

Thermal and Photoisomerisation of Ion Pairs of the 1,3-Diphenyl-2-aza-allyl Carbanion

By Ronald N. Young* and Muhanad A. Ahmad, Department of Chemistry, The University, Sheffield S3 7HF

Upon irradiation with white light, the predominant conformation of the 1,3-diphenyl-2-aza-allyl carbanion is changed from *trans,trans* to *cis,trans*. The kinetics of the reverse dark reaction have been studied. The loose ion pairs with lithium, sodium, and potassium all have very similar Arrhenius parameters; the tight ion pairs with sodium and potassium, but not with lithium, have smaller values of both E and A . The electronic spectrum depends upon the conformation and, to some extent, upon the nature of the ion pairing.

EARLY studies of the 1,3-diphenylallyl carbanion using n.m.r. spectroscopy led to the conclusion that the conformation adopted is *trans,trans*.¹⁻⁴ More recently, it has been reported that there is in fact *ca.* 7% of the *cis,trans*-conformer present in equilibrium with the *trans,trans* at ambient temperatures.⁵ Previous work in this laboratory has shown that solutions in a number of ether solvents are acutely photosensitive, white light causing *trans,trans* \rightarrow *cis,trans* isomerisation to an extent that is strongly temperature dependent.^{6,7} Interestingly, it was found that when methylamine is employed as solvent, the extent of photolysis to the *cis,trans*-conformation is quite limited.⁶ Subsequent study has shown that when liquid ammonia is the solvent, the conformation of the diphenylallyl carbanion exhibits no significant sensitivity to light.⁸ The cause of this dependence of the extent of photoisomerisation upon solvent is unknown.

The related species, 1,3-diphenyl-2-aza-allyl ion (DAA⁻), is of particular synthetic interest since it readily undergoes cycloaddition with a wide range of alkenes yielding pyrrolidine salts; the addition proceeds with retention of stereochemistry which is in accord with the predictions of the Woodward-Hoffmann rules.⁹ Under suitable conditions, ring opening of 2,3-diphenylaziridine occurs: the *cis*-isomer initially yields *cis,trans*-DAA⁻, but relaxation to the more stable *trans,trans*-DAA⁻ occurs rapidly.¹⁰ The possibility of employing photochemical procedures to generate the metastable *cis,trans*-conformers of DAA⁻ and analogous ions has considerable synthetic attraction and provided motivation for the present study, in addition to our desire to extend our earlier studies.

EXPERIMENTAL

Benzyl-*N*-benzylideneamine was prepared by the condensation of benzylamine with benzaldehyde in boiling toluene. 1-(Biphenyl-4-yl)-3-phenyl-2-azapropene was prepared in a similar manner from biphenyl-4-carbaldehyde and benzylamine. *cis*-2,3-Diphenylaziridine was synthesised by reduction of the oxime of deoxybenzoin with lithium aluminium hydride.¹¹ Much improved yields were obtained by shortening the reduction time from 3 to 0.5 h; † it is evident that the remarkable series of colour changes

† 1 h = 60 min = 3 600 s.

noted by the original authors is associated with ring opening of the aziridine.

Diethyl ether, 2-methyltetrahydrofuran (MTHF), tetrahydrofuran (THF), and 1,2-dimethoxyethane (DME) were degassed and dried under high vacuum by stirring over sodium-potassium alloy in the presence of a little benzophenone; the formation of the blue colour of the negative ions of the latter indicated dryness. Methylamine, condensed from a cylinder of the compressed gas, was dried by dissolving a little sodium-potassium alloy in it.

Solutions of 1,3-diphenyl-2-aza-allyl ion were prepared under high vacuum in all-glass reactors fitted with optical cells of 1 mm pathlength. The lithium salts were formed by reacting benzyl-*N*-benzylideneamine or diphenylaziridine with *n*-butyl-lithium in the appropriate solvent. The sodium and potassium salts were prepared from the same precursors by reaction with the corresponding salts of the dimeric dianion of α -methylstyrene. A few solutions were prepared from benzyl-*N*-benzylideneamine by reaction with alkali metal; care was taken to limit contact between these since it has been reported that the analogous diphenylallyl carbanion can be further reduced by alkali metal to a tri-negative ion.¹² The sodium salt in methylamine can be conveniently prepared from diphenylaziridine or benzyl-*N*-benzylideneamine by reaction with sodamide; since the powerful solvating species ammonia is produced simultaneously, this procedure is inappropriate in ether solvents.

