Ion Pairing of 1,5-Diarylpentadienyl Carbanions

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The 1,5-diarylpentadienyl carbanions exist in solution as mixtures of tight and loose ion pairs. The thermodynamic parameters for the change tight $\longrightarrow$ loose ion pair have been determined for several combinations of solvent and counterion. The introduction into the rings of electron-releasing substituents increases the magnitude of ΔH and ΔS; a similar effect is produced by increasing the chain length from pentadiene to heptatriene and nonatetraene.

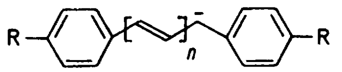
PREVIOUS results from this laboratory[1-3] have shown that the visible absorption spectra of the alkali-metal salts of substituted 1,3-diphenylpropenes can be interpreted in terms of the presence of tight (contact) and loose (solvent separated) ion pairs.[1-3] The spectra of the loose ion pairs of these anions are indistinguishable from those of the corresponding free anions formed by dissociation. However, in the tight ion pairs the perturbation of the molecular orbital energy levels arising from the ion association is considerable. The ground state is stabilised to a greater extent than is the excited state, and consequently the absorption maxima of the tight pairs are shifted to the blue by an amount which increases with decreasing cation radius. The existence of two kinds of ion pairs has been confirmed by n.m.r. spectroscopy.[4]

Early n.m.r. studies showed[4-7] that the diphenylallyl carbanion adopts the *trans,trans* conformation unless there is a substituent such as an alkyl group in the allylic 2-position, in which case the stable conformation is the *cis-trans*.[8] A later study showed[9] that there is, in fact, *ca.* 7% of the *cis-trans*-conformer present in solutions of the 1,3-diphenylallyl anion at ambient temperatures. More recently, we discovered[10] that under appropriate conditions it is possible to change the conformation almost completely to *cis,trans* by photolysis with white light. The rate of relaxation in the dark is very sensitive to the nature of the ion pairing, being greater for tight ion pairs than for the loose.[10]

The objective of the present study was to investigate the influence upon such ion pairing equilibria of lengthening the chain connecting the aromatic moieties as a prelude to photochemical studies. To this end we have prepared several 1,5-diarylpentadienyl anions and have made a limited study of the 1,7-diphenylheptatrienyl and 1,9-diphenylnonatetraenyl anions.

EXPERIMENTAL

Trimethylene(bistriphenylphosphonium) dibromide was prepared as described by Horner *et al.*[11] This compound was converted into the corresponding bis-ylide by stirring in dry diethyl ether with the calculated volume of 2M-butyl-lithium solution in hexane. Following the procedure described by Wittig *et al.*,[12] reaction of the bis-ylide with freshly distilled benzaldehyde yielded 1,5-diphenylpenta-1,4-diene (DP5). Purification was effected by vacuum distillation followed by chromatography on an alumina column, using hexane as eluant.



R	H	CH_3	CH_3O	$(CH_3)_2N$	C_6H_5	H	H
n	2	2	2	2	2	3	4
Designation	DP5	DT5	DA5	DM5	DB5	DP7	DP9

1,5-Di-*p*-tolylpenta-1,4-diene (DT5), 1,5-bis-*p*-methoxyphenylpenta-1,4-diene (DA5), 1,5-bis-(*p*-dimethylaminophenyl)penta-1,4-diene (DM5), and 1,5-bis(biphenyl-4-yl)-penta-1,4-diene (DB5) were prepared analogously from the reaction of the above bis-ylide with the appropriate aldehyde. The similar reaction with cinnamaldehyde yielded 1,9-diphenylnona-1,3,6,8-tetraene (DP9).

Reaction of the above bis-ylide with an equimolar mixture of cinnamaldehyde and benzaldehyde yielded a product which was a mixture of DP5, DP9, and 1,7-diphenylhepta-1,3,6-triene (DP7), in the proportions *ca.* 1 : 1 : 4. Attempts to isolate DP7 by chromatography on alumina met with limited success, probably because of the large number of geometric isomers of the components present in the mixture. Accordingly, it was necessary to employ this impure material to obtain some estimate of the properties of the $DP7^{-}M^{+}$ ion pairs.

The procedures used for the purification of the solvents have been described previously.[1] The lithium ion pairs were generated in solution in the appropriate solvent from the parent hydrocarbons by the removal of a proton by reaction with butyl-lithium under high vacuum conditions; the sodium ion pairs were formed similarly using the sodium salt of the dimer dianion of α-methylstyrene. In contrast to the diphenylallyl anion, the higher vinylogous anions were not cleanly formed by reaction of the parent hydrocarbon with alkali metal, but were formed accompanied by variable amounts of several other carbanions of undetermined constitution.

