Nuclear Magnetic Resonance Spectroscopy of Diphenylallyl Carbanions. Part I. The Determination of Equilibrium Constants for Ion Pairing

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The results of a study of the ^{1}H n.m.r. spectra of the alkali-metal salts of 1,3-diphenylpropene in several different ethers provide further evidence for the existence of contact and solvent-separated ion pairs. The thermodynamic parameters $\Delta H°$ and $\Delta S°$ have been determined for the solvation process for the sodium salt in tetrahydrofuran and 2-methyltetrahydrofuran and for the potassium salt in tetrahydrofuran. The composition of ether complexes in C_6D_6 and the effect of methyl substitution in the 1-position have also been investigated.

THE alkali-metal salts of 1,3-diphenylpropene (DPP$^-$M$^+$) and 1,3-diphenylbut-1-ene (DPB$^-$M$^+$) exist as mixtures of contact and solvent-separated ion pairs in ether solutions.[1,2] Although the use of visible absorption spectroscopy to study such phenomena has been extensive,[3-7] the use of n.m.r. has been somewhat limited.[8,9] N.m.r. presents a direct means of estimating π-electron densities within a molecule or ion. In aromatic systems, the chemical shift of a proton is particularly sensitive to the π-electron density at the carbon atom to which the proton is attached and some workers have suggested that there is a linear relationship (1),[10,11] where δ is

$$\delta = K\Delta\rho \tag{1}$$

the chemical shift of a given proton relative to benzene, $\Delta\rho$ is the excess charge density at the carbon atom (also relative to benzene), and K is the constant of proportionality. Schaeffer and Schneider[9] applied this equation in a study of the mono- and di-negative ions of several polycyclic hydrocarbons and obtained reasonable agreement between the experimentally determined π-densities and the results of HMO and SCF calculations. These workers, however, recognised that other factors, such as ring currents, solvent effects, and cation–anion association should also be important in determining the chemical shifts of protons in aromatic systems.

In a previous communication[12] we reported that the ^{1}H n.m.r. spectrum of DPP$^-$M$^+$ is sensitive to the nature of the cation in tetrahydrofuran (THF) solutions. Cox[8] conducted a similar study of the alkali-metal salts of fluorene (Fl$^-$M$^+$) in THF and concluded that his results presented evidence for the existence of contact and solvent-separated ion pairs in these systems. Dixon, Gwinner, and Lini[13] extended this work to C_6D_6 solutions of the ether complexes of Fl$^-$Li$^+$; a study of the ^{1}H resonances of both the anion and of the ether proved to be most useful in establishing the structure of the complexes. We now present the results of an investigation of DPP$^-$M$^+$ in tetrahydropyran (THP), 2-methyltetrahydrofuran (MTHF), 1,2-dimethoxyethane (DME), and C_6D_6 as well as of DPB$^-$M$^+$ in THF and in DME.

EXPERIMENTAL

1,3-Diphenylpropene[14] and 1,3-diphenylbut-1-ene[2] were prepared and purified as previously described. n-Butyllithium (Kodak) supplied as a 2·4 molar solution in hexane was divided into ampoules containing about 0·5 cm^3 of solution. All the solvents used were commercially available except for *cis*- and *trans*-2,5-dimethyltetrahydrofuran (2,5-DMTHF); these latter solvents were separated (better than 98% pure) from an equimolar mixture of the isomers (Fluka) by distillation through a spinning-band column. The solvents were dried and purified by distillation under high vacuum from sodium–potassium alloy to which a little benzophenone had been added to act as indicator.

Solutions of DPP$^-$M$^+$ and DPB$^-$M$^+$, approximately one molar, were prepared under high vacuum in Pyrex vessels with conventional n.m.r. tubes attached. A weighed quantity of the appropriate hydrocarbon was introduced into the vessel. Except for lithium, which was added to the vessel in small pieces, the alkali metals were sublimed in from a side-arm. The appropriate solvent was distilled in, together with tetramethylsilane to act as internal reference, and the vessel was sealed and detached from the vacuum line. The reaction was allowed to proceed to completion overnight before the n.m.r. tube was filled and sealed off. DPP$^-$Li$^+$ and DPB$^-$Li$^+$ were also prepared by treating the parent hydrocarbons with butyl-lithium, following essentially the same procedure. The hexane solution of butyl-lithium was introduced into the vessel from an ampoule *via* a breakseal; the hexane was removed under vacuum and replaced by the appropriate solvent.