In order to record the absorption spectrum and to effect photolysis, the cell was placed in an unsilvered Dewar vessel partially filled with ethanol and placed in the cell compartment of a Perkin-Elmer 554 spectrophotometer. An appropriate volume of solution was transferred to the side arm bearing the cell and was diluted by distilling the remainder of the solvent from the reactor. This procedure eliminated the danger of further dilution occurring during a kinetic run. A coil of thin copper tubing was immersed in the ethanol and cold alcohol was pumped through it from an external thermostat. This arrangement permitted control of the cell temperature to ± 0.2 °C. Photolysis was effected using a 50 W quartz-halogen lamp located *ca.* 5 cm away from the sample, a typical photolysis time being 30 s. Kinetic data were obtained following photolysis by recording the change of absorbance with time at the absorption maximum of the *trans,trans* conformation.

RESULTS AND DISCUSSION

The visible absorption spectrum of DAA⁻M⁺ consists of a single band, the location of the maximum of which is sensitive to counterion and solvent (Table 1). In di-

ethyl ether, the maximum moves to longer wavelength as the cation radius increases, the lithium, sodium, and potassium salts absorbing at 534, 540, and 543 nm, respectively. This behaviour is entirely analogous to that of the tight ion pairs of the diphenylallyl carbanion^{13,14} and can be explained in simple molecular orbital terms.^{15,16} The association of the anion with the cation results in stabilisation of the ground state, relative to that of the free carbanion. In contrast, the Franck-Condon excited state is only weakly stabilised since the site of greatest electron density on the anion is not the same in the excited state as it is in the ground state. The absorption band is accordingly blue-shifted, relative to the free carbanion, to an extent that increases with decreasing cation radius.

TABLE 1

Solvent and counterion dependence of absorption maximum (nm) of 1,3-diphenyl-2-aza-allyl carbanion at 20 °C

Solvent	Li ⁺	Na ⁺	K ⁺
Ether	534	540	543
MTHF	563	547	547
THF	563	549	548
DME	560	558	
Methylamine	556	556	556

The spectra of DAA⁻M⁺ in THF and in MTHF differ from those in diethyl ether in that the lithium salt absorbs at longer wavelength (563 nm) than the sodium or potassium salts (*ca.* 548 nm; see Table 1). By analogy with the spectra of the ion pairs of the diphenylallyl carbanion,^{13,14} it would seem that DAA⁻Li⁺ exists largely, if not entirely, as the tight ion pair in the weakly solvating medium diethyl ether but as the loose ion pair in THF and MTHF, both of which have considerable solvating power; DAA⁻Na⁺ and DAA⁻K⁺ exist as the tight ion pairs in all these solvents. In methylamine, a powerful solvating solvent, the Li⁺, Na⁺, and K⁺ ion pairs are all loose pairs and have the same absorption maximum; as is generally observed, spectra in amine solvents are slightly blue-shifted with respect to those in ethereal media.

The spectra of solutions of DAA⁻M⁺ differ from those of the corresponding diphenylallyl ion pairs in that none of the systems examined show separate bands attributable to the simultaneous presence of tight and loose ion pairs at any temperature. It seems clear that this is largely due to the rather small difference between the absorption spectra of the tight and loose ion pairs.

