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NUCLEAR MAGNETIC RESONANCE STUDIES OF 1,1-DIPHENYL-n-BUTYLLITHIUM IN MIXED SOLVENTS OF BENZENE AND TETRAHYDROFURAN

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SUMMARY

1,1-Diphenyl-n-butyllithium (DPB^-), 1,1-diphenyl-n-butyllithium-3,4-d_5 ($DPB\text{-}d^-$), and 1,1-diphenyl-n-hexyllithium (DPH^-) were prepared by the reactions of 1,1-diphenylethylene with corresponding alkyllithiums in benzene and benzene-d_6. The NMR spectra of these anions were measured in mixed solvents of benzene and tetrahydrofuran (THF). The chemical shifts of the aromatic and aliphatic protons showed minima at $THF/DPB^- = 2$ and those of methylene protons of THF moved to downfield rapidly up to the same ratio of THF to DPB^-. These phenomena were explained by assuming the dimer formation of DPB^- in benzene.

INTRODUCTION

In the anionic polymerization involving a lithium counterion, the polarity of solvent has a great influence upon initiation and propagation reactions[1]. The NMR spectra of living anions can provide us rather direct information about the chemical structures of active species. A number of NMR spectra have been measured on organolithium compounds[2-14]. Most recently, McKeever and Waack reported the study of ^{13}C, ^7Li, and ^1H NMR of benzyllithium and 1,1-diphenyl-n-hexyllithium in a variety of solvents[15]. The solvent dependency of the NMR was interpreted as evidence that the α-carbons of these arylmethyllithiums have appreciable sp^3 character which increases with decreasing solvent polarity[15].

In the present study we measured the NMR spectra of DPB^-, $DPB\text{-}d^-$, and DPH^- in the continuous mixtures of benzene and THF, and discussed the structures of the anions in these solvents.

EXPERIMENTAL

Materials.

Ethyllithium-d_5 was prepared from ethyl-d_5 bromide and metallic lithium in benzene at 50°. After reaction for 1 h, solid parts were separated by filtration. The resultant solution including unchanged ethyl-d_5 bromide was distilled *in vacuo* immediately, and then dry benzene-d_6 was distilled onto the residue. The ethyllithium-d_5

obtained was recrystallized in the solvent using a high vacuum system[16]. The benzene-d_6 solution of the product gave no peak except that of benzene. Ethyllithium was prepared by the same method described above.

n-Butyllithium was prepared in benzene according to the method of Ziegler[17].

Each anion, DPB$^-$, DPB-d^-, and DPH$^-$ was prepared in benzene or benzene-d_6 by an equimolar reaction of 1,1-diphenylethylene with the corresponding alkyllithium compound for 72 h at 40° under an atmosphere of dry argon in a glass ampul[18,20].

NMR Spectrum

The NMR spectrum was taken on a JNM-4H-100 spectrometer (JEOL) at 100 MHz using benzene as an internal standard at 22.5° and the chemical shift toward higher magnetic field from that of the standard was taken as positive. A sample was prepared by transferring a benzene solution of the anion and THF into a completely dry NMR tube with syringes under dry argon. The molar ratio of THF to the anion was estimated from the areas of their resonance peaks up to a ratio of THF/DPB$^-$ = 9.2. The value was in accord with that calculated from the quantities added to the tube within an error of ±7%. Above THF/DPB$^-$ = 9.2, the ratio was calculated from the quantities added. The concentration of the anion was 0.40–0.50 mol/l. The precision of the measurement of chemical shift was ±0.3 Hz.

RESULTS

The NMR spectra of DPB$^-$ and DPB-d^- in benzene-d_6 are shown in Fig. 1. In the mixtures of benzene and THF the spectral patterns of the aromatic protons were quite similar to those in Fig. 1. The chemical shifts and the coupling constants of DPB$^-$, DPB-d^- and DPH$^-$ obtained by the first-order analysis are collected in

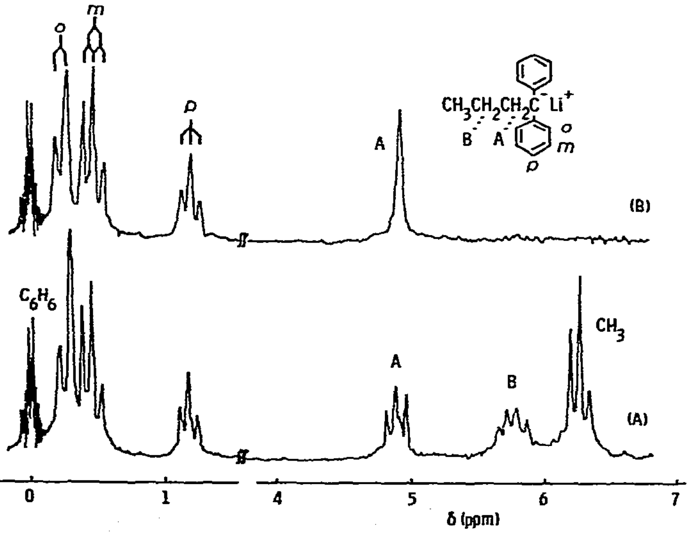


Fig. 1. NMR spectra of DPB$^-$ (A) and DPB-d^- (B) in benzene-d_6.

