Thermal Decomposition of Lithium Amides: a Matrix Isolation Investigation

Robert Withnall,[a] **Ian R. Dunkin** [*,a] **and Ronald Snaith** [*,b]

[a] *Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, UK G1 1XL*

[b] *University Chemical Laboratory, Lensfield Road, Cambridge, UK CB2 1EW*

Lithium dimethylamide, lithium diethylamide and lithium diisopropylamide decompose, probably *via* an αβ-lithium hydride elimination mechanism, to give *N*-methylenemethylamine, *N*-ethylidene-ethylamine and *N*-isopropylideneisopropylamine, respectively. Lithium dibenzylamide and lithium bis(trimethylsilyl)amide exhibited different behaviour. Lithium dibenzylamide decomposes *via* the rupture of carbon–nitrogen and carbon–carbon bonds, to give toluene and benzene, and lithium bis(trimethylsilyl)amide volatilizes without decomposition.

There have been a number of studies of the thermal decomposition of alkyllithium compounds.[1-4] The mechanism of such decompositions is widely believed to be an αβ-hydride elimination, yielding lithium hydride and the appropriate alkene. Alternative decomposition pathways are thought to be important only when the alkyllithium lacks β-hydrogens. For example, methyllithium has been reported to disproportionate to give dilithiomethane; this product was characterized by its solid phase ^{13}C NMR spectrum using cross polarization magic angle spinning.[5]

In this study, matrix isolation coupled with IR spectroscopy has been used to observe the products of the thermal decompositions of lithium amides. There have been no previous reports on the thermolysis of such lithium compounds. The technique of matrix isolation was used in order that any unstable products could be trapped and observed spectroscopically. In particular, these electron-deficient compounds are known to cluster and exist as oligomers in the solid state, and it seemed possible that, on heating, lower oligomers or even monomers could be evolved. Finally, this study is relevant to the use of lithium amides in organic synthesis, as a knowledge of the mechanisms of their thermal decompositions could have implications regarding the mechanisms of synthetic reactions involving these compounds.[6]

Experimental

Synthesis of Lithium Amides.—An equimolar amount of butyllithium in hexane was added to the appropriate amine with constant stirring in a Schlenk tube under argon. The amide, which was precipitated, was filtered off and dried by pumping.

Synthesis of Imines.—*N*-Ethylideneethylamine and *N*-isopropylideneisopropylamine were prepared by the standard literature method.[7] *N*-Isopropylideneisopropylamine formed a ternary azeotrope (which boiled at 39 °C) with the acetone and isopropylamine precursors. The imine was subsequently separated incompletely using preparative gas chromatography. The GC column was packed with 20% carbowax on a Chromosorb G support and the oven temperature was kept at 60 °C. The acetone and amine impurities were estimated at 6% each from GC analysis.

Equipment.—The low temperature cell was similar to that described in detail previously.[8] It consisted of a CsI window cooled by an APD Cryogenics model HC-2 closed cycle helium refrigerator and enclosed in a stainless steel vacuum-shroud

fitted with external KBr or CsBr windows and several inlet ports.

IR spectra were recorded on a Perkin-Elmer model 684 spectrometer interfaced to a Perkin-Elmer 3600 Data Station. UV–VIS spectra were recorded on a Shimadzu model UV250 instrument. The mass spectrum of lithium bis(trimethylsilyl)-amide was recorded on a Krato MS-50 mass spectrometer.

Thermolyses and Matrix Deposition.—The moisture-sensitive lithium amides were transferred to an evacuable Pyrex glass container in a glove box under an argon atmosphere. The container was then connected to the deposition inlet of the vacuum shroud which housed the cold window. Nichrome wire was wound around the glass container in order to heat it resistively, and the temperature was monitored and controlled by means of chromel–alumel thermocouples. Argon (BOC, research grade) was passed over the lithium compound at a rate of approximately 5 mmol h^{-1}, and the resulting gas mixture was condensed on the CsI cold window, which was maintained at a temperature of 15 K. The temperature of the lithium amide sample was incremented progressively (maximum temperature *ca.* 350 °C), and matrix IR spectra were recorded periodically over the region 4000–200 cm^{-1}.

Lithium dibenzylamide was also heated in a stainless steel Knudsen cell mounted inside the vacuum shroud which housed the cold window.[9] Temperatures of *ca.* 800 °C were attained using this arrangement.