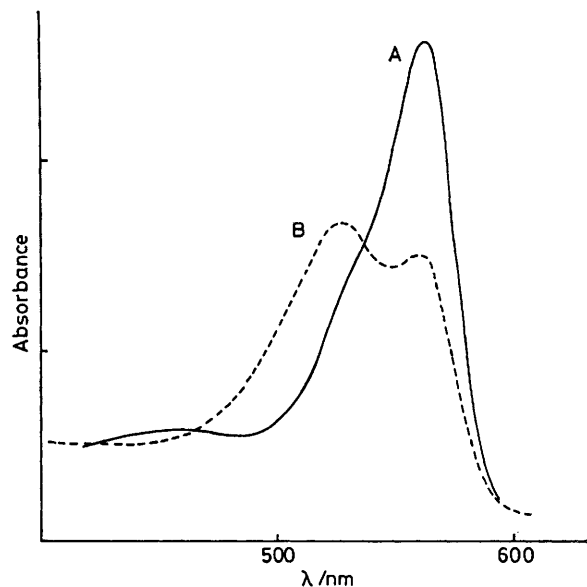
An alternative possible interpretation of the difference in the degrees of sensitivity of DAA⁻ and diphenylallyl ion pairs to changes of temperature or counterion would be to propose differences in the locations of the cations with respect to these two anions. Comparative studies have been made of the nitranion formed by the deprotonation of carbazole, with the related carbanion derived from fluorene.¹⁷ Whereas ⁷Li n.m.r. spectroscopy of the lithium salt showed that the Li signal in fluoren-9-yl-lithium is 6.2 p.p.m. upfield from that in aqueous LiCl, that in carbazol-9-yl-lithium is 0.13 p.p.m. downfield.

It was concluded that whereas the cation is located in the π -cloud of the fluoren-9-yl anion, it is specifically associated with the carbazol-9-yl nitrogen, probably in the plane of the nitranion. In THF, the ¹H n.m.r. spectra show that the carbazolyl protons are shielded in the order Rb > K > Na whereas in DME the order is reversed: Li > Na > K. These observations were explained¹⁷ on the basis that there are only tight ion pairs in THF, but that appreciable fractions of loose ion pairs are present in DME. The electronic spectra of the nitranions from carbazole and 4,5-iminophenanthrene were found to be insensitive to the nature of the ether employed as solvent and to temperature.¹⁸ It was concluded that only tight ion pairs are formed with lithium and potassium, in THF and DME. Comment on the seriousness of the apparently conflicting interpretations of the ¹H n.m.r. and absorption spectroscopy must await quantification of the fractions of the loose ion pairs present. The significant sensitivity of the electronic spectrum of DAA⁻ to the nature of the counterion and solvent contrasts with the insensitivity of the nitranion spectra and would seem to provide strong evidence against the proposal that specific interaction occurs between the cation and the nitrogen atom in DAA⁻. There is, of course, a fundamental difference between the nitrogen atom in DAA⁻ and those in the carbazolyl and iminophenanthrenyl ions; the latter bear a considerable proportion of the anionic charge whereas the former does not. Consequently, specific association with DAA⁻ would have to depend almost entirely upon interaction with the lone pair of electrons on nitrogen. It has been argued that less highly delocalised nitranions are more likely to form π -complexes than σ -complexes.¹⁹ If this generalisation applies to the aza-allyl ions then a further piece of indirect evidence that DAA⁻M⁺ is a π -complex is the observation²⁰ that the absorption band of the tight ion pair of the related species 1-(biphenyl-4-yl)-3-phenyl-2-aza-allyl-lithium in 2,5-dimethyltetrahydrofuran is quite distinct from that of the loose ion pair. The latter is located at longer wavelength (619 nm) than the former (580 nm). As the temperature is lowered, the intensity of the band due to the loose ion pair increases at the expense of that due to the tight ion pair: spectra at different temperatures pass through an isobestic point. Such behaviour is typical of π -complexed ion pairs.