DPP$^-$Li$^+$ (2,5 DMTHF)$_n$ was prepared as a crystalline precipitate by treating DPP with lithium in 2,5-DMTHF. This complex was collected by filtration and washed by back-distillation of solvent to remove traces of 2,3-dibenzyl-1,4-diphenylbutane, which is also produced during the reduction.[12] After final removal of solvent, solutions were made up in C_6D_6. Since DPP$^-$Li$^+$ is freely soluble in THF and THP, purification by crystallisation was impossible: accordingly, complexes of these ethers were prepared from

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[1] J. W. Burley and R. N. Young, *Chem. Comm.*, 1969, 1127.

[2] J. W. Burley and R. N. Young, *J. Chem. Soc.* (*B*), 1971, 1018.

[3] R. V. Slates and M. Szwarc, *J. Amer. Chem. Soc.*, 1967, **89**, 6043.

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[10] G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, 1960, **82**, 5846.

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[12] J. W. Burley, R. Ife, and R. N. Young, *Chem. Comm.*, 1970, 1256.

[13] J. A. Dixon, P. A. Gwinner, and D. C. Lini, *J. Amer. Chem. Soc.*, 1965, **87**, 1379.

[14] J. W. Burley and R. N. Young, *J. Chem. Soc.* (*C*), 1971, 3780.

DPP⁻Li⁺ (2,5-DMTHF)$_n$ by solvent exchange. THF (or THP) was distilled onto a sample of DPP⁻Li⁺ (2,5-DMTHF)$_n$. The solution so obtained was evaporated to dryness under vacuum. The residue was washed with C_6H_6, again evaporated to dryness and finally dissolved in C_6D_6.

Spectra.—Spectra were recorded on a Varian Associates HA 100 instrument. In most cases a sweep width of 1000 Hz was used, but several spectra were also run at a reduced sweep of 100 Hz.

RESULTS AND DISCUSSION

When DPP was reduced by lithium in THF, the n.m.r. spectrum of the resulting solution was as shown in Figure 1a. This is in essence identical, except for the presence of additional aromatic absorptions at τ 2·9 and 3·1, with the spectrum of the solution produced by treating DPP with butyl-lithium in THF (Figure 1b). The latter spectrum has been reported previously and suitably interpreted.[15] Since the visible spectrum of the solution obtained upon treatment of DPP with lithium exhibited no absorption maxima other than those produced by treatment with butyl-lithium, the absorptions at τ 2·9 and 3·1 were clearly due to the presence of an uncharged hydrocarbon. Mass spectrometric and n.m.r. analysis of this hydrocarbon proved that it was the dihydro-dimer of DPP (2,3-dibenzyl-1,4-diphenylbutane) and the overall reaction sequence can be represented by Scheme 1.

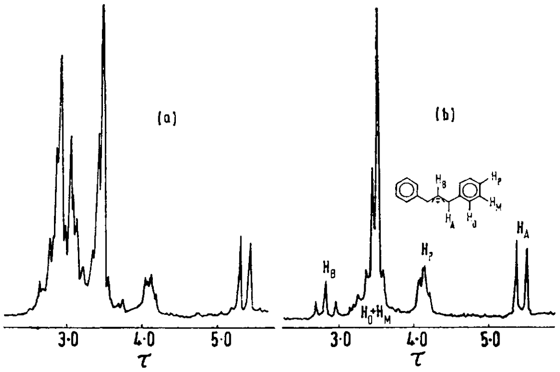
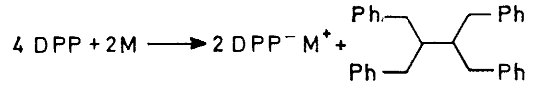


FIGURE 1 (a) The n.m.r. spectrum of DPP⁻Li⁺ in tetrahydrofuran, prepared by reaction of DPP with lithium metal. (b) The n.m.r. spectrum of DPP⁻Li⁺ in tetrahydrofuran, produced by reaction of DPP with butyl-lithium



