Structural Studies on some 1,3,4-Thiadiazolium-2-aminides and their Rearrangement Isomers using ^{15}N and ^{13}C NMR Spectroscopy

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^{15}N and ^{13}C NMR data are reported for some triaryl-1,3,4-thiadiazolium-2-aminides, I, (both as free bases and as hydrochloride salts) and for their rearranged 1,3,4-triazolium-2-thiolate, II, free base isomers. The structures of the compounds and their interconversion processes have thereby been re-studied. The $^1J(^{13}C-^{15}N)$ coupling constants have proved to be the most direct means of differentiating the isomeric structures. Nitrogen CPMAS NMR studies of I, as their hydrochlorides, and II using ^{15}N natural abundance, show that protonation takes place on the exocyclic NHPh moiety in the former series. ^{13}C CPMAS NMR studies show that I can undergo isomerization to II in the solid state.

5-Aryl-N,4-diphenyl-1,3,5-thiadiazolium-2-aminides I, also called thioisosydnonimines † in this work, and the corresponding isomeric 5-aryl-1,4-diphenyl-1,3,4-triazolium-2-thiolates II are members of the class of compounds known as mesoionic (Fig. 1).[1] Potts et al.[2a] and Ollis and Ramsden[2b] have discussed the formation of 1,3,4-triazolium-2-thiolates by the reaction of 1,4-diphenylthiosemicarbazide with acid chlorides followed by basification, as illustrated in Scheme 1. The triaryl-1,3,4-triazolium-2-thiolates thus formed have been known for many years,[3] while the possibility of two isomeric structures was suggested by Schönberg in 1938.[4] Baker and co-workers suggested in 1957[5] that the true structure of the reaction product might be that of the isomeric triaryl-1,3,4-thiadiazolium-2-aminides. However, it has been shown since
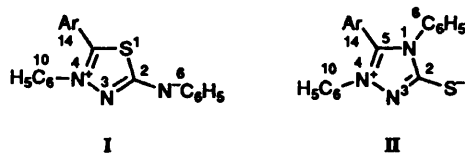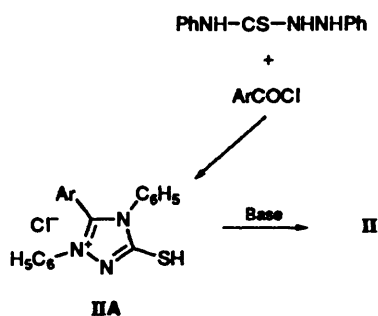
that the correct structure is that of the 1,3,4-triazolium-2-thiolate system[6] and the early dispute was settled.[1a] Moreover, more recent studies[2b,7] have demonstrated the formation of such thioisosydnonimines, I, as illustrated by Scheme 2, although compound I ($R^1 = R^2 = C_6H_5$ and $R^3 = Ar$) has not been synthesized via this route.

Fig. 1 Chemical structures and numbering systems for 1,3,4-thiadiazolium-2-aminides, I and 1,3,4-triazolium-2-thiolates, II

Scheme 1 Reaction scheme, previously reported, for obtaining mesoionic 5-aryl-1,4-diphenyl-1,3,4-triazolium-2-thiolates
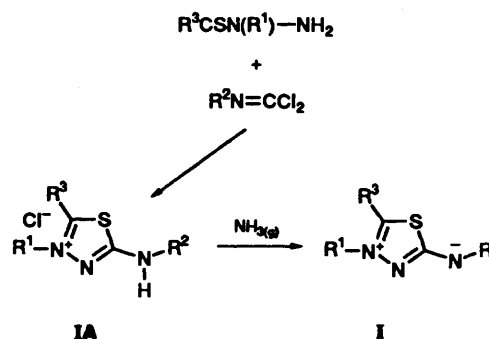
Scheme 2 Reaction scheme for obtaining mesoionic 1,3,4-thiadiazolium-2-aminides[6]