Results

Typical spectra resulting from the thermolysis of each amide are presented below and compared with matrix IR spectra of authentic samples of the decomposition products.

Lithium dimethylamide. Fig. 1 shows the matrix IR spectrum over the region 4000–400 cm^{-1} obtained on heating lithium dimethylamide to a temperature of 200 ± 5 °C and co-depositing the products with 2.5 mmol of argon over a period of 0.5 h. All the observed bands can be assigned either to *N*-methylenemethylamine (labelled I in Fig. 1) or to dimethylamine (labelled A). The band assignments to *N*-methylene-methylamine and dimethylamine were made by comparison with the literature matrix IR spectra;[10,11] frequencies agreed within ± 2 cm^{-1}. The two sets of bands (A and I) clearly showed different rates of evolution with temperature. The I bands first appeared at a reaction temperature of about 155 °C, but the A bands were present at lower temperatures. Both sets of bands increased in intensity at reaction temperatures above 155 °C.

Table 1 IR bands (cm^{-1}) of N-ethylideneethylamine and diethylamine in solid argon at 15 K (Ar–imine or Ar–amine = 100:1)[a]

N-Ethylideneethylamine	Diethylamine	N-Ethylideneethylamine	Diethylamine
1679vs[b]			1098
	1489	1095	
1470		1068w	
	1464	1058	
	1457	1049sh	1049
	1452		1036
1451		941	
1437s	1437		888
1383		872	
	1378	868sh	
1372		859	
1356			821w
1335		819sh	
	1328	801	
	1290w	780	737s
	1261		
	1189	527	495w
1165			
	1142s	446	
1118		330	

[a] Only bands below 1700 cm^{-1} are included. [b] vs very strong, s strong, w weak, sh shoulder.

Table 2 IR bands of diisopropylamine in solid argon at 15 K (Ar–amine = 100:1)[a]
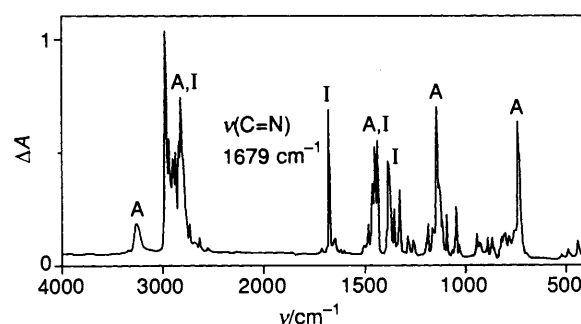
v/cm^{-1}	v/cm^{-1}
1481	1170
1467	1141
1454w[b]	1116
1448w	1091
1436	1018
1380	950w
1372	914w
1364	845
1337	825
1322w	704
1309w	503
1183	

[a] Only bands below 1700 cm^{-1} are included. [b] weak.
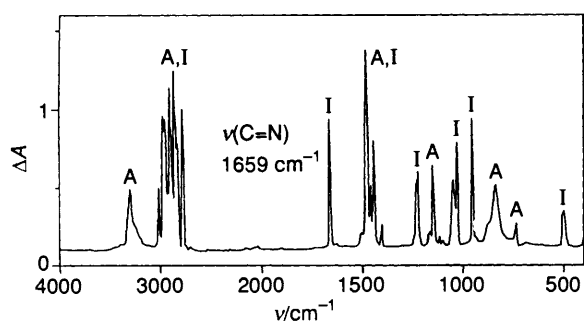
Fig. 1 IR spectrum obtained on heating lithium dimethylamide to 200 ± 5 °C and co-depositing the products with 2.5 mmol of argon over a period of 0.5 h. The bands labelled I and A belong to N-methylenemethylamine and dimethylamine, respectively.

Fig. 2 IR spectrum obtained on heating lithium diethylamide to 200 ± 5 °C and co-depositing the products with 2.5 mmol of argon over a period of 0.5 h. The bands labelled I and A belong to N-ethylideneethylamine and diethylamine, respectively.

Lithium diethylamide. Fig. 2 shows the matrix IR spectrum over the region 4000–400 cm^{-1} obtained on heating lithium diethylamide to a temperature of 200 ± 5 °C and co-depositing the products with 2.5 mmol of argon over a period of 0.5 h. The observed bands belong to either N-ethylideneethylamine (I) or diethylamine (A), as indicated in Fig. 2. They were identified by comparison with the IR spectra of authentic samples (this work), which are listed in Table 1; frequencies agreed to within ± 1 cm^{-1}.