SCHEME 1

Although treatment of DPP with butyl-lithium in THF produced completely homogeneous solutions and resulted in the formation of DPP⁻Li⁺ only, other solvents did not behave so simply. When 1,4-dioxan was used as solvent, the n.m.r. spectrum of the resulting solution corresponded closely to that of the THF solution. This was surprising in view of the very different solvating abilities of these two ethers[2] and also in view of the fact that n.m.r. spectra of carbanions are sensitive to the solvent used.[13,16] This result can, however, be rationalised in terms of cross-association between DPP⁻Li⁺ and butyl-lithium in 1,4-dioxan. Solutions of DPB⁻Li⁺ in dioxan have been shown[17] to be particularly susceptible to this effect and it has been pointed out that the visible absorption spectrum of the associate is closely similar to that of the solvent-separated ion pair—the predominant form of DPP⁻Li⁺ in THF. DPP reacted with lithium metal in dioxan to produce DPP⁻Li⁺ but the solution could not be made sufficiently concentrated for n.m.r. purposes. Evidently, cross-association increases the solubility of the salt.

The n.m.r. spectrum of the solution produced by treatment of DPP with butyl-lithium in MTHF in no way resembled that of DPP⁻Li⁺ (Figure 2). The absorptions at τ 4·24 and 5·04 completely disappeared when the solution was treated with methanol, clearly indicating that they represented the presence of a carbanion. The resulting hydrocarbon had a molecular weight of 252 and gave a n.m.r. spectrum with signals at τ 2·88, 7·50, 8·73, and 9·14. There were no olefinic protons and the ratio of the integrated intensities of aromatic and aliphatic signals was 10 : 14. On this basis, and in the light of the ratio of the integrated intensities of the signals in the spectrum of the carbanion, τ 2·95 : 4·24 : 5·04 = 5 : 2 : 3, the carbanion responsible for this spectrum is $PhCH_2{\cdot}CHBu{\cdot}\bar{C}HPh$ (the resonances being due to phenyl, *m*-, *o*-, and *p*-benzylic protons respectively). This carbanion is produced by the addition of butyl-lithium to the olefinic double bond of DPP (Scheme 2). That the aromatic proton resonances of this substituted benzyl carbanion occur at such high field is not surprising in view of recent

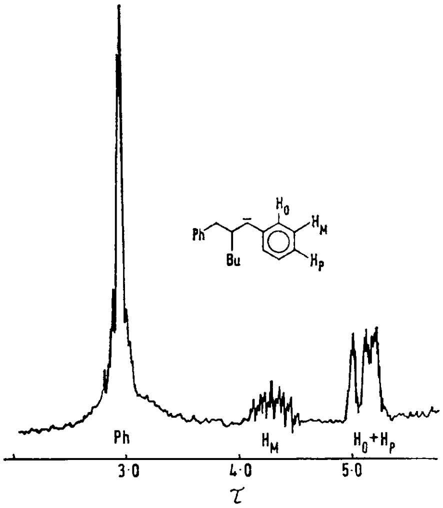


FIGURE 2 The n.m.r. spectrum of $PhCH_2{\cdot}CHBu{\cdot}\bar{C}HPh$ Li⁺ in 2-methyltetrahydrofuran

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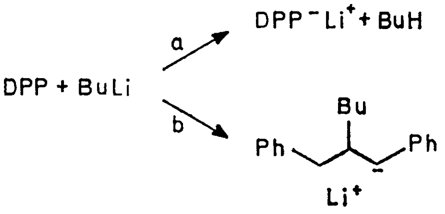
[15] H. H. Freedman, V. R. Sandel, and B. P. Thill, *J. Amer. Chem. Soc.*, 1967, **89**, 1762.

[16] L. D. McKeever and R. Waack, *J. Organometallic Chem.*, 1971, **28**, 145.

[17] J. W. Burley and R. N. Young, *Chem. Comm.*, 1970, 991.

work by Takahashi and his co-workers[18] who reported similar high-field positions for protons in the alkali-metal salts of the dimer dianion of α-methylstyrene and of dimethylbenzylpotassium. A solution of DPP$^-$Li$^+$ in MTHF was successfully produced by reaction of DPP with lithium.