The spectra were obtained using 1 mm pathlength cells and employing an alcohol-filled unsilvered Dewar vessel as thermostat. Cooling was effected by passing liquid nitrogen through a coil of narrow-bore copper tubing immersed in the alcohol. In order to exclude any possibility of photolysis, the spectroscopic measurements on the solutions, necessarily conducted with the cell compartment lid open because of the considerable dimensions of the glassware, were made with the laboratory in complete darkness. In general, the spectra consisted of overlapping bands due to the tight and loose ion pairs. The method of obtaining the equilibrium constants (defined as K = [loose pair]/[tight pair]) has been described.[1] In the case of the solutions of $DP7^-M^+$ the spectral analysis was complicated by the presence of $DP5^-M^+$ and $DP9^-M^+$; the concentration of $DP7^-M^+$ loose ion pair was determined from the absorbance at 647 nm. The total concentration of $DP7^-M^+$ was obtained from spectra recorded at a temperature sufficiently low to ensure that only the loose ion pairs were present, due allowance being made for solvent contraction.

RESULTS AND DISCUSSION

The ^1H n.m.r. spectrum of a solution of $DT5^-Li^+$ in tetrahydrofuran (THF) was determined (Perkin-Elmer R34). The aromatic protons gave rise to a singlet at δ 6.8, the pentadienyl 1- and 5-H gave a doublet at 4.97 (J 13.6 Hz), and 3-H a triplet at 5.08 (J 12.1 Hz). The signal due to the ring methyl groups was hidden by the broad solvent resonance, whilst the multiplet due to the pentadienyl 2- and 4-H was partially obscured by noise. Despite the incompleteness of the spectrum, it can be deduced from the ^1H–^1H coupling constants that the predominant (if not the only) conformer present is the all-*trans* one, since an extensive study of pentadienylic anions by Bates *et al.* established[13] that the ^1H–^1H coupling constants are respectively *ca.* 6.5 and 12 Hz for *cis*- and *trans*-configurations about inner bonds, whereas about outer bonds the corresponding values are 7.5—9 for *cis* and 16 Hz for *trans*. Brenner and Klein studied[14] the ^1H n.m.r. spectrum of $DP5^-Li^+$ in [$^2H_{10}$]diethyl ether solution and concluded that this species also has the all-*trans*-conformation. They reported resonances at δ 6.93 (10 H, ArH), 5.20 (pentadienyl H-1 and -5, d, J 14.4 Hz), and 4.81 (pentadienyl H-3, t, J 11.2 Hz). The reversal of the relative resonance positions of H-3 and H-1 and -5 in moving from $DP5^-Li^+$ to $DT5^-Li^+$ must be due to the combined effects of introducing electron-releasing substituents and of changing from the tight ion pair (ether) to the loose (tetrahydrofuran).

Solutions of the αω-diarylpolyenylic carbanions were found to exhibit the characteristics expected of solutions containing tight and loose ion pairs in equilibrium. Except when rather strongly solvating solvents were employed which supported some dissociation, the electrical conductivity was very small and the spectra were insensitive to concentration. The band at shorter wavelength (Table 1) due to the tight ion pair predominates at high temperatures and its position is very sensitive to the choice of cation and solvent. Conversely, the formation of the loose ion pair is favoured on lowering the temperature and the position of its absorption maximum is comparatively insensitive to the cation and solvent.

TABLE 1

Absorption maxima (nm) and the ratio of loose ion pair to tight ion pair concentrations [L]/[T] at 20 °C

Anion	Cation	Solvent	Tight $\lambda_{max.}$	Loose $\lambda_{max.}$	[L]/[T]
$DP5^-$	Li^+	THF		595	>50
	Li^+	MTHF	535	595	1.81
	Li^+	DMTHF	514		0.08
	Na^+	THF	562	599	1.74
	Na^+	MTHF	549		0.02
$DT5^-$	Li^+	MTHF	530	597	1.98
	Li^+	DMTHF	514	596	<0.01
	Na^+	THF	560	601	0.53
$DA5^-$	Li^+	MTHF	510	586	0.69
	Li	DMTHF	507		<0.01
	Na^+	THF	546	590	0.35
$DM5^-$	Li^+	MTHF	530	600	0.38
	Li^+	DMTHF	519		<0.01
	Na^+	THF	558		0.19
$DB5^-$	Li^+	DMTHF	575		0.01
	Na^+	THF		721	>50
	Na^+	MTHF	630		0.08
$DP7^-$	Li^+	THF		647	>50
	Li^+	DMTHF	556		0.11
$DP9^-$	Li^+	MTHF		709	>50
	Li^+	DMTHF	598	704	0.25
	Na^+	MTHF	644		0.24

THF = Tetrahydrofuran, MTHF = 2-methyltetrahydrofuran, DMTHF = 2,5-dimethyltetrahydrofuran.