TABLE 1

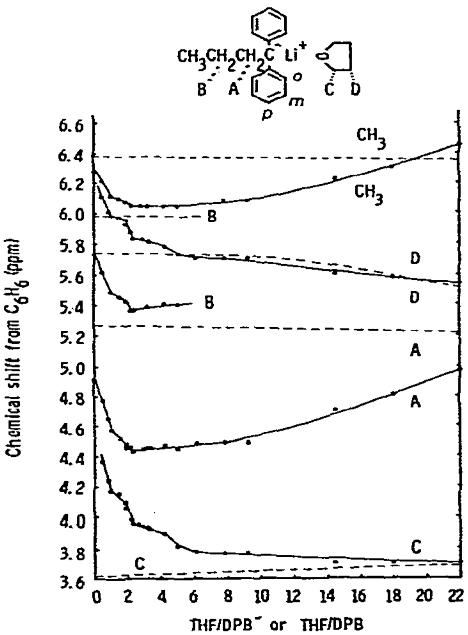
CHEMICAL SHIFTS AND COUPLING CONSTANTS OF DPB^-, $DPB\text{-}d^-$, AND DPH^- IN BENZENE-d_6 AND THF

Anion	Solvent	Chemical shift (ppm)			Coupling constant (Hz)	
		δ_o	δ_m	δ_p	J_{o-m}	J_{m-p}
DPB^-	C_6D_6	0.23	0.46	1.20	8.0	6.7
$DPB\text{-}d^-$	C_6D_6	0.24	0.48	1.21	8.0	7.0
$DPB\text{-}d^-$/2 THF	C_6D_6	−0.22	0.10	0.85	8.2	7.3
DPB^-	THF	0.44	0.86	1.73	8.7	6.9
DPH^-	C_6D_6	0.28	0.46	1.19	7.9	6.6
DPH^- [a]	THF	0.43	0.82	1.69		

[a] Data shown in ref. 6.

Table 1. The chemical shifts and the coupling constants of the three anions were very similar in the same solvent.

The changes of the chemical shifts of DPB^- in benzene/THF mixtures are shown in Figs. 2 and 3. As a molar ratio of THF to DPB^- increased, all of the peaks of DPB^- shifted downfield up to $THF/DPB^- = 2$ with breaks at $THF/DPB^- = 1$, and above 2 they turned to shift upfield. On the other hand, the two methylene resonances of THF shifted downfield with at least two breaks at $THF/DPB^- = 1$ and 2, as the ratio increased. When the solvent was evaporated off from the solution of DPB^- with $THF/DPB^- = 9$ for 1 h under vacuum (0.02 mm) at 40°, the molar ratio



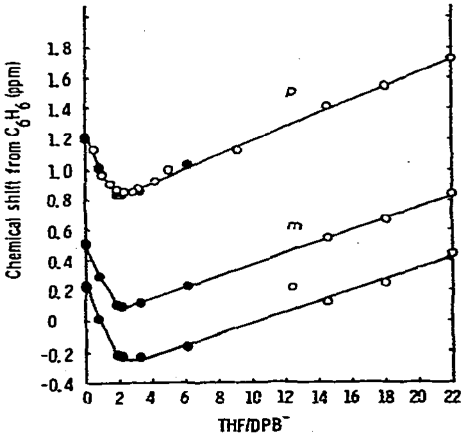


Fig. 2. Chemical shifts of DPB^-, $DPB\text{-}d^-$, DPB, and THF. Dotted lines are for DPB.

Fig. 3. Chemical shifts of aromatic protons of DPB^- (○) and $DPB\text{-}d^-$ (●).

of THF to DPB$^-$ in the residue was 2.4 by means of NMR spectroscopy. This seems to indicate a tight coordination of two moles of THF to DPB$^-$.

The results of the NMR of a neutral compound, n-$C_3H_7CH(C_6H_5)_2$ (DPB), are also shown in Fig. 2*. The difference between the chemical shifts of this compound in benzene and in THF was rather small. In this figure, the chemical shift at THF/DPB=22 corresponds to that in THF. Generally the peaks of the aliphatic protons in DPB$^-$ appeared at lower field than those of DPB, and in the same solvents, the differences between the chemical shifts of DPB$^-$ and DPB decreased as the protons were located at an increasing distance from the α-carbon (benzylic carbon).