The isomerization of thioisosydnonimines, I, to 1,3,4-triazolium-2-thiolates, II, in alkaline conditions was studied by Grashey et al. in 1972.[8] The isomerization under the influence of heat and in alkaline conditions has also been studied by Ollis and Ramsden and by Potts et al.[1,2] Nevertheless, the reaction scheme shown in Scheme 1 continues to be used for obtaining 5-aryl-1,4-diphenyl-1,3,4-triazolium-2-thiolates both as the conjugate acids, IIA, and as the free bases, II.[9]

Thioisosydnonimines, I as free bases, are unstable in solution since they isomerize to 1,3,4-triazolium-2-thiolates, II, however, the hydrochlorides retain the 1,3,4-thiadiazolium-2-aminide ring structure. It is now also demonstrated, by ^{13}C CPMAS NMR experiments, that compounds I can nevertheless undergo isomerization to compounds II even in the solid state.

As part of an ongoing study of the chemistry and biological activity of mesoionic compounds[10] the above reactions have been carefully re-investigated using, in particular, ^{15}N and ^{13}C NMR[11] to characterize the compounds obtained.

Table 1 ^{15}N NMR chemical shifts $[\delta(^{15}N)]$ and $^1J(^{13}C-^{15}N)$ coupling constants for compounds A[a]

Aroyl substituent	$\delta(^{15}N)$[b]	$^1J(^{13}C-^{15}N)$/Hz	
H	88.9 (a)[c]	(a) –C-2	23.1 ± 1.5
		(a) –C-6	15.1 ± 1.5
	213.6 (c)	(c) –C-5	18.1 ± 1.5
		(c) –C-10	16.1 ± 1.5
CH₃O	88.9 (a)	(a) –C-2	23.1 ± 1.5
		(a) –C-6	14.1 ± 1.5
	258.4 (b)	(b) –C-2	<2
	209.4 (c)	(c) –C-5	14.1 ± 1.5
		(c) –C-10	16.1 ± 1.5
NO₂	90.9 (a)	(a) –C-2	23.1 ± 1.5
		(a) –C-6	14.1 ± 1.5
	257.7 (b)	(b) –C-2	<1
	216.3 (c)	(c) –C-5	16.1 ± 0.8
		(c) –C-10	16.1 ± 0.8

[a] See text for explanation. [b] (a), (b) and (c) distinguish the labelled nitrogen atoms as follows: $C_6H_5-N^{(a)}H-CS-N^{(b)}H-N^{(c)}H-C_6H_5$. [c] (b) has not been measured.

Results and Discussion

The reaction of phenyl isothiocyanate obtained from ^{15}N labelled aniline with carbon disulfide and ethyl chloroformate was used to obtain specifically labelled $C_6H_5-^{15}NH-CS-NH-NH-C_6H_5$.[12] The other two nitrogen atoms were also labelled: first by making $C_6H_5{}^{15}NHNH_2$ from ^{15}N labelled aniline by diazotization and reduction (no scrambling was observed);[13] the second nitrogen atom in the phenyl hydrazine was specifically labelled by carrying out the diazotization using $Na^{15}NO_2$, thereby generating a second phenylhydrazine with both nitrogen atoms labelled.

The three differently labelled 1,4-diphenylthiosemicarbazides thus obtained were treated with three different aroyl chlorides (benzoyl chloride, 1; p-methoxybenzoyl chloride, 2 and p-nitrobenzoyl chloride, 3) to give a range of specifically labelled products.

The ^{15}N NMR chemical shifts and $^1J(^{13}C-^{15}N)$ coupling constants obtained for the first formed products, designated A, from the reactions of 1,4-diphenylthiosemicarbazide with aroyl chlorides are given in Table 1.

The three labelled nitrogen atoms in compounds A are identified in Table 1 as $C_6H_5-N^{(a)}H-CS-N^{(b)}H-N^{(c)}H-C_6H_5$. The carbon atoms to which the various nitrogen atoms are attached in the cyclic compounds are C-2, C-5, C-6 and C-10 as shown in structure I. Coupling constants were obtained by comparison of the ^{13}C NMR spectra with and without the labelled nitrogen atoms.