The colours of solutions of the polyenyl carbanions deepen with increasing chain length, as anticipated by elementary quantum theory. A plot of the frequency of the absorption maximum of the loose ion pairs against the chain length is approximately linear, and conforms to the equation ($10^{-3}\,\gamma_{max.}/cm^{-1} = 19.4 - 0.56x$ where x is the number of carbon atoms in the polyenylic moiety. The polarisability of these anions, and in consequence the extent to which the molecular orbital energy levels are perturbed by ion association, is also expected to increase with increasing chain length. This is indeed observed: the difference in colour between the tight and loose ion pairs is more marked in the higher vinylogues (Table 2). Typical spectra are exemplified by those of $DP5^-Na^+$ in MTHF (Figure 1) and $DP9^-Li^+$ in DMTHF (Figure 2); in both cases the band at shorter wavelength is that due to the tight ion pair.

TABLE 2

Colour of the ion pairs of the polyenylic anions

$C_6H_5\overset{-}{C}H(CH = CH)_mC_6H_5M^+$

m	Tight ion pair	Loose ion pair
1	Yellow	Red
2	Red	Mauve
3	Lilac	Blue
4	Blue	Green

The values of the equilibrium constant for the interconversion of the tight and loose ion pairs were determined for a number of systems over as wide a range of temperature as possible within the limitations imposed by the boiling or freezing of solvent. The van't Hoff plots of these results were found to be linear and enabled the determination of the changes in entropy (ΔS) and enthalpy (ΔH) for the process tight $\rightleftharpoons$ loose ion pair. These values are collected in Table 3 and are believed to be accurate to *ca.* $\pm 7\%$.

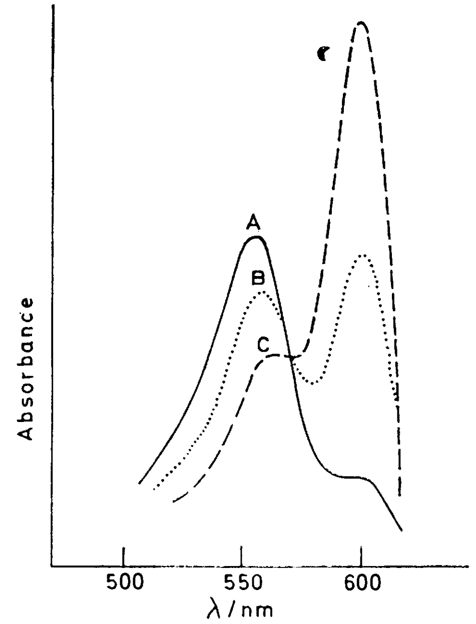


FIGURE 1 Absorption spectrum of 1,5-diphenylpentadienyl sodium in 2-methyltetrahydrofuran: A, $-38°$; B, $-72°$; C, $-95°$

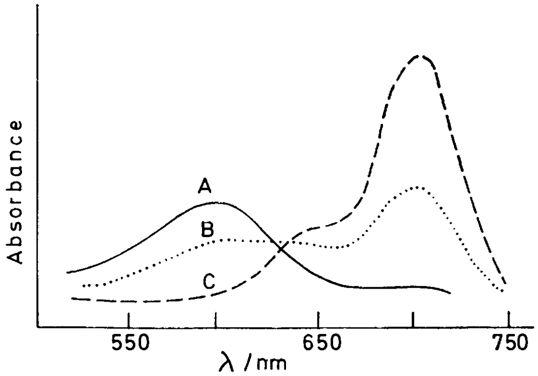


FIGURE 2 Absorption spectrum of 1,9-diphenylnonatetraenyllithium in 2,5-dimethyltetrahydofuran: A, 5°; B, $-17°$; C, $-53°$

In an earlier publication[15] we drew attention to the existence of an extrathermodynamic relationship for the interconversion of ion pairs of a wide variety of carbanions in media of low dielectric constant: for a given solvent and counterion, the enthalpy and entropy changes are related by equation (1) where α and β are

$$\Delta H = \alpha \Delta S + \beta \qquad (1)$$

constants. It is of interest to test whether or not the present results conform to equation (1). Figure **3** shows the points (ΔH, ΔS) for each of the lithium salts studied in 2-methyltetrahydrofuran (MTHF) and 2,5-dimethyltetrahydrofuran (DMTHF) solutions, together with the lines drawn for these cation–solvent combinations on the basis of the values of α and β previously reported.[15] It can be seen that the four points for MTHF solutions lie quite close to the relevant line. In contrast, in the case of the DMTHF solutions although three systems lie near the line (*viz.* $DA5^-Li^+$, $DP5^-Li^+$, and $DT5^+Li^+$) the other three ($DP7^-Li^+$, $DP9^-Li^+$, and $DB5^-Li^+$) are far from the line. Since the parameters for $DP7^-Li^+$ were obtained from data based on measurement of a single absorption band (that due to the loose ion pair) as a

