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CIRCULAR DICHROISM INDUCED ON ARYLMETHYL CARBANIONS

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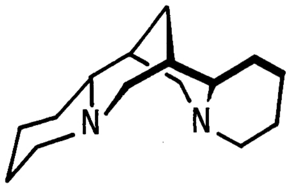
Circular dichroism spectra of fluorenyllithium, benzyllithium, diphenylmethyllithium, triphenylmethyllithium, and 1,1-diphenylhexyllithium were measured in the presence of chiral tertiary diamines, (-)-sparteine, (+)- and (-)-2,3-dimethoxy-1,4-bis(dimethylamino)butane. All the carbanions showed induced circular dichroism (ICD) in nonpolar mediums.

The behavior and structure of carbanions in solutions have been extensively investigated by a variety of techniques such as electronic, nuclear magnetic resonance, and electron spin resonance spectroscopies.$^{1)}$ For example, the electronic spectra of fluorenylalkali metal salts show clear evidence for the existence of two distinct ion pairs, contact and solvent separated (or loose) ion pairs,$^{2)}$ and ^{1}H, ^{7}Li, and ^{13}C NMR spectra of arylmethyllithiums afford important information on the delocalization of the carbanions.$^{3)}$ In this letter we describe the circular dichroism (CD) spectra of fluorenyllithium and arylmethyllithiums induced by chiral tertiary diamines, (-)-sparteine (**1**), (+)- and (-)-2,3-dimethoxy-1,4-bis(dimethylamino)butane (**2**).

Figure 1 shows the UV and CD spectra of fluorenyllithium in the presence of equimolar amount of **1** in toluene.$^{4)}$ The UV spectral pattern is consistent with that reported for the fluorenyllithium existing as a contact ion pair$^{2)}$ and CD was



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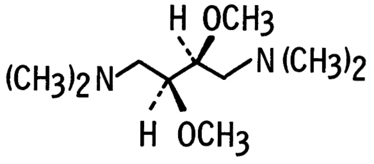

(+)-**2**

induced near the UV absorption maxima. The UV and CD spectral pattern and their relative intensity were not varied by the existence of excess 1 up to fivefold, suggesting that a 1 : 1 complex was formed between the lithium salt and 1. The coordination of two molecules of 1 appears to be prohibited because of sterical reason. The observation of the induced CD (ICD) suggests that 1 exists in a position close to fluorenyl anion by coordinating to Li cation. This is also supported by the fact that fluorenyllithium-1 complex is an effective chiral initiator in the asymmetric polymerization of triphenylmethyl methacrylate.[5)] Although the existence of this type of a contact ion pair (coordinated contact ion pair) in solution has been postulated for fluorenyllithium in the presence of a powerful coordinating agent like dimethyl sulfoxide, no spectral evidence has been obtained because the contact ion pair and the coordinated contact ion pair of fluorenyllithium show undistinguishable UV spectra.[2)]

When (+)- and (-)-2 were used as chiral ligands, 1,1-diphenylhexyllithium gave UV and CD spectra depicted in Fig. 2. The CD patterns were mirror images to each other whose intensities were comparable to the corresponding UV intensities and the concentrations of the lithium compound.

The UV and CD data of fluorenyllithium, benzyllithium, diphenylmethyllithium, triphenylmethyllithium, and 1,1-diphenylhexyllithium in the presence of 1 are summarized in Table 1. All lithium salts displayed the ICD spectra. The relative intensity of the ICD to the optical density of UV absorption depended greatly on

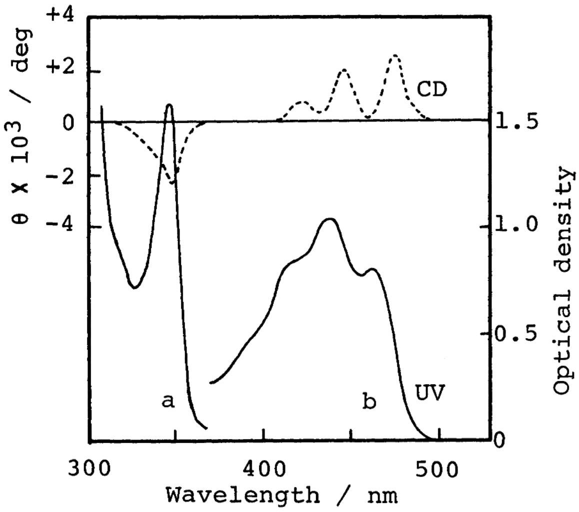

Fig. 1. UV and CD spectra of fluorenyllithium in the presence of 1 in toluene at -78 °C. Concentration: 0.010 mol l^{-1} for a and 0.050 mol l^{-1} for b. Path length of cell 0.015 cm.

