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1-Phenyl-3-biphenylyl-2-azaallyl-lithium and -sodium: ion pairing and the kinetics of *cis,trans* to *trans,trans* isomerisation

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Abstract

Phenylbiphenylylallyl-lithium and -sodium tight and loose ion pairs have different absorption spectra. Photolysis causes the conformation to change from *trans,trans* to *cis,trans*: the Arrhenius parameters have been determined for the subsequent relaxation process in several solvents. The activation energy and the pre-exponential factor are substantially larger for the tight ion pair than for the loose. Replacing the phenyl by a *p*- or *o*-anisyl group causes little change in kinetics although there is some evidence that the *o*-anisyl compounds have a chelate structure.

Introduction

The alkali-metal salts of 1,3-diphenylallyl carbanion exist in non-aqueous solvents as mixtures of tight (contact) and loose (solvent-separated) ion pairs in equilibrium with the free ions formed by their dissociation [1,2,3]. At the concentrations normally used for spectrophotometry (ca. 10^{-4} M) the extent of dissociation is generally less than 5%. The absorption spectrum of the free carbanion is indistinguishable from that of the loose ion pair. However, in the tight ion pair the intimate association of the ions results in considerable perturbation of the molecular orbital energy levels. The cation is located at the position of greatest electron density of the anion in the ground state but not in the (Franck–Condon) excited state and, consequently, the greater stabilisation of the ground state results in a blue-shift of the absorption spectrum that is the greater the smaller the cation radius [4]. The equilibrium constant for the interconversion of the tight and loose ion pairs can be determined from the absorption spectrum by making due allowance for band overlap.

The ion pairs of the 1,3-diphenylallyl-2-azaallyl carbanion differ from those of its hydrocarbon analog in that the tight and loose ion pairs do not give rise to distinguishable absorption bands [5]. Instead, the single absorption maximum is located at longer or shorter wavelength in qualitative accord with expectation of the

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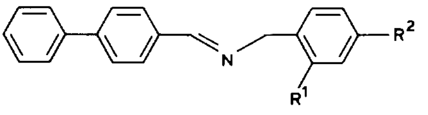
nature of the ion pairing and the observed spectrum is evidently the envelope of unresolved bands due to the two ion pairs. The two families do, however, have in common the property of being converted from the preferred *trans,trans* conformation into the *cis,trans* on exposure to white light [5,6,7].

Preliminary tests showed that the tight and loose ion pairs of the 1-biphenylyl-3-phenyl-2-azaallyl carbanion have different absorption spectra, permitting the unambiguous classification of the type of ion pairing and offering the possibility of determining the pertinent thermodynamic parameters. In addition, it was found that photolysis converts a fraction of the solute from the *trans,trans* conformation into the *cis,trans* and that the subsequent relaxation proceeds at a convenient rate for spectrophotometric study. On these grounds, it seemed that a systematic study might give some insight into the influence of the nature of the ion pairing upon the barriers to rotation about the carbon–nitrogen bond.

Experimental

1-Phenyl-3-biphenylyl-2-azapropene (**1a**) was prepared by refluxing an equimolar mixture of benzylamine and biphenyl-4-carboxaldehyde in benzene under a Dean–Stark trap. Purification was affected by recrystallisation from hexane and confirmed by chromatography. The *o*-anisyl (**1b**) and *p*-anisyl (**1c**) analogs were prepared similarly. 1-Phenyl-3-biphenylyl propene was prepared by reducing the chalcone formed by the condensation of biphenyl-4-carboxaldehyde with acetophenone by $LiAlH_4$ and dehydrating the resulting alcohol by distillation from $KHSO_4$. Purification was affected by column chromatography in cyclohexane on alumina.



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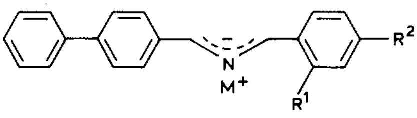

(2)

(**a** : R^1 = H, R^2 = H ; **b** : R^1 = OCH_3, R^2 = H ; **c** : R^1 = H, R^2 = OCH_3)

The solvents were dried by standing over sodium-potassium alloy in the presence of a little benzophenone to act as an indicator. Dryness was indicated by the appearance of a permanent blue colour but no solvent was distilled out until complete reduction of the benzophenone had taken place thereby converting it to the involatile ion.