Even without discussing the magnitudes (see below) of the chemical shifts, it can readily be seen from the coupling constants that the nitrogen atoms (a) are directly attached to two carbon atoms only. These first-formed compounds A cannot therefore be the 1,3,4-triazolium-2-thiolate hydrochlorides reported previously since the labelled nitrogen atoms in these compounds would be directly attached to three carbon atoms: N-1–C-2, –C-5 and –C-6. Thus, by far the most likely hypothesis is that these first-formed compounds—the kinetic products, are the thiadiazolium-aminide hydrochlorides, IA, as shown in Scheme 3, and not IIA as in Scheme 1—these being the thermodynamic products.

In order to confirm this hypothesis, we have obtained the corresponding thioisosydnonimine free bases, I, by neutralization of their conjugate acids, IA, with NH₃ gas and also isomerized compound IA directly to the 1,3,4-triazolium-2-thiolate free base II using pyridine; we have also converted I into II directly, thus clearly supporting the concept of
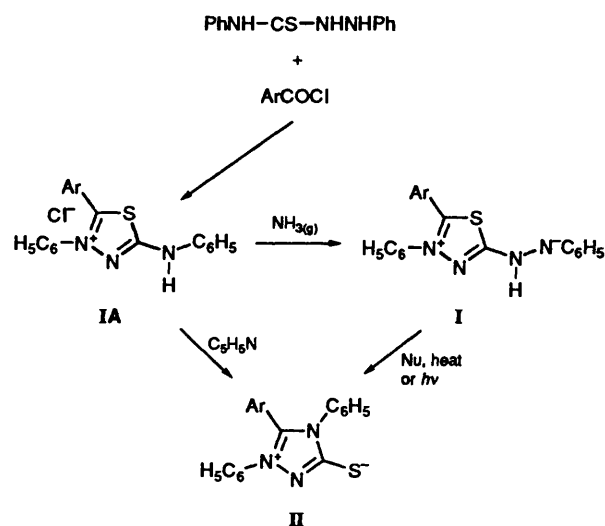
interconversion of the kinetic product to the thermodynamic product of these isomeric mesoionic systems. The relevant ^{15}N chemical shifts and $^1J(^{13}C-^{15}N)$ coupling constants are reported in Table 2. The reactions involved are summarized in Scheme 3 and the procedures can be found in the Experimental section.

The nitrogen chemical shifts given in Table 2 are consistent with the structures for the thioisosydnonimines I and the 1,3,4-triazolium-2-thiolates II. A point of special interest is that the alternative isomers, in which the ring heteroatom in position-1, in II, is exchanged with the corresponding exocyclic heteroatom, in I, do not show a large difference in their chemical shifts and this is associated with the fact that N-1 in II has its lone-pair electrons conjugated in a π-system while in I it is an imine-like moiety.

An additional point of interest concerns the close similarity of the N-3 and N-4 chemical shifts in both series. It is well known from nitrogen NMR studies that when a nitrogen atom acquires a positive charge there is an appreciable increase in the shielding of the nitrogen nucleus,[11c,14,15] since the nucleus deshielding is quenched and some shielding may even occur. Thus, as expected, N-4 is shielded when compared with N-3 and these nitrogen NMR data constitute a sensitive probe to distinguish between them. Jażwinski et al. also found this behaviour in the ^{15}N NMR chemical shifts for two 1,2,3,4-oxatriazolium-5-thiolates and two 1,2,3,4-thiatriazolium-5-olates.[16] The same behaviour was found in the solid state study; see Table 3. A similar discussion is valid for the other compounds shown in Table 1.

Table 2 reports the ^{15}N and ^{13}C NMR chemical shifts together with $^1J(^{13}C-^{15}N)$ coupling constants, for carbon atoms directly attached to ^{15}N enriched nitrogen atoms, in thioisosydnonimines, I and 1,3,4-triazolium-2-thiolates, II, both as free bases. The data presented strongly suggest that the isomeric systems are both cyclic. The coupling constants shown in Table 2 have values consistent with a delocalized π-electron system. It is, however, noteworthy that the magnitudes for C-2–N-3 and C-2–N-1, in II, suggest less N-3 and N-1 lone-pair electron delocalization towards C-2, than N-4 to C-5 or N-1 to C-5, for instance. The broadness of the ^{13}C NMR resonance signals for I is also most interesting and remains to be studied (see below).