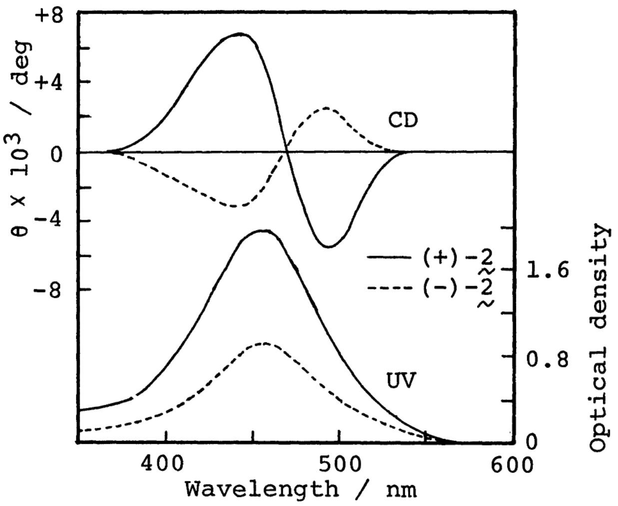

Fig. 2. UV and CD spectra of 1,1-diphenylhexyllithium in the presence of equimolar amount of 2 in toluene at -78 °C. Concentration: 0.010 mol l^{-1} for (+)-2 and 0.005 mol l^{-1} for (-)-2. Path length of cell 0.010 cm.

the carbanions. Benzyllithium showed two positive CD peaks at 332 and 410 nm, indicating that there exists an electronic transition at around 400 nm which is a shoulder in the UV spectrum and difficult to detect. The ICD of diphenylmethyllithium showed a simple weak positive peak near the UV maximum, whereas intense positive and negative ICD peaks were observed for triphenylmethyllithium. The CD spectral pattern of 1,1-diphenylhexyllithium was very similar to that shown in Fig. 2 and completely different from that of diphenylmethyllithium. It was rather similar to that of triphenylmethyllithium in respect of the appearance of positive and negative peaks.

The difference in the ICD of these three arylmethyllithiums may be related with the sterical hindrance of phenyl rings. It is known that three phenyl rings of triphenylmethyllithium have a propeller geometry.6) The existence of chiral **1** may result in the formation of either right- or left-handed propeller in excess.

Table 1. UV and CD spectral data of organolithiums in the presence of **1** at -78 °Ca)

Lithium compound	Solvent	Concentrationb) mol l^{-1}	Path length cm	UV		CD	
				λmax nm	ε	Wavelength nm	Δε cm^2 mmol^{-1}
Fluorenyl-Li	Toluene	0.010	0.015	347	10000	346	0.45
		0.050	0.015	418	1100c)	420	0.03
				438	1400	445	0.08
				465	1000	475	0.11
Benzyl-Li	Toluene	0.0092	0.011	333	14000	295	-2.4
				400	1700c)	313	0
						332	2.2
						410	1.4
	Heptane	0.010	0.015	329	13000	297	-2.2
				380	1200	310	0
						324	2.4
						402	0.57
Diphenylmethyl-Li	Heptaned)	0.0030	0.050	407	13000	408	0.69
Triphenylmethyl-Li	Heptane	0.0046	0.050	437	7500	374	7.5
				400	5800c)	415	0
						448	-3.2
						480	-3.3
1,1-Diphenylhexyl-Li	Toluene	0.0043	0.012	450	19000	435	6.1
						468	0
						498	-5.6
	Toluenee)	0.0043	0.012	446	15000	435	4.0
						475	0
						500	-1.9
	Heptane	0.0050	0.015	440	17000	422	3.9
						458	0
						492	-2.7

a) Molar ratio of Li compound to **1** was 1 : 1. b) Estimated from the amounts of BuLi added. c) Shoulder. d) Solubility at -78 °C was very low. Measured at 25 °C. e) Measured at 25 °C.

Because the propeller structure is chiral,[7) the CD spectrum of triphenylmethyllithium may arise partly from this chirality. Contribution of this type of chirality seems to decrease in the order of triphenylmethyllithium > 1,1-diphenylhexyllithium > diphenylmethyllithium. The ICD for the carbanions decreased with an increase of temperature as shown for 1,1-diphenylhexyllithium in Table 1. This may be due to the fact that the coordination of the chiral ligands is more tight at lower temperatures.

The results reported in this letter appear to be the first observation of the ICD on carbanions, which provides new information on the structure of carbanions. The application of the present method to other carbanion systems such as the anionic polymerizations of styrene and methyl methacrylate is underway.

References

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4) Carbanions were prepared in a vessel equipped with a quartz optical cell and a spacer under dry nitrogen. 9-Fluorenyl, benzyl, diphenylmethyl, and triphenylmethyllithiums were prepared by exchange reaction between corresponding hydrocarbons and butyllithium (BuLi) in the presence of **1**. 1,1-Diphenylhexyllithium was obtained by addition reaction of BuLi to 1,1-diphenylethylene. The UV and CD spectra were measured with a Hitachi 124 spectrophotometer and a JASCO J40 CD apparatus, respectively. A quartz Dewar vessel with optical windows and an Oxford ND704 cryostat were used for low-temperature measurements.

5) Y. Okamoto, T. Takeda, and K. Hatada, unpublished data; the complex afforded quantitatively the THF-soluble (+)-poly(triphenylmethyl methacrylate) which is useful to prepare the chiral packing material for high-performance liquid chromatographic resolution of enantiomers; cf. Y. Okamoto, S. Honda, I. Okamoto, H. Yuki, S. Murata, R. Noyori, and H. Takaya, J. Am. Chem. Soc., 103, 6971 (1981) and references cited therein.

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