The azaallyl carbanions (**2a,2b,2c**) were prepared under high vacuum in a reservoir attached to a glass spectroscopic cell with a 1 mm pathlength. The base employed to remove one acidic proton from (**1a,1b,1c**) was either butyllithium in hexane or the disodium salt of the dimer of α-methylstyrene in the appropriate ether.

Sufficient stock solution was added to the spectroscopic cell and was then diluted by distilling all the residual solvent from the reservoir. The cell was thermostatted by placing in an alcohol-filled unsilvered Dewar located in the cell compartment of a Perkin–Elmer 554 spectrophotometer and the temperature controlled to ±0.1° C by passing cold nitrogen through a coil of copper tubing immersed in the alcohol under the control of a thermocouple. When spectra were studied at temperatures below −80 °C cells of 1 cm path-length were employed and the alcohol was replaced by a suitably machined brass block. Photolysis was by means of a 50 W quartz-halogen lamp placed near the Dewar flask.

Results and discussion

The absorption spectrum of **2a**-Li + in MTHF is shown in Fig. 1 and at 2 °C consists of a single band at 587 nm. Successive spectra run at lower temperatures pass through an isosbestic point at 592 nm and the progressive formation of a new absorption band at 620 nm is clearly seen. Such behaviour is entirely analogous to that of the diphenylallyl carbanion and the short and long wavelength bands are attributable to the presence of the tight and loose ion pairs respectively. The equilibrium constant (K), defined as the ratio of the concentrations of the loose and the tight ion pairs, was obtained from the spectra by measuring the absorbances at their respective absorption maxima. Making allowance for band overlap was difficult because of its severity but the resulting plot of ln K vs. $1/T$ was linear and yielded the parameters shown in Table 1 which are believed accurate to about ±10%. The systems **2a**-Li + in DMTHF, **2a**-Li + and **2a**-Na + in MTHF generated linear Van 't Hoff plots. The derived thermodynamic parameters are listed in Table 1.

It is of interest to compare the spectra of **2a**-Li + in DMTHF with the corresponding lithium salt derived from 1-phenyl-3-biphenylylpropene (PBA).

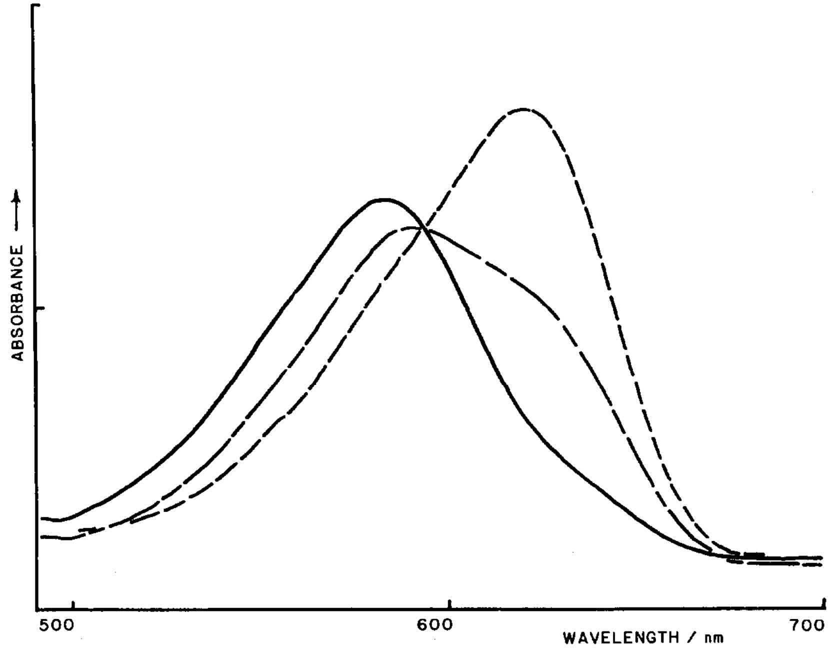

Fig. 1. Absorption spectrum of 1-phenyl-3-biphenylyl-2-azaallyllithium +15 °C ———, −10 °C -—-—-, −33 °C — — —.

Table 1

Absorption maxima and thermodynamics of tight to loose ion pair conversion

Anion	Cation	Solvent	λ_t (nm)	λ_l (nm)	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
2a	Li	DMTHF	580	620	27	180
2a	Li	MTHF	581	620	40	155
2a	Na	MTHF	592	626	14	96
2b	Li	MTHF	610	645		
2b	Na	MTHF	612	644		
2b	Na	THF	600	650		
2c	Li	DMTHF	588	621	34	243
2c	Li	MTHF	585	624		
PBAl [a]	Li	DMTHF	520	619		
PBAl	Na	MTHF	554	618	32	151

[a] PBAl = 1-phenyl-3-biphenylylallyl.