TABLE 3

Thermodynamic parameters for the conversion of tight to loose ion pairs

Anion	Cation	Solvent	$-\Delta H$/ kJ mol^{-1}	$-\Delta S$/ J K^{-1} mol^{-1}
$DP5^-$	Li^+	MTHF	31.1	101
	Li^+	DMTHF	37.1	156
	Na^+	THF	26.1	84
	Na^+	MTHF	21.7	105
$DT5^-$	Li^+	MTHF	50.8	168
	Li^+	DMTHF	43.5	211
	Na^+	THF	38.3	136
$DA5^-$	Li^+	MTHF	32.2	113
	Li^+	DMTHF	25.1	125
	Na^+	THF	33.2	122
$DM5^-$	Li^+	MTHF	33.4	122
	Na^+	THF	30.5	118
$DB5^-$	Li^+	DMTHF	54.4	222
	Na^+	MTHF	25.9	109
$DP7^-$	Li^+	DMTHF	41.5	160
$DP9^-$	Li^+	DMTHF	55.9	202
	Na^+	MTHF	26.7	103

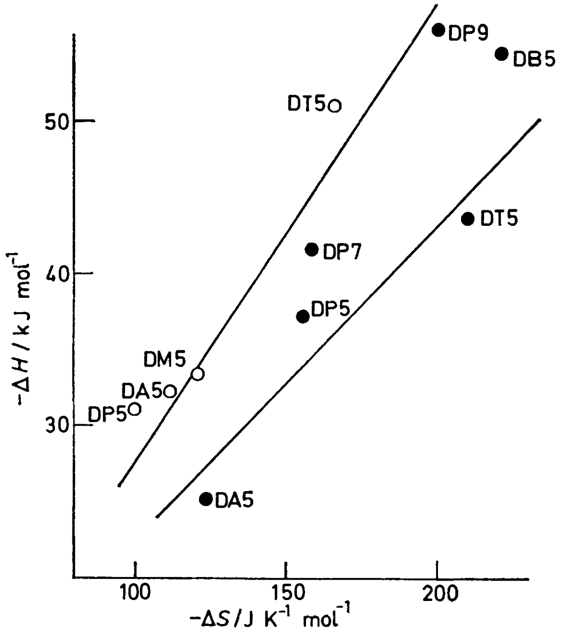


FIGURE 3 Plot of thermodynamic parameters for ion pairs with lithium: ●, data in DMTHF; ○, data in MTHF. Upper line (MTHF) and lower line (DMTHF) drawn from ref. 15

function of temperature, the deviation of this point from the line might be ascribed to the greater inaccuracies inherent in such a method of analysis. However, such considerations do not apply to the studies of $DP9^-Li^+$ or $DB5^-Li^+$. The applicability of equation (1) to the interconversion of ion pairs was rationalised by appealing to the treatment of the dissociation of ion pairs by Denison and Ramsey [16] in which they assumed that the solvent behaves as a continuous dielectric and that the ions are approximately spherical. It is probably significant that the anions $DP9^-$ and $DB5^-$ are more grossly non-spherical than are the ions which appear to conform with equation (1), such as diphenylallyl, naphthyl, and fluorenyl.

As can be seen from Table 3, the effect of introducing electron-releasing substituents into the 1,5-diphenylpentadienyl carbanion is generally to increase ΔH (and ΔS). An alternative parameter which serves as a basis for the comparison of these systems is the temperature at which the populations of tight and loose ion pairs are equal (T_{eq}). For the sodium salts in THF, the values of T_{eq} are DM5 (−14°), DA5 (−1°), DT5 (9°), and DP5 (36°); similarly, the values for the lithium salts in MTHF are DM5 (0°), DA5 (12°), DT5 (30°), and DP5 (33°). Since an increase in the electron density in the anion will increase the attractive force exerted on a cation, these observations occasion no surprise.

Increasing the length of the polyenylic chain increases the polarisability of the carbanions and the enthalpy of the process tight ⟶ loose ion pair. For the lithium salts in DMTHF, the values of T_{eq} for the αω-diphenylcarbanions are: allyl (−70°), pentadienyl (−36°), heptatrienyl (−12°), and nonatetraenyl (2°).

[9/1805 *Received, 12th November, 1979*]

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