The temperature evolution of the amine and imine bands was similar to that observed in the case of lithium dimethylamide. The N-ethylideneethylamine bands first appeared at a temperature of ca. 150 °C unlike the diethylamine bands, which were present at lower temperatures. Both sets of bands increased in intensity above 150 °C. In a separate experiment, lithium diethylamide was heated to 150 °C for 0.5 h, while argon was passed over it. The resulting sample was then cooled to room temp. and stored for 24 h. Subsequent heating of the solid at temperatures above 150 °C evolved the N-ethylideneethylamine as evidenced by its characteristic IR spectrum, but not diethylamine. Instead there was a strong band at 1651 cm^{-1}.

Lithium diisopropylamide. Fig. 3 shows the matrix IR spectrum over the region of 4000–400 cm^{-1} obtained on heating lithium diisopropylamide to a temperature of 300 ± 5 °C and co-depositing the products with 2.5 mmol of argon over a period of 0.5 h. The strong, diagnostic 1671 cm^{-1} band is attributed to N-isopropylideneisopropylamine by comparison with an authentic sample, which unfortunately contained approximately 6% acetone and 6% isopropylamine impurities (see Experimental). Further IR band assignments to the imine could not be made with confidence on account of these impurities. Diisopropylamine was also identified by comparison of the spectrum of Fig. 3 with an IR spectrum of an authentic sample (see Table 2); frequencies agreed to within ± 2 cm^{-1}.

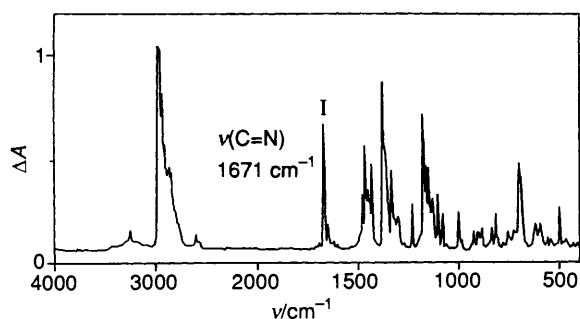**Fig. 3** IR spectrum obtained on heating lithium diisopropylamide to 300 ± 5 °C and co-depositing the products with 2.5 mmol of argon over a period of 0.5 h. The band labelled I belongs to *N*-isopropylideneisopropylamine.
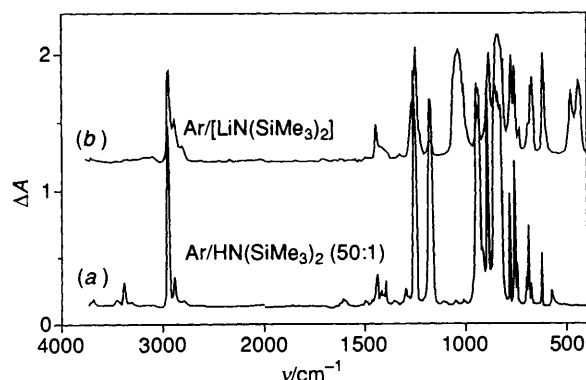

Fig. 4 (*a*) IR spectrum of a sample of 2 mmol of Ar–HN(SiMe₃)₂ (50:1) at 15 K; (*b*) IR spectrum obtained on heating lithium bis(trimethylsilyl)amide to 110 ± 5 °C and co-depositing with 2.5 mmol of argon over a period of 0.5 h

The strong 1671 cm⁻¹ band, due to the C=N stretch of *N*-isopropylideneisopropylamine, first appeared at a reaction temperature of about 55 °C along with the diisopropylamine bands, which first appeared at lower temperatures. Both the amine and the imine bands increased in intensity at temperatures above 55 °C.

Lithium bis(trimethylsilyl)amide. Fig. 4(*b*) shows the matrix IR spectrum over the region 4000–400 cm⁻¹ obtained on heating lithium bis(trimethylsilyl)amide to a temperature of 110 ± 5 °C and co-depositing the products with 2.5 mmol of argon over 0.5 h. This is compared with the IR spectrum of a sample of 2 mmol of Ar–HN(SiMe₃)₂ at a dilution of 50:1 [Fig. 4(*a*)]. Important differences in the two spectra are (*i*) a band at 3400 cm⁻¹, which is present in Fig. 4(*a*) and absent from Fig. 4(*b*), and (*ii*) strong broad bands at 430, 472 and 1037 cm⁻¹, present in Fig. 4(*b*) and absent from Fig. 4(*a*).