Whereas the loose ion pairs have very similar absorption maxima (620 and 619 nm, respectively) the tight ion pairs have their absorption maxima at very different wavelengths. Clearly, the structural details of the tight pairs differ. It is known that the cation is located in the π-electron cloud in the hydrocarbon ions [2]. In contrast, the fluorescence and ^1H NMR spectra of the ion pairs of the carbanions derived from indole and carbazole show that the cation is σ-bonded to nitrogen [8,9,10]. ^7Li NMR spectroscopy also shows that the lithium is coordinated to nitrogen in the lithium salt of carbazole. Although the nitrogen atom in the 2-azaallylics is associated with a much lower charge density, it does not seem unreasonable to propose that similar σ-bonding with the cation might exist. Such a structural difference between the ion pairs of the allylics and their aza counterparts might be the cause of several unusual features of Table 1: (i) With hydrocarbon ions the position of the absorption maximum of the loose ion pair is normally independent of the nature of the cation and ethereal solvent. It is clear from Table 1 that the absorption maxima of the sodium loose ion pairs are red-shifted with respect to their lithium counterparts for **2a**, **2b** and **2c**. (ii) A unifying feature that links the ion pairing equilibria of the allylics and a wide range of other structurally unrelated carbanions is that the ratio of the enthalpy and entropy changes (effectively the temperature at which the equilibrium constant is unity) has a characteristic value for a given combination of solvent and cation [11]. The azaallylics of Table 1 have temperatures that are very different from these (in parentheses): Li-DMTHF 150 K (206), Li-MTHF 258 K (301) and Na-MTHF 146 K (198). (iii) The considerable bathochromic shift of the ion pairs of **2b** with respect to those of **2a** or **2c** is also unexpected. If the cation is associated with the nitrogen atom it might be supposed that the *ortho* methoxy group in **2b** might also coordinate with the cation, effectively forming a six-membered chelate. (iv) Although THF is a more powerful solvating agent than MTHF the absorption maximum of the tight ion pair of **2b** (but no **2a** nor **2c**) with sodium is at longer wavelength in the latter solvent. Speculatively, one might suggest that the *o*-anisyl oxygen is coordinated to sodium in MTHF but not in THF.

If the postulated involvement of the *o*-anisyl group in chelate formation is correct, it might be further supposed that this would prevent the ion from adopting the conformation in which the anisyl group is *cis*-possibly altering the course of

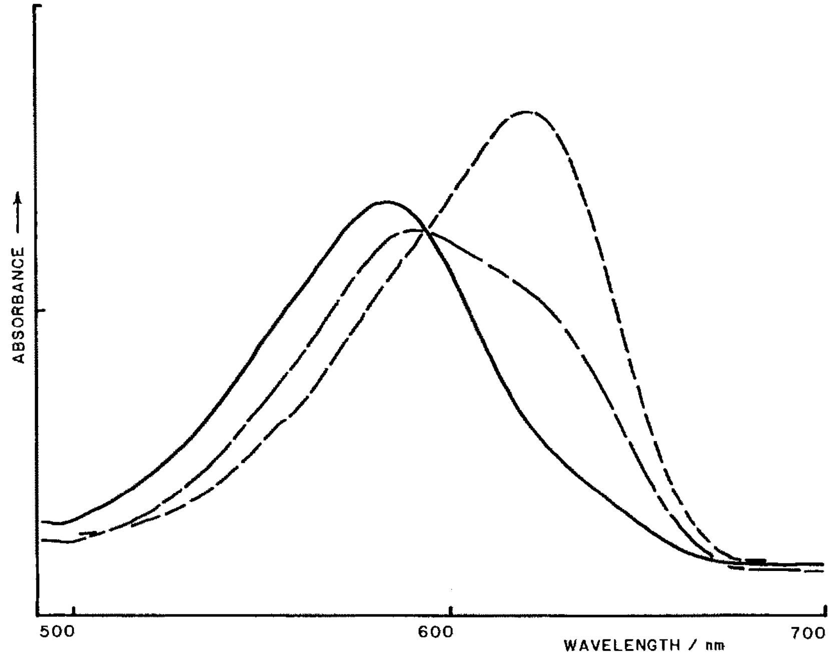

Fig. 2. Absorption spectrum of photostationary state of 1-phenyl-3-biphenylyllithium in MTHF: −128 °C ———, −140 °C - — - — -, −146 °C. — — —.

photolysis. To explore this possibility a systematic study was undertaken of the photolytic behaviour of **2**, **2b** and **2c**.