Scheme 2

The Effect of Temperature, Cation, and Solvent upon the Spectrum of DPP$^-$M$^+$.—The spectra of DPP$^-$M$^+$ in a variety of solvents are presented in Table 1. In every case the chemical shifts of the *ortho*- and *meta*-protons are identical, whereas the *para*-protons are distinctly to higher field. The low-field position of the H_B signal has been attributed to ring currents.[15] As the size of the alkali-metal cation is increased (Na$^+$ to Cs$^+$), the spectrum of DPP in THF is progressively displaced to higher field. The lithium salt, however, appears to be anomalous since the chemical shifts of this species are at even higher field than those of the caesium salt. Accepting that the chemical shift of a proton is dependent upon the electron density of the carbon atom to which it is attached, then, except for the lithium salt, the highest electron density on the anion occurs when it is paired with the caesium cation. If the Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ salts are considered to be predominantly contact ion pairs, the observed order of the spectra can be rationalised as follows. In a contact ion pair, some portion of the charge of the anion will reside between the cation and the anion, thereby giving some degree of covalency to this bond. The amount of electron density in this position will be governed by the polarising power of the cation, which, for the above series, is greatest for Na$^+$. In the Na$^+$ ion pair, relatively little electron density will remain on the anion, whose proton resonances will therefore occur at lowest field. If the lithium salt existed as a contact ion pair in THF, the proton resonances would occur at even lower field than those of the sodium ion pair. The observed spectrum indicates the maximum possible electron density on the anion and the predominant form of the lithium salt must therefore be solvent-separated—no electron density residing between the anion and the cation. Studies of the visible absorption spectra of the solutions of these salts in THF have indeed shown[2] that all are contact ion pairs except for the lithium salt which is solvent-separated. A similar series of results was obtained for MTHF solutions where again the lithium salt is mainly solvent-separated. The lithium salt of DPP is almost entirely solvent-separated in DME, but the resonances are downfield from the signals from DPP$^-$Li$^+$ in THF. Whilst we can offer no rigorous explanation of this effect, it must arise from some specific solvent interaction. Since the other ethers (THF, THP, and MTHF) are all very similar in structure, we consider it valid to compare the results obtained in these solvents. In fact the n.m.r. spectra of DPP$^-$Na$^+$ in THP and MTHF are almost identical—as are the visible spectra of this salt in these two solvents, (THP solution $\lambda_{max.}$ 518 nm, MTHF solution $\lambda_{max.}$ 516 nm).

Table 1

The n.m.r. spectrum (τ values) of DPP$^-$M$^+$ in various solvents at 30° (sweep width 1000 Hz)

M	Solvent	H_B	H_o + H_m	H_p	H_A	J_{AB}/Hz
Li	THF	2·78	3·46	4·11	5·37	13
Na	THF	2·58	3·37	3·94	5·23	13
K	THF	2·68	3·37	3·95	5·26	13
Rb	THF	2·74	3·35	3·96	5·28	13
Cs	THF	2·74	3·34	3·93	5·33	13
Li	MTHF	2·70	3·37	3·93	5·35	13
Na	MTHF	2·51	3·32	3·86	5·17	13
K	MTHF	2·69	3·30	3·87	5·25	13
Rb	MTHF	2·76	3·30	3·90	5·27	13
Li	THP	*a*	3·37	3·96	5·34	13
Na	THP	2·50	3·30	3·87	5·18	13
Li	DME	2·77	3·41	4·05	5·27	13
Na	DME	2·73	3·42	4·06	5·24	13
Li	1,4-Dioxan	2·77	3·41	4·03	5·34	13

[a] This signal was masked by the aromatic protons of 2,3-dibenzyl-1,4-diphenylbutane.

The results presented in Table 1 indicate that all the lithium salts, and the sodium salt in DME, are predominantly solvent-separated, whereas the other salts exist as contact ion pairs. An exact interpretation of every proton chemical shift is impossible owing to the differing ability of each cation both to withdraw charge from the anion and also to perturb the remaining charge on the anion. The shape of the doublet at *ca.* τ 5·37 (H_A) is unaffected by cation and this appears to be the most reliable resonance for determining the nature of the ion pairing of a given salt in any solvent. Solutions of DPP$^-$Na$^+$ in THF and in MTHF and of DPP$^-$K$^+$ in THF gave spectra which showed distinct shifts to higher field as the temperature was lowered, indicating the formation of solvent-separated ion pairs. The H_A signal was studied using a sweep width of 100 Hz for several systems and a selection of the results is shown in Table 2.