Photolysis of a solution of DAA⁻Li⁺ in DME at -30 °C* resulted in a major change in the absorption spectrum (Figure). The intensity of the normal absorption band (λ_{max} 560 nm) was greatly diminished, and a new band appeared, having its absorption maximum at 526 nm. On storing the sample in darkness, its spectrum progressively reverted to the original form over a period of several minutes. Analogous behaviour was observed following the photolysis of the lithium, sodium, and potassium salts of DAA⁻ in a wide range of ethereal and amine solutions. The nature of the spectral change consequent upon photolysis is very similar to that

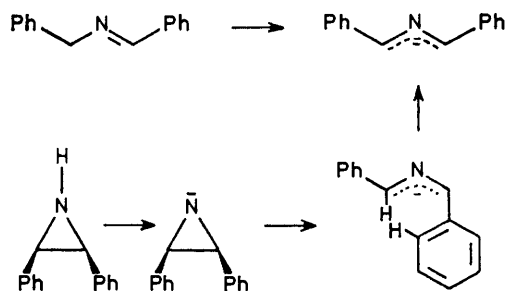
* °C = K - 273.15.

previously described⁶ for the 1,3-diphenylallyl carbanion which is converted from its preferred *trans,trans*-conformation into *cis,trans*. The *trans,trans*-conformer is planar. However, in the *cis,trans*-isomer interaction between the allylic 1-proton and an *ortho*-proton on the 3-phenyl group (Scheme 1) results in twisting out of



The absorption spectrum of 1,3-diphenyl-2-aza-allyl-lithium in 1,2-dimethoxyethane at $-30\text{ }^{\circ}\text{C}$: A, before photolysis; B, after photolysis

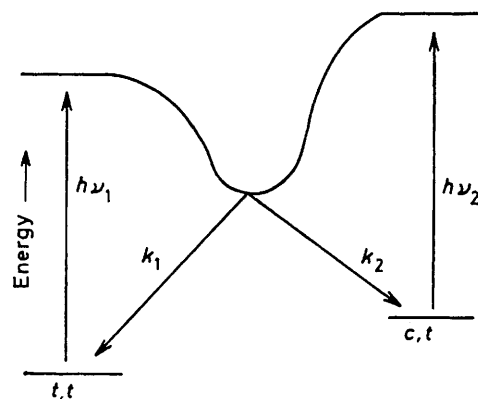
planarity with a consequent blue-shift of the absorption band. Stereochemical analysis of the cyclic adduct formed from $\text{DAA}^{-}\text{Li}^{+}$ and stilbene has shown¹⁰ that the equilibrium conformation of $\text{DAA}^{-}\text{Li}^{+}$ is indeed *trans,trans*. In a similar fashion, it has been demonstrated that the initial product of ring opening of the *cis*-2,3-diphenylaziridine anion at $50\text{ }^{\circ}\text{C}$ is *cis,trans*- $\text{DAA}^{-}\text{Li}^{+}$.



SCHEME 1

We treated a solution of *cis*-2,3-diphenylaziridine in methylamine with sodamide at $-40\text{ }^{\circ}\text{C}$ in darkness. The spectrum of the solution obtained exhibited two maxima, at 528 and 556 nm, due to the presence of both the *cis,trans* and the *trans,trans* ions. Although conformational relaxation is slow at this temperature, it proceeds at a rate comparable with that of the opening of the aziridine ring. Warming the solution to ambient

temperature caused the disappearance of the band at 528 nm and a corresponding intensification of that at 556 nm. Photoisomerisation of DAA^{-} into the *cis,trans*-conformation proceeds substantially to completion, regardless of the nature of the solvent or counterion employed, and independently of temperature in the range studied (typically from -90 to $-20\text{ }^{\circ}\text{C}$, above which temperature thermal relaxation becomes significant). Such behaviour contrasts dramatically with that of solutions of the diphenylallyl carbanion, some of which scarcely photolyse (solutions in methylamine⁶ and especially liquid ammonia⁸); those which do photolyse exhibit a very pronounced sensitivity of the position of the photostationary equilibrium to the temperature, low temperature favouring the *trans,trans*-conformation.⁷ The energy level scheme shown in Scheme 2 can rationalise the behaviour of DAA^{-} . Skeletal twisting of the *cis,trans* or *trans,trans*-conformers in their excited states may lead to the corresponding ground states with rate constants k_1 and k_2 respectively; evidently $k_1 \ll k_2$. The analogous energy level scheme for the diphenylallyl carbanion differs in that there is an activation barrier to twisting the excited state of the *trans,trans* (but not the *cis,trans*)-conformer.⁷ In addition to satisfactorily accounting for the temperature dependence of the photostationary state in a quantitative fashion, this also explains why, at low temperature, the *trans,trans*-diphenylallyl carbanion becomes intensely fluorescent whereas the *cis,trans*-ion does not seem to fluoresce at all. Solutions of $\text{DAA}^{-}\text{M}^{+}$ in MTHF or THF exhibit rather weak fluorescence at low temperature (which we have not yet investigated in detail), which would seem to make improbable one obvious alternative to Scheme 2 in which there are barriers to twisting the excited states of both conformers which are identical in height.