Photolysis of solutions of the salts of **2a**, **2b** and **2c** results in the loss of intensity from the normal absorption band and the corresponding appearance of additional absorbance at shorter wavelengths; on standing in darkness these systems relax to their original states. These changes are entirely analogous to those exhibited by the ion pairs of 1,3-diphenyl-allyl and -2-azallyl anions which have been shown to correspond to the conversion of the *trans,trans* conformer to the *cis,trans*. A photostationary state was established after a short period of illumination (ca. 15 s). Clearly, the presence of an *o*-methoxy substituent does not prevent photoisomerisation. A number of systems were investigated to observe the influence of temperature upon the position of the photostationary state. Broadly, two classes of behaviour were observed: (i) Systems in which only loose ion pairs are present give rise to photostationary states (using white light) that are strongly temperature dependent, favouring the *cis,trans* conformer at higher temperatures and the *trans,trans* at lower temperatures. The spectra of the photostationary states all pass through an isosbestic point. (ii) Systems in which the ratio of tight and loose ion pairs is changing with temperature give rise to photostationary states that exhibit a complex temperature dependence and no isosbestic points are seen in their spectra. An example of the first category, **2a**-Li in MTHF, is shown in Fig. 2.

Four solvents were chosen for a survey of the influence of the nature of the ion pairing upon the post-photolytic dark relaxation of azaallylic ion pairs: 1,2-dimethoxyethane (DME), a powerful solvating agent capable of chelating lithium and

Table 2

Arrhenius parameters A (s^{-1}) and E (kJ mol^{-1}) for *cis,trans* to *trans,trans* isomerisation

Cation	Solvent	**2a**			**2b**			**2c**		
		log A	E	λ_{max}	log A	E	λ_{max}	log A	E	λ_{max}
Li	DME	9.6	55.8	619	8.9 [a]	54.3	633	8.6	52.4	622
Li	THF	11.4	67	621	11.6	69.4	596	10.6	65.0	626
Li	DEE	12.8	74.1	570				11.9	71.7	570
Li	DMTHF	12.4	74.0	573	12.8 [a]	77.4	593	12.7	79.0	575
Na	DME	12.1	65.5	619	12.5	66.1	635	11.8	64.5	621
Na	THF	11.0	64.9	589	14.3	81.5	603	12.0	71.2	591
Na	DEE	13.4	77.6	575				13.0	77.3	579
Na	DMTHF	13.2 [a]	77.3	580	14.4 [a]	82.1	581			

[a] Data from single preparation of solution.

sodium; THF, a moderately strong solvating agent; diethyl ether (DEE) and equimolar *cis*- and *trans*-2,5-dimethyltetrahydrofuran (DMTHF), both very weak solvating media. The study was limited to lithium and sodium ion pairs; the absorption maximum are listed in Table 2. For the study of the kinetics of the *cis,trans* to *trans,trans* isomerisation it was found convenient to operate in the temperature range +5 to −30 °C. The extent of the conversion was modest (10–15%) with the tight ion pairs but was considerable (30–40%) with the loose ion pairs. The post-photolysis relaxation was monitored at the absorption maximum of the *trans,trans* conformer. Analysis of the data gave accurately linear first order plots over several half-lives with the exceptions of **2b**-Li in THF and **2b**-Na in DME which showed pronounced curvature, the gradient decreasing with time. To enable some sort of comparison with the other systems the gradient of the later stages of the relaxation where the curvature was small was measured and used to determine the Arrhenius parameters. Except where indicated, the data summarised in Table 2 was derived from results obtained from at least two separate preparations of each ion pair stock solution; in several cases separate preparations of the precursors **1a**, **1b** and **1c** were also undertaken. Reproducibility was good provided that the solutions had been freshly prepared. Systems were typically studied over a range of 25 °C; linear Arrhenius plots were obtained and the resulting parameters are believed accurate to about ±5%.