It has been shown that in the conjugate acids of the thioisosydnonimines, the protonation site is on N-3,[2b] e.g. IA,

Scheme 3 Reaction scheme used in this work. 1, Ar = C_6H_5; 2, Ar = 4-$MeOC_6H_4$; 3, Ar = 4-$O_2NC_6H_4$. (Py = pyridine, Nu = nucleophile).

Table 2 ^{15}N and ^{13}C chemical shifts and $^1J(^{13}C^{-15}N)$ for 1,3,4-thiadiazolium-2-thiolates and 1,3,4-triazolium-2-thiolates[a]

Compound	Atom no.	$\delta(^{15}N)$	$\delta(^{13}C)$	$^1J(^{13}C^{-15}N)$/Hz
I.1	C-6–N-exo	175.8	135.2	16.6 ± 1.5
	C-2–N-exo	175.8	152.1	b
I.2	C-2–N-exo	174.6	152.3	c
	C-2–N-3	243.5	152.5	36.6 ± 3.0[d]
	C-5–N-4	213.5	162.0	15.3 ± 3.0[d]
	C-6–N-exo	174.6	135.6	c
	C-10–N-4	213.5	138.5	17.1 ± 3.1
I.3	C-2–N-3	249.6	152.1	b
	C-2–N-exo	177.5	152.0	30.0 ± 0.8[d]
	C-5–N-4	221.2	159.9	14.5 ± 0.8[d]
	C-6–N-exo	177.5	132.0	20.1 ± 3.0[d]
	C-10–N-4	177.5	138.3	16.1 ± 0.8
II.1	C-2–N-1	177.4	169.9	4.0 ± 1.5
	C-5–N-1	177.4	148.2	19.2 ± 1.5
	C-6–N-1	177.4	134.4	16.1 ± 1.5
II.2	C-2–N-1	177.0	169.7	4.0 ± 1.5
	C-5–N-1	177.0	148.3	18.1 ± 1.5
	C-6–N-1	177.0	134.5	16.1 ± 1.5
	C-2–N-3	257.0	169.7	3.0 ± 0.8
	C-5–N-4	195.1	148.3	19.1 ± 0.8
	C-10–N-4	195.1	136.2	19.1 ± 0.8
II.3	C-2–N-1	177.5	170.4	4.0 ± 1.5
	C-5–N-1	177.5	146.4	20.1 ± 1.5
	C-6–N-1	177.5	134.0	16.1 ± 1.5
	C-2–N-3	258.6	170.4	3.0 ± 0.8
	C-5–N-4	196.8	146.4	20.1 ± 0.8
	C-10–N-4	196.8	135.7	18.1 ± 0.8

[a] Structures are to be found in Scheme 3. Some data have not been reported since they were not obtained. [b] Not observed. [c] Not measured, ^{13}C NMR signal taken when the compound was used with natural abundance nitrogen. [d] Broad peak.

Table 3 ^{15}N CPMAS NMR data for 1,3,4-thiadiazolium-2-aminides, IA and 1,3,4-triazolium-2-thiolates, II[a]

Compound	$\delta(^{15}N)$[b]	W_H(Hz ± 7 Hz)
IA.1	N-exo 89.7	149
	N-3 257.6	62
	N-4 210.4	99
IA.2	N-exo 90.3	137
	N-3 256.1	99
	N-4 203.6	124
IA.3	Nitro 341.3	62
	N-exo 94.0	124
	N-3 260.3	124
	N-4 210.7	99
II.1	N-1 174.0	50
	N-3 261.0	62
	N-4 194.1	99
II.2	N-1 173.5	25
	N-3 256.8	74
	N-4 193.9	112
II.3	Nitro 349.5	62
	N-1 173.8	37
	N-3 262.4	99
	N-4 196.9	99

[a] Structures are shown in Scheme 3. [b] Chemical shifts are reported with respect to 5 mol dm^{-3} ^{15}NH$_4$NO$_3$ in 2 mol dm^{-3} HNO$_3$ as secondary reference. Compare with the solution-state data, Tables 1 and 2.