In order to establish the degree of association of lithium bis(trimethylsilyl)amide in the vapour phase, its mass spectrum was determined after vaporization at approximately 100 °C of a solution of the amide in benzene (60 mg cm⁻³). The highest mass peak was found at *m*/*z* 334, corresponding to the dimer [⁷LiN(Me₃Si)₂]₂, accompanied by peaks at 333 (⁷Li⁶Li) and 332 (⁶Li₂), which confirm the presence of two Li atoms. No monomer peaks at *m*/*z* 167 (⁷Li) and 166 (⁶Li) were observed.

Lithium dibenzylamide. Fig. 5 shows the matrix IR spectra over the region 800–600 cm⁻¹ obtained on heating lithium dibenzylamide to temperatures of (*a*) 170, (*b*) 210 and (*c*) 260 °C followed by co-deposition of the products with argon. Dibenzylamine bands were present at reaction temperatures below 150 °C but did not grow in intensity above this temperature. Toluene bands at 695 and 729 cm⁻¹ were first observed at a reaction temperature of *ca.* 150 °C. As can be seen
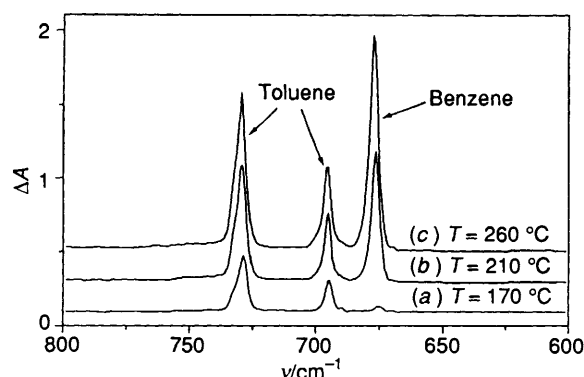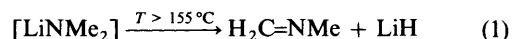

Fig. 5 IR spectrum of the matrix isolated decomposition products of lithium dibenzylamide heated to (*a*) 170, (*b*) 210 and (*c*) 260 °C. The lithium dibenzylamide solid was maintained at each temperature for a period of 0.5 h.

from Fig. 5(*a*), these two toluene bands are much more intense than the benzene band at 676 cm⁻¹. On increasing the reaction temperature to 210 °C, however, the benzene band at 676 cm⁻¹ became comparable in intensity to the toluene band at 729 cm⁻¹ and more intense than the 695 cm⁻¹ band [Fig. 5(*b*)]. At a reaction temperature of 260 °C the benzene band became more intense than both toluene bands in the 800–600 cm⁻¹ region [Fig. 5(*c*)]. The toluene and benzene bands did not grow in intensity above 300 °C. Furthermore, the amount of toluene produced from lithium dibenzylamide was determined quantitatively. This was done by depositing a known amount of an argon–toluene (50:1) mixture, which reproduced exactly the toluene spectrum resulting from the thermal decomposition. By this method it was deduced that [LiN(CH₂Ph)₂] decomposes to an equimolar amount of toluene. Unfortunately it was not possible to make a quantitative determination of the amount of benzene produced, as attempts to deposit known amounts of benzene were thwarted by the formation of films on the surfaces of the vacuum manifold.
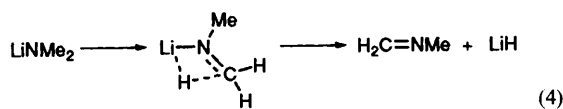
On heating the solid lithium amide to 600 ± 5 °C for 1.5 h in a stainless steel Knudsen cell, while co-depositing the products with argon, new bands appeared at 2083 cm⁻¹ (with a weaker satellite at 2100 cm⁻¹) and 646 cm⁻¹. The 646 and 2083 cm⁻¹ bands are assigned to lithium isocyanide monomer, LiNC, by comparison with the literature matrix IR spectrum,[12,13] and the weak band at 2100 cm⁻¹ is attributed to lithium isocyanide dimer, (LiNC)₂, by comparison with its literature matrix IR spectrum.[14] Fine, shiny, black crystals remained in the Knudsen cell, the identity of which still remains to be established.
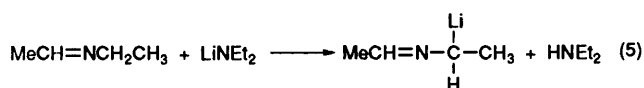
Discussion