Using the relationship, $\rho=\Delta\delta/10.7$[5,6,8,15], where ρ is the absolute charge density on a carbon atom and $\Delta\delta$ is the proton chemical shift from benzene (ppm), we calculated the charge distributions on the phenyl rings. The results are collected in Table 2. It seems that in most instances the electron is most delocalized on the phenyl ring in THF.

TABLE 2

NEGATIVE CHARGE DISTRIBUTION DETERMINED FROM CHEMICAL SHIFT[a]

Anion	Solvent	Charge density, ρ			
		o	*m*	*p*	Total[b]
DPB$^-$	C_6D_6	0.022	0.044	0.112	0.488
DPB-*d*$^-$/2 THF	C_6D_6	−0.021	0.009	0.080	0.112
DPB$^-$	THF	0.041	0.079	0.162	0.804
DPH$^-$	C_6D_6	0.026	0.043	0.111	0.498
DPH$^-$ [c]	THF	0.040	0.077	0.158	0.784

[a] Determined by using the relationship, $\Delta\delta=10.7\times\rho$[5,6,8]. [b] $4o+4m+2p$. [c] Data shown in ref. 6.

DISCUSSION

The resonances of the aromatic protons of DPB$^-$ and DPH$^-$ in THF were in accord with those for DPH$^-$ reported by Waack and Doran[6]. The peaks of n-propyl group of the DPB$^-$ were observed at lower field than those of DPB (Fig. 2). The chemical shifts of both the aromatic and aliphatic protons appeared at lower field in benzene than in THF, but did not change monotonously with variation of the compositions in the solvent mixtures. They showed minima at THF/DPB$^-$=2.

Alkyllithium compounds are known to exist as tightly bonded agglomerates such as hexamer or tetramer in hydrocarbon solvents and even in THF[20−22]. On the other hand, organolithium compounds involving resonance-stabilized groups, such as benzyl, allyl, diphenylmethyl, and styryl, are found to be dimeric in hydrocarbon solvents[1,23−25]. A basic compound such as THF dissociates these dimeric lithium compounds and converts them to solvated monomeric species.

Waack *et al.*[26] reported that the addition of THF to DPH$^-$ in benzene gives two etherates, probably DPH$^-$·2 THF and DPH$^-$·4 THF, and that the former must have a high formation constant, whereas the constant is small for the latter, which

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* The aromatic protons of DPB gave a peak at almost the same position as that of benzene.

may be essentially the species in 100% THF. On the other hand, Hogen-Esch and Smid[27] reported that fluorenyllithium, which is structually similar to DPH$^-$ and DPB$^-$, forms only contact ion-pairs in toluene, but the fraction of solvent-separated ion-pair is substantial in THF at room temperature.

The DPB$^-$ may exist as a dimer in benzene and mainly as solvent separated ion-pairs in THF. On the addition of THF to the benzene solution the dimer dissociates to form a monomeric dietherate through the monoetherate. The etherates exist as contact ion-pairs, which are gradually transformed, by the subsequent addition of THF, into solvent-separated ion-pairs[27], probably tetra or higher etherates. The sharp breaks appeared in the NMR spectra as shown in Figs. 2 and 3 indicate that the dissociation of the dimeric DPB$^-$ into monomeric etherates is complete at the addition of two molex of THF to the lithium compound.

It has been reported that the α-carbon of triphenylmetyllithium, diphenylmethyllithium, and benzyllithium are substantially sp^2 hybridized in THF[7,15]. The calculation of the charge density upon the phenyl rings in DPB$^-$ indicated that the electron density on the α-carbon may be highest at THF/DPB$^-$ = 2, and lowest in THF. Since the α-carbon atom has no attached proton, the charge density at this position can not be experimentally obtained. However, the negative charge seems to be extensively delocalized on the phenyl rings of DPB$^-$ in THF. In THF the α-carbon and the two phenyl rings may have a coplanar conformation, while the dietherate will have a tetrahedral arrangement forming an "outside coordinated contact ion-pair"[1,28]. The increasing amount of THF must bring the increasing distance between the anionic center and the lithium cation, resulting in the electron delocalization. The upfield shifts of both the aliphatic and aromatic protons at THF/DPB$^-$ > 2 may be attributed to the charge distribution.

Contrary to DPB$^-$ in THF the anion in benzene solution seems to exist in a complicated state. From the lithium resonance of fluorenyllithium/THF complex it was reported that the lithium is situated above the plane of the fluorenyl anion[9], leading to a sandwich structure[27,29]. On the other hand, the dimerization of polystyryllithium in hydrocarbon solvent is considered to arise from electrostatic interactions leading to the formation of quadrupole from two dipoles[1,30]. Although the situation of DPB$^-$ in benzene solution is not known, the downfield shifts of the peaks of DPB$^-$ up to THF/DPB$^-$ = 2 may be well explained if the DPB$^-$ in benzene associates in a structure in which its resonance peaks are shifted upfield by the diamagnetic effect of the ring current induced in the phenyl groups of another DPB$^-$ in the dimer*. The addition of THF to the benzene solution dissociates the dimer, resulting in the downfield shifts.