Table 2

The chemical shift of H_A (τ values) for several systems at a sweep width of 100 Hz

		Temperature			
M	Solvent	30°	0°	−30°	−60°
Li	THF	5·351			
Na	THF	5·211	5·258	5·320	
K	THF	5·255	5·273	5·291	5·327
Rb	THF	5·282			
Cs	THF	5·316			
Na	MTHF	5·169	5·182	5·193	5·214
K	MTHF	5·234			5·235
Rb	MTHF	5·285			

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[18] K. Takahashi, M. Takaki, and R. Asami, *J. Phys. Chem.*, 1971, **75**, 1062.

In the typical example of DPP$^-$Na$^+$ in MTHF, the position of the H_A doublet varied from τ 5·169 at 30° to τ 5·214 at −60° but showed only slight broadening at the lowest temperatures (most probably due to the increased viscosity of the solvent since all the other signals also broadened). This indicates that the exchange process between contact and solvent separated ion pairs is still fast at −60°, as studied by the n.m.r. technique. In fast exchange, the observed chemical shift δ is given by equation (2) where α is the fraction of contact ion pairs,

$$\delta = \alpha\delta_c + (1 - \alpha)\delta_s \qquad (2)$$

δ_c is the chemical shift of the contact ion pair, and δ_s that of the solvent-separated ion pair. The equilibrium constant for the contact–solvent-separated ion pair equilibrium is given by (3)

$$K_{eq} = \frac{1 - \alpha}{\alpha} = \frac{\delta_c - \delta}{\delta - \delta_s} \qquad (3)$$

It was observed that δ for DPP$^-$K$^+$ in MTHF was independent of temperature in the range 30 to −60°. Visible absorption spectroscopy has shown that only contact ion pairs are present in this system and this result demonstrates that δ_c is independent of temperature. The value of δ_c for DPP$^-$K$^+$ was assumed to be the same in THF as in MTHF. Similarly, it was assumed that DPP$^-$Na$^+$ has the same value of δ_c in MTHF and in THF: since there are no solvent-separated ion pairs in MTHF at 30°, δ_c was taken at τ 5·169. It was further assumed that δ_s is independent of solvent and cation and was taken as τ 5·351—the value for DPP$^-$Li$^+$ in THF. δ Was measured at 10—15° intervals for DPP$^-$Na$^+$ in THF and MTHF, and for DPP$^-$K$^+$ in THF. K_{eq} Was calculated using equation (3) and $\Delta H°$ and $\Delta S°$ were determined from a plot of ln K_{eq} against reciprocal temperature. The results are presented in Table 3 and are in reasonable agreement with results previously obtained [19] for the analogous system DPB$^-$M$^+$ by absorption spectrometry. Although the n.m.r. technique is intrinsically less accurate than that using absorption spectrometry, it does potentially have advantages. For example, it is unnecessary to determine extinction coefficients and overlap does not present a serious problem.

TABLE 3

Thermodynamic parameters for the contact–solvent-separated ion pair equilibrium of DPP$^-$M$^+$

M	Solvent	$-\Delta H°$/kJ mol^{-1}	$\Delta S°$/J mol^{-1} K^{-1}
Na	THF	25·4	93·4
K	THF	17·0	68·6
Na	MTHF	11·5	63·2

The N.m.r. Spectrum of DPB$^-$M$^+$.—The n.m.r. spectrum of DPB$^-$Li$^+$ in THF (prepared using BuLi), is shown in Figure 3. The spectrum is more complex than that of DPP$^-$Li$^+$ since the two phenyl groups are inequivalent due to the methyl group which perturbs the distribution of the π-electron density within the anion. This spectrum was interpreted by comparison with that of DPP$^-$Li$^+$, since the ($H_o + H_m$) high field signal (τ 3·52) is similar in shape to that of DPP$^-$Li$^+$ whilst the low field signal (τ 3·31) is almost its mirror image (Figures 1b and 3). The assignment of the absorption at τ 3·52 to ($H_o + H_m$) of Ph$_b$ was also supported by the appearance of the H_A signal at τ 5·51—*ca.* τ 0·15 to higher field than the corresponding signal in DPP$^-$Li$^+$, indicating a higher π electron density in this position of the DPB$^-$ anion relative to DPP$^-$. The *para*-proton resonances at τ 4·02 and 4·18 were assigned to the relevant protons by comparison with the order of the ($H_o + H_m$) signals.