It appears from the foregoing that, in general, lithium amides decompose to imines as long as the amides have β-hydrogens. For example, lithium dimethylamide, lithium diethylamide and lithium diisopropylamide decompose to *N*-methylenemethylamine, *N*-ethylideneethylamine and *N*-isopropylideneisopropylamine, respectively [eqns. (1)–(3)].

$$[LiNMe_2] \xrightarrow{T > 155\,°C} H_2C=NMe + LiH \qquad (1)$$

$$[LiNEt_2] \xrightarrow{T > 150\,°C} MeCH=NEt + LiH \qquad (2)$$

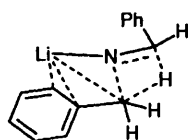$$[LiNPr^i_2] \xrightarrow{T > 55\,°C} Me_2C=NPr^i + LiH \qquad (3)$$

The fact that these decompositions occur at relatively low temperatures suggests that there is a low energy pathway involved. This could be the case if the $\alpha\beta$-lithium hydride elimination proceeds *via* a four-centre transition state [eqn. (4)], as has been suggested for analogous $\alpha\beta$-hydride eliminations from alkyllithium compounds.[3]

$$\text{LiNMe}_2 \longrightarrow \text{Li—N} \begin{smallmatrix} \text{Me} \\ \\ \\ \text{C—H} \\ \text{H} \end{smallmatrix} \longrightarrow \text{H}_2\text{C=NMe} + \text{LiH}$$
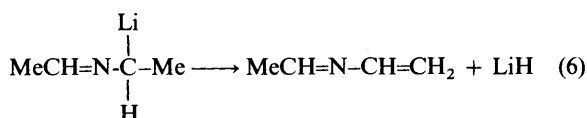
(4)

In each case, imine formation was accompanied by amine formation, beginning at a lower temperature. The initial amine formation was probably due to hydrolysis of the lithium amide by traces of water introduced during transfer of the amide into the matrix equipment. At more elevated temperatures, however, both the amine and imine bands continued to grow, and a *second source* of the amine seems likely at this stage. We thus propose that, once formed, the imine would almost certainly react with excess amide, which would attack the acidic hydrogen, as in, for example, eqn. (5)

$$\text{MeCH=NCH}_2\text{CH}_3 + \text{LiNEt}_2 \longrightarrow \text{MeCH=N—}\overset{\overset{\displaystyle \text{Li}}{|}}{\underset{\underset{\displaystyle \text{H}}{|}}{\text{C}}}\text{—CH}_3 + \text{HNEt}_2 \quad (5)$$

This would probably be followed by further $\alpha\beta$-hydride elimination at more elevated temperatures [eqn. (6)].

1

$$\text{MeCH=N-}\overset{\overset{\displaystyle \text{Li}}{|}}{\underset{\underset{\displaystyle \text{H}}{|}}{\text{C}}}\text{-Me} \longrightarrow \text{MeCH=N-CH=CH}_2 + \text{LiH} \quad (6)$$

It is quite possible that the bands at 1651 and 1654 cm^{-1}, which were observed on decomposing lithium diethylamide and lithium diisopropylamide respectively, are due to such $\alpha\beta$-unsaturated imines, as it is well known that conjugation of the C=N linkage with a single ethylenic double bond slightly lowers the C=N stretching frequency.[15] Similar secondary decomposition was reported for butyllithium, which gave butadiene, this then subsequently polymerizing in the presence of an excess of butyllithium.[3]

Lithium bis(trimethylsilyl)amide is the sole amide of this study which does not contain β-hydrogens; consequently it cannot decompose *via* an $\alpha\beta$-hydride elimination pathway. A gas-phase electron diffraction study of this amide indicated that it goes into the gas phase in a lower state of association than in the solid.[16] The electron diffraction data indicate that at a temperature of *ca.* 130 °C the amide exists mainly as a dimer, whereas X-ray crystallographic studies have established that it is a trimer in the solid.[17,18] Our mass spectral measurements confirm the dimeric state of this amide in the vapour phase at about 100 °C; so that it is virtually certain that the species trapped in solid argon was also the dimer. The matrix IR spectra do not enable the state of association of the matrix isolated species to be determined directly, though it is conceivable that experiments with precursors enriched with ^{6}Li might provide this information.