Inspection of the data shows that an isokinetic principle applies, the dividend E (kJ mol^{-1})/ln A having an average value of 6.0 for the lithium and 5.7 for the sodium salts. In practice, this manifests itself in all of the systems of Table 2 relaxing with similar ranges of rate constant in the experimental temperature interval of +5 to −30 °C. Generally, the values of A and E vary little on interchanging the anions **2a**, **2b** and **2c** while holding the cation and solvent constant. The location of the absorption maximum indicates the nature of the ion pairing which is expected to be virtually identical for the *trans,trans* and *cis,trans* conformations. All the salts in DME are loose ion pairs whereas all those in DEE and DMTHF are tight pairs. In the case of the loose ion pairs, the A and E values are distinctly larger for sodium salts than for lithium. In contrast, the values for all the tight ion pairs are similar and no clear trend can be seen. The solutions in THF cannot be compared quite so easily. With lithium as counterion, **2a** and **2c** are loosely paired but **2b** is tightly paired; nonetheless, the Arrhenius parameters are very similar for all three salts. Contrarily, with sodium as counterion **2a**, **2b** and **2c** all form mainly (> 90%) tight ion pairs yet the E and A values are very like those for other tight ion pairs only in the case of **2b**.

A plausible mechanism for the conformational isomerisation of allylic carbanions invokes an intermediate in which one terminal aromatic substituent has twisted into a position perpendicular to the rest of the structure. In the case of the 1,3-diphenylallyl carbanion, the twisting effectively creates a benzyl carbanion, probably tightly paired, and a styrene moiety. Close proximity of the counterion would be expected to facilitate the localisation of negative charge on an allylic terminal carbon atom. This appears to be the situation with this hydrocarbon carbanion whose tight ion pair relaxes faster than the loose. In the case of the azaallylics, however, if the cation is coordinated by the nitrogen atom, any advantage offered by its proximity must be offset by the disadvantage of being bound. This raises the question whether the cation in the azaallylic loose pair is also σ-bonded to nitrogen or located in the

π-cloud as in the hydrocarbon counterpart [2]: the solid state structure of the monoetherate of 1,3-diphenylallyllithium has been shown to involve η^3-bonding [12]. An unusual feature that might be construed as evidence for the former location is the systematic red-shift of the absorption maximum of the loose ion pair on changing the cation from lithium to sodium; under comparable conditions loose ion pairs derived from hydrocarbons show no shift.

The interpretation of the Arrhenius parameters presents a number of difficulties. The tight ion pairs where the cation is closest to the anion would be reasonable expected to show considerable sensitivity to the cation radius and to the nature of the solvent. However, the tight ion pairs constitute a group with very similar parameters; in fact, the pre-exponential factors are typical of those shown for non-ionic unimolecular processes. The corollary, that loose pairs having large interionic separations would be insensitive to cation and solvent is also untrue. The A factors are lower than for the tight pairs, particularly for the lithium salts in DME. This implies that the loose ion pairs do not change conformation by a tightly paired transition state since the accompanying release of solvent would decrease the entropy of activation thereby raising the A factor. It seems that the tight and loose ion pairs must isomerise via different transition states. The literature contains few studies of the effect of a change of counterion upon the kinetics of intramolecular rotation processes. The *cis,trans* to *trans,trans* isomerisation of 1,3-diphenylallyllithium in THF has a log A/s^{-1} value of 13.3 [13] while that for phenyl rotation of the same ion pair in liquid ammonia has the value 11.5 [14]; phenyl rotation in 1,3-diphenyl-2-azaallylsodium in methylamine has a log A of 11.7 [15]. All these are loosely paired systems. The alkali metal neopentylallylics are much less highly delocalised species and comparison with the ions of the present work should probably not be pressed too far. However, it is interesting to note that the activation energies for *cis* to *trans* isomerisation in THF [16] increase in the order $\mathrm{Li} < \mathrm{Na} < \mathrm{K}$ (respectively 57, 72 and 93 kJ mol^{-1}) as do the log A values (9, 11 and 13).

The unsymmetrically substituted azaallylic carbanions can, in principle, form two transition states by associating the cation and negative charge at either allylic terminal carbon atom. The failure of an *o*-methoxy substituent to prevent photoisomerisation does not, therefore, disprove the existence of the chelation suggested. Indeed, the transition state involving the more highly delocalised biphenylylmethyl carbanion is expected to be the more favoured i.e. the residue expected to become *cis* is the biphenylyl.

The failure of two systems to conform to first order kinetics is interesting. One possibility is that the isomerisation proceeds via some intermediate which has not been detected. Further study is in progress.

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