The chemical shifts of the protons of THF moved downfield with an increasing ratio of THF to DPB$^-$ above two and approached to those of pure THF. A rapid exchange must occur between coordinated and uncoordinated molecules of THF, because two kinds of THF could not be observed at any ratios of THF to DPB$^-$. The methylene resonance of diethyl ether coordinating with ethyllithium in benzene shifted downfield[19]. Therefore, the upfield shift of the THF coordinating with DPB$^-$ at low fraction of THF must be caused by the ring current of the anion. The large upfield

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* In this case the charge distribution upon the phenyl rings in a benzene solution must be smaller than the observed values (Table 2).

shifts of THF in the monoetherate compared with those in the dietherate suggest that the THF in the former is situated to be more easily subject to the diamagnetic effect of the ring current than in the latter. It will be presumed that the monoetherate still associates to form the dimer.

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REFERENCES

1 M. Szwarc, *Carbanions, Living Polymers, and Electron-transfer Processes*, Interscience, New York, 1968, p. 476.
2 C. S. Johnson Jr., M. A. Weiner, J. S. Waugh and D. Seyferth, *J. Amer. Chem. Soc.*, 83 (1961) 1306.
3 H. H. Freedman, V. R. Sandel and B. P. Thill, *J. Amer. Chem. Soc.*, 89 (1967) 1762.
4 V. R. Sandel, S. V. McKinley and H. H. Freedman, *J. Amer. Chem. Soc.*, 90 (1968) 495.
5 V. R. Sandel and H. H. Freedman, *J. Amer. Chem. Soc.*, 85 (1963) 2328.
6 R. Waack and M. A. Doran, *J. Amer. Chem. Soc.*, 85 (1963) 4042.
7 R. Waack, M. A. Doran, E. B. Baker and G. A. Olah, *J. Amer. Chem. Soc.*, 88 (1966) 1272.
8 T. Schaefer and W. G. Schneider, *Can. J. Chem.*, 41 (1963) 966.
9 J. A. Dixon, P. A. Gwinner and D. C. Lini, *J. Amer. Chem. Soc.*, 87 (1965) 1379.
10 R. H. Cox, *J. Phys. Chem.*, 73 (1969) 2649.
11 R. Waack, L. D. McKeever and M. A. Doran, *J. Chem. Soc. D*, (1969) 117.
12 M. Morton, R. D. Sanderson and R. Sakata, *J. Polymer Sci., Part B*, 9 (1971) 61.
13 F. E. Naylor, H. L. Hsieh and J. C. Randall, *Macromolecules*, 3 (1970) 486.
14 F. Schue, D. J. Worsfold and S. Bywater, *Macromolecules*, 3 (1970) 509.
15 L. D. McKeever and R. Waack, *J. Organometal. Chem.*, 28 (1971) 145.
16 M. Morton, A. A. Rembaum and J. L. Hall, *J. Polymer Sci., Part A*, 1 (1963) 461.
17 K. Ziegler and A. Colonius, *Justus Liebigs Ann. Chem.*, 479 (1930) 135.
18 A. G. Evans and D. B. George, *J. Chem. Soc.*, (1961) 4653; (1962) 141.
19 Z. K. Cheema, G. W. Gibson and J. F. Eastham, *J. Amer. Chem. Soc.*, 85 (1963) 3517.
20 R. Waack and M. A. Doran, *J. Amer. Chem. Soc.*, 91 (1969) 2456.
21 P. West, R. Waack and J. I. Purmort, *J. Amer. Chem. Soc.*, 92 (1970) 840.
22 H. L. Lewis and T. L. Brown, *J. Amer. Chem. Soc.*, 92 (1970) 4664.
23 D. J. Worsfold and S. Bywater, *Can. J. Chem.*, 38 (1960) 1891.
24 A. F. Johnson and D. J. Worsfold, *J. Polymer Sci., Part A*, 3 (1965) 449.
25 M. Morton and L. J. Fetters, *J. Polymer Sci., Part A*, 2 (1964) 3311.
26 R. Waack, M. A. Doran and P. E. Stevenson, *J. Amer. Chem. Soc.*, 88 (1966) 2109.
27 T. H. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, 88 (1966) 307.
28 R. V. Slates and M. Szwarc, *J. Amer. Chem. Soc.*, 89 (1967) 6043.
29 S. Toppet, G. Slinckx and G. Smets, *J. Organometal. Chem.*, 9 (1967) 205.
30 A. F. Johnson, D. J. Worsfold and S. Bywater, *Can. J. Chem.*, 42 (1964) 1255.