A comparison of the spectra of Figs. 4(*a*) and 4(*b*) reveals similarities in the majority of absorptions, as might be expected for HN(SiMe$_3$)$_2$ and [LiN(SiMe$_3$)$_2$]. The band at 3400 cm^{-1} in Fig. 4(*a*) is due to the N–H stretch of the amine and is obviously not present in Fig. 4(*b*). The broad band at 1037 cm^{-1} in Fig. 4(*b*) is due to the Si–N–Si antisymmetric stretch of the amide, which is blue-shifted from this mode in the amine by approximately 100 cm^{-1} due to back-donation of p-electron density from the N atom of the amide to empty d-orbitals on the Si atoms, so strengthening the Si–N bonds.[18] The bands at 430 and 472 cm^{-1}, which are present in Fig. 4(*b*) and absent from Fig. 4(*a*), are probably due to skeletal Li–N stretches.

Although lithium dibenzylamide has β-hydrogens, it also does not decompose *via* the $\alpha\beta$-hydride elimination mechanism discussed earlier. If it did decompose by eliminating LiH, it would give N-benzylidenebenzylamine as a product, but this is not the case. The temperature evolution of the toluene and benzene products suggests one of two possibilities. Either there are two possible decomposition pathways and the pathway which releases toluene has a lower activation energy barrier than that which releases benzene, or else the toluene is produced in the primary decomposition and benzene is a secondary decomposition product. As toluene is produced quantitatively from [LiN(CH$_2$Ph)$_2$], it seems likely that it is a primary decomposition product [eqn. (7)].

$$[\text{LiN(CH}_2\text{Ph)}_2] \xrightarrow{T > 150\,°C} [\text{LiN=CHPh}] + \text{PhMe} \quad (7)$$
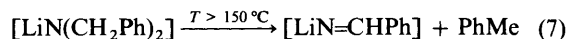
Benzene could then be produced as a secondary product from the decomposition of the imide [eqn. (8)].

$$[\text{LiN=CHPh}] \xrightarrow{T > 170\,°C} \text{LiNC} + \text{PhH} \quad (8)$$
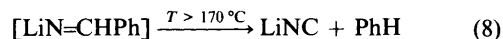
This mechanism is supported by the observation of lithium isocyanide monomer, LiNC, and dimer, (LiNC)$_2$, when the reaction temperature was raised to 600 °C.

The fact that the lithium dibenzylamide decomposes at mild temperatures suggests that there is a low energy pathway. The lithium interaction with the organic ligand almost certainly influences the decomposition pathway. This could, indeed, explain why LiH is not eliminated here as the electron-deficient Li atom can interact with the electron-rich phenyl groups, unlike in the other lithium dialkylamides which did not contain aromatic substituents. Lithium interactions with benzyl α-C, o-C and methylene C atoms have previously been discussed in connection with the X-ray crystal structure of lithium dibenzylamide.[19] A low energy transition state which includes such interactions can be envisioned 1.

Conclusions

N-Methylenemethylamine, N-ethylideneethylamine and N-isopropylideneisopropylamine were produced in the thermal decompositions of lithium dimethylamide, lithium diethylamide and lithium diisopropylamide, respectively.

Lithium dibenzylamide was exceptional as it did not decompose to the corresponding imine. Instead, carbon–nitrogen and carbon–carbon bonds were ruptured, giving toluene and benzene. A lithium imide intermediate can be postulated to account for the temperature evolution of these products.

All of the primary decompositions occurred under mild conditions ($T < 155$ °C), suggesting that the decomposition proceeded *via* a low energy pathway.

Finally, one of the amides studied, lithium bis(trimethylsilyl)-

amide, was itself volatile at temperatures > 70 °C. Mass spectrometry confirmed that it exists in the gas phase, and therefore probably in Ar matrices, as a dimer, but the exact state of association in matrices could not be obtained from the present study.

Acknowledgements

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