The effect of the methyl group upon the n.m.r. spectrum can be explained on the following basis. It is well established that alkyl groups are ' σ-donating ' when attached to aromatic systems and this will result in the production of a higher electron density at C-1 than at C-3. There will, however, be a complementary adjustment of the π-electron density distribution, resulting in a higher charge density at C-3 than at C-1. Accordingly, the $H_o + H_m$, and H_p signals of Ph$_a$ are shifted downfield.

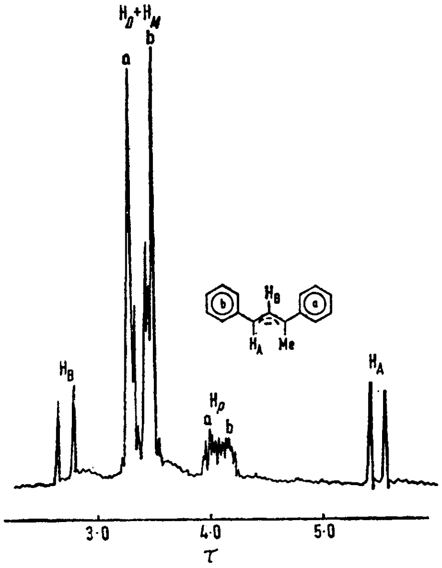

FIGURE 3 The n.m.r. spectrum of DPB$^-$Li$^+$ in tetrahydrofuran

The spectra of DPB$^-$Li$^+$ and DPB$^-$Na$^+$ in THF and DME are summarised in Table 4. As with DPP$^-$Li$^+$, the spectrum of DPB$^-$Li$^+$ in DME occurs downfield of that of the THF solution. The spectrum of DPB$^-$Na$^+$ is at lower field than that of DPB$^-$Li$^+$, both salts in THF solution, in accordance with optical measurements which showed that the Li$^+$ salt is completely solvent-separated whereas the Na$^+$ salt is *ca.* 95% contact ion pairs. Likewise, the spectra of DPB$^-$Li$^+$ and DPB$^-$Na$^+$ in DME are very similar, both salts being in the form of solvent-separated ion pairs.

Complexes of DPP$^-$Li$^+$ *with Ethers.*—In an attempt to obtain some information on the structure of DPP$^-$Li$^+$ in solution, we studied the ^{1}H resonances of both the anion and the complexed ether molecules of C_6D_6 solu-

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[19] J. W. Burley and R. N. Young, *J.C.S. Perkin II*, 1972, 835.

TABLE 4

The n.m.r. spectra (τ values) of DPB^-M^+ in THF and DME at 30°

M	Solvent	H_B	$(H_o + H_m)_a$	$(H_o + H_m)_b$	H_pa	H_pb	H_A	Me	J_{AB}/Hz
Li	THF	2·74	3·31	3·52	4·02	4·18	5·51	*a*	13
Na	THF	2·56	3·20	3·36	3·86	4·06	5·44	*a*	13
Li	DME	2·70	3·24	3·44	3·95	4·08	5·41	8·27	13
Na	DME	2·68	3·25	3·42	3·97	4·12	5·41	8·26	13

[a] This signal was masked by the high field signal of THF.

tions, prepared as described in the Experimental section. Dixon, Gwinner, and Lini [13] studied the analogous solutions of fluorenyl-lithium solvated by DME, THF, and diethyl ether in C_6D_6 and they concluded from observations of both ^1H and ^7Li resonances that the lithium cation is located in the π-cloud of the anion. The ether molecules remained complexed to the lithium cation and the shielding effect caused by ring currents within the anion more than compensated for any deshielding resulting from co-ordination of the ether oxygen atom. Consequently the ether protons experienced upfield shifts. It seems likely that the ether complexes of DPP^-Li^+ will adopt a basically similar structure, presumably with the lithium cation symmetrically located over the allyl portion of the anion. In accordance with this view, a single set of aromatic proton signals was observed (Table 5) and the complexed ether molecules experienced an upfield shift. In contrast to the fluorenyl anion complexes, the shifts are small—10—30 Hz as compared to 80—100 Hz. Presumably the polycyclic nature of the fluorenyl anion is responsible for the larger shifts.