SCHEME 2

The thermal conformational relaxation process following photolysis was found to be accurately of the first order over several half-lives. For all the systems studied, data were collected over a range of *ca.* $15\text{ }^{\circ}\text{C}$ and the linearity of the Arrhenius plots was very satisfactory. In general, the solutions containing lithium as counterion were stable for at least a day. Those employing

sodium, and even more so potassium, had to be used for kinetic study within a few hours in order to obtain reproducible results. Although storage for a day or so resulted in no sign of heterogeneity developing, and although the spectra were unchanged, anomalously low values of the activation energy were obtained (as low as 35 kJ mol⁻¹). It may be that cross-association of DAA⁻M⁺ with a colourless decomposition product catalyses the relaxation process. The results presented in Table 2 represent concordant values of E and A found for at least a pair of solutions of each of the compositions specified, which were in many cases prepared by different routes.

TABLE 2

Arrhenius activation energy (E /kJ mol⁻¹) and pre-exponential factor (A /s⁻¹) for the thermal relaxation *cis*-*trans* → *trans*,*trans*-1,3-diphenyl-2-aza-allyl ion pairs

	Li ⁺		Na ⁺		K ⁺	
	E	$\log A$	E	$\log A$	E	$\log A$
Ether	79.7	14.8	66.4	11.7	65.7	12.0
MTHF	89.2	15.2	73.8	12.4		
THF	82.5	14.8	82.9	13.8	65.8	11.2
DME	78.0	14.0				
Methylamine	84.9	14.0	85.3	14.1	84.9	14.8

The failure of the absorption spectrum of DAA⁻M⁺ to provide quantitative information concerning the relative proportions of tight and loose ion pairs obviously makes detailed interpretation of the results of Table 2 impossible. The observed similarity of the Arrhenius parameters for the Li, Na, and K salts in methylamine, and the broad similarity of these to the Li salts in DME, THF, and MTHF, is in accord with the belief that these are all predominantly loose ion pairs: in such pairs the cation is sufficiently far from the anion that a change of cation, or of the solvent molecules that solvate it, will cause no profound change in rate. The large values of the A factor imply an increase in entropy in forming the transition state complex. One possibility is that the transition state is a tight ion pair formed by the loss of a solvent molecule. In accord with this proposal are the much lower values of E and A observed for the tightly paired systems, Na⁺-ether, K⁺-ether, and K⁺-THF. In the absence of quantitative information concerning the nature of ion pairing, little comment can be made about the systems Na-MTHF and Na-THF. The values for Li-ether are anomalous in that they are much greater than would be predicted on the foregoing basis for a tight ion pair system. It is inconceivable that this system could be loosely paired. A more plausible explanation

would be that, as is very common in organolithium solutions in media of low dielectric constant, the ion pairs are further associated into aggregates, and that partial disaggregation is required prior to conformational change. In principle, it is possible to test this hypothesis by study of the effect of dilution upon relaxation; the practicality of such an investigation would depend heavily upon the actual numerical value of the equilibrium constant of aggregation.

The behaviour of the ion pairs of DAA⁻ thus differs from that of the ion pairs of the diphenylallyl carbanion in several respects: (a) the conformational photo-stationary state is independent of temperature, (b) extensive conversion to the *cis*,*trans*-conformation occurs even in amine solvents, (c) the spectrum is relatively insensitive to the nature of solvent and the counterion. These differences are both interesting and unexpected. At the present time it seems unlikely that their cause is σ -bonding of the counterion to nitrogen. However, it is clear that this possibility must be explored further and, to this end, a study by ⁷Li n.m.r. is already in hand.

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