon coordination to Li–DTBC. This is due to the following reasons. Assuming that the Li–O distance and the Li–O–Li angle of the Li_2O_2 ring (Fig. 1) are 1.95 Å and 90°, respectively, the magnitude of higher field shifts of the THF methylene proton signals due to the ring current of the benzene rings of the DTBC molecules is estimated to be 0.1 ~ 0.2 ppm.[18] Such a high field shift due to the ring current of aromatic rings has been reported for fluorenyllithium-THF complex.[19] Furthermore, the anisotropic effect of the C–O bonds of the DTBC molecules contributes to a high field shift of the THF methylene proton signals. The higher field shift observed in this work is contrary to the general observation that, upon coordination to alkali metals, the proton signals of donor molecules are shifted to a lower field by 0.1 ~ 0.3 ppm due to a decrease in electron density of the donor atom.[14-17] However, the present anomaly rather supports the proposed structure because of the reasons mentioned above. Table II shows that these shifts are larger in benzene than in carbon tetrachloride. This is because the solvent molecules exert and additional anisotropic effect on the THF protons in benzene solution.[20-22]

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Table III. Far-infrared spectra of Li–DTBC–THF and Li–DMP (cm^{-1})

^{6}Li–DTBC–THF				^{6}Li–DMP			
Nujol		THF		Nujol		THF	
ν	Δν[a]	ν	Δν[a]	ν	Δν[a]	ν	Δν[a]
681 (w)	1	681 (w)	3	690 (s)	0	696 (m)	6
574 (s)	5	574 (s)	7	584 (s)	3	580 (sh)	1
556 (s)	11	556 (s)	12	558 (s)	17	532 (s)	3
531 (s)	21	531 (sh)	19	505 (s)	24	496 (sh)	2
475 (m)	6	471 (m)	2	470 (m)	17	440 (s)	17
444 (w)	2	446 (w)	1	419 (m)	19	360 (m)	12
404 (m)	4	406 (m)	7	330 (m)	2		
352 (m)	1	353 (m)	0	288 (w)	0		
282 (w)	10		---[b]	238 (m)	14		---[b]

[a] ν(^{6}Li)–ν(Li). Li(natural abundance) contains 7.4% of ^{6}Li and 92.6% of ^{7}Li. [b] Obscured by solvent absorption. Intensity designation: s, strong; m, medium; w, weak; sh, shoulder.

Table III compares the far-infrared frequencies of ^{6}Li–DTBC–THF and its Li (natural abundance; ^{6}Li, 7.4% and ^{7}Li, 92.6%) analog in Nujol mull and THF solution. It is seen that two bands at 556 and 531 cm^{-1} of the former are shifted to lower frequencies by the isotopic substitution. The dimer structure proposed in Fig. 1 belongs to C_{2h} point group, in which two Li–O stretching modes are infrared active. Thus, these two isotope-sensitive bands must be assigned to the Li–O stretching vibrations of the Li$_2$O$_2$ ring. Table III also shows that the band near 282 cm^{-1} of the ^{6}Li–DTBC–THF is shifted by 10 cm^{-1} to a lower frequency by the isotopic substitution. This band may be assigned to the O–Li–O bending mode of the Li$_2$O$_2$ ring.

The spectrum of Li–DTBC–THF in Nujol mull is very similar to that of the THF solution. This result indicates that Li–DTBC–THF is dimeric even in the crystalline state.

Li–DMP. Li–DMP is dimeric in dioxane solution. However, its molecular weight in THF could not be determined. Table III shows, however, that Li–DMP in THF solution exhibits only two bands (*ca.* 440 and 360 cm^{-1}) which are sensitive to the isotopic substitution. This result may indicate that the Li–DMP molecules in THF solution take a dimeric structure similar to that of Li–DTBC–THF discussed previously. In this case, however, the Li atom of the Li$_2$O$_2$ ring may be coordinated by two THF molecules to attain a tetrahedral environment. Such a structure is probable since steric hindrance of the methyl groups of DMP is much smaller than that of the tert-butyl groups of DTBC.

As is shown in Table III, the (Li–DTBC–THF)$_2$ molecule exhibits two Li$_2$O$_2$ stretching bands at 556 and 531 cm^{-1} whereas the (Li–DMP)$_2$ molecule exhibits them at 440 and 360 cm^{-1} in THF solution. Lowering of the Li–O stretching frequencies in going from (Li–DTBC–THF)$_2$ to (Li–DMP)$_2$ in THF also supports the proposed tetrahedral environment of the Li atom in the latter, since an increase in the coordination number greatly reduces the stretching frequency.

Table III shows that the spectrum of Li–DMP in Nujol mull is markedly different from that of a THF solution. The former shows at least four bands between 560 and 410 cm^{-1} which are sensitive to the isotopic substitution of the lithium atom. This result may suggest that crystalline Li–DMP is polymeric as found for solid ethyllithium.[23]

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