TABLE 5

The n.m.r. spectra (τ values) of etherate complexes of DPP^-Li^+ in C_6D_6

Anion spectra

Ether	H_B	$H_o + H_m$	H_p	H_A	J_{AB}/Hz
cis-2,5-DMTHF	2·25	2·86	3·30	5·05	14
trans-2,5-DMTHF	2·22	2·85	3·30	5·05	13
THF	2·25 (0·53)	2·87 (0·59)	3·34 (0·77)	5·01 (0·36)	14
THP	—	2·88	3·32	5·05	13

Ether spectra

Ether	α–CH_2–	β–CH–	Me	*n*
cis-2,5-DMTHF	6·24 (0·04)	8·47 (0·19)	9·04 (0·19)	4·0
trans-2,5-DMTHF	6·11 (0·12)	8·39 (0·26)	9·06 (0·15)	3·3
THF	6·73 (0·29)	8·70 (0·22)		3·6
THP	6·57 (0·07)	8·72 [a] (0·14)		12

Values in parentheses are upfield shifts for the ether protons relative to the free ether signals in C_6D_6 and downfield shifts for the protons of the carbanion relative to their values in THF.

[a] This signal also includes the γ-protons of THP.

The number of ether molecules (*n*) bound to the cation was determined from the ratio of the integrated intensities of the ether α proton signal to that of H_A. Plausible values of *n* were obtained for the ether complexes involving *cis*- and *trans*-2,5-DMTHF and THF but the improbably high value of 12 was found for THP, suggesting serious inadequacies in the technique used for the preparation of this complex. The crystalline complexes of *cis*- and *trans*-2,5-DMTHF presented no synthetic problems, but both the complex with THF and that with THP appeared to be amorphous and susceptible to occlusion of free ether. Washing with C_6H_6 decreased the importance of this occlusion phenomenon with THF complexes, but did (after several washings) reduce the solubility in C_6D_6, suggesting the formation of a less-soluble and less-solvated complex:

$$DPP^-Li^+ (THF)_n \rightleftharpoons DPP^-Li^+ (THF)_{n-x} + x\,THF \quad (4)$$

We have in fact observed [2] a similar phenomenon in solutions of $DPP^-Li^+(THF)_n$ in diethyl ether. In the case of the etherate of THP, washing with C_6H_6 appeared to be ineffective.

It was of some interest to verify that equilibrium (4) is operative in hydrocarbon solutions of ether complexes. To this end, it was necessary to study the ^1H n.m.r. spectrum as a function of temperature and toluene was used in place of C_6D_6 (f.p. 6·5°) as solvent. The α-protons of the ether complexes of DPP^-Li^+ with THF and 2,5-DMTHF moved upfield by 10 and 8 Hz respectively when the temperature was lowered from 30 to $-60°$, whereas the signals of the pure ethers in toluene were independent of temperature. Since the position of the ether signals in the complexes is dependent upon the weighted average of bound and unbound ether molecules, the upfield shifts indicate a displacement of equilibrium (4) to the left upon lowering of the temperature.

In contrast to solutions of the etherates of fluorenyl-lithium,[13] the spectrum of DPP^-Li^+ was independent of the nature of the solvating ether. Essentially the same species must therefore be present in every case—*viz.* the poorly solvated contact ion pair. It is informative to examine the downfield shifts of individual protons of DPP^-Li^+ in C_6D_6 relative to the corresponding values in THF. The H_p proton moves downfield by 77 Hz, indicating particularly low electron density on the aromatic rings whereas the H_A signal shows the much smaller shift of 36 Hz. In THF solution, the distribution of electron density within the anion is largely determined by electron–electron interactions since the carbon–metal bond is entirely ionic. However, in C_6D_6 the formation of a contact ion pair gives some degree of covalency to this bond and results in a large polarisation of π electron density towards the allyl portion of the molecule.

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