Scheme 3. ^{15}N NMR data constitute a sensitive probe in this respect[14,15] and there is an increase in the chemical shift of the nitrogen nucleus of about 100 ppm. This was observed in the neutralization IA→I (Scheme 3): $\delta_{N\text{-}exo}$ changes of about 86 ppm. Thus, it seems clear from our results that protonation occurs on N-exo, as shown in Scheme 3. Moreover, it was possible to observe the $^{15}N_{exo}$–^{1}H splitting both in the ^{15}N

and ^{1}H NMR spectra; the coupling constants are of the order of 90 Hz, typical for $^1J(^{15}N^{-1}H)$.[17]

The experiments carried out for the mesoionic systems studied, using ^{15}N CPMAS NMR, have the advantage of using natural abundance materials and solve the problem of their low solubility, although longer periods are needed to obtain the spectra.

The ^{15}N CPMAS spectra in the solid state exhibit three resonances for compounds IA–II and (1 and 2) and four for the nitro derivative (Scheme 3). The assignments are based on the assumption that the structures are actually as shown and bearing in mind the results obtained in solution when enriched materials were used. The chemical shifts and resonance line widths are given in Table 3.

There is a further point of interest in the labelled ^{15}N NMR spectra of I and IA (1, 2 and 3). In solution, compounds I show N-exo with a chemical shift of about δ 175, whereas an increase in the shielding of about 85 ppm occurs when protonation leading to IA takes place. In the solid state the chemical shift for this moiety, in compound IA, has the largest increase in shielding of nitrogen in the spectra. An unambiguous assignment of this signal appears in the ^{15}N CPMAS–NQS[18] spectrum, where the protonated nitrogen nucleus does not give a signal and it is assigned by difference. This is an interesting result since it shows the site of protonation in the solid state to be the same as in solution, viz., on the N-exo moiety. It has not been possible to demonstrate any exchange in the site of protonation either in the solid state or in solution.

The mesoionic compounds so far studied can be classified in relation to their thermodynamic stability (see above), with respect to the interconversion I→II where there is an exchange between the exocyclic and endocyclic heteroatoms or groups.[1a] Furthermore, the NMR data show another striking difference in their physico-chemical properties. The free bases I (1, 2 and 3) gave no signal in the ^{15}N CPMAS NMR spectra. This difference has been attributed to a longer relaxation time with these molecules, although additional study is needed in order to clarify it. However, it constitutes a noteworthy difference between the two isomeric systems, and can be used to distinguish one from the other in a pair of isomeric compounds.

Thioisosydnonimines I are deeply-coloured viscous oils (1 and 2 are red, while 3 is violet). They solidify when dried in vacuo for 3 h, but they isomerize to 1,3,4-triazolium-2-thiolates II over longer periods. This behaviour has been studied and Table 4 shows the ^{13}C CPMAS NMR data for the isomerized compounds (II, 1 and 2). The assignment of the chemical shift for C-2 at ca. δ 170 supports their identification as compounds II.1 and II.2, and not I.1 or I.2.

Experimental

The preparation of compounds I and II and the interconversion I→II were carried out by published procedures.[2]

Reagents. ^{15}N enriched 1,4-diphenylthiosemicarbazide was prepared essentially according to methods described in ref. 12(a). ^{15}N enriched aniline was prepared by nitration of benzene with 1 g H^{15}NO$_3$, 40% aqueous solution (MSD Isotopes), in 10 cm^3 trifluoroacetic anhydride in an ice–water bath.[12c] The resulting nitrobenzene was reduced (Sn–HCl) to aniline which was then treated with carbon disulfide and ethyl chloroformate (equivalent quantities) to afford phenyl isothiocyanate quantitatively. Its reaction with phenylhydrazine yields the desired thiosemicarbazide. This reacts with acid chlorides giving labelling on N-exo in the thioisosydnonimines and on N-1 in the 1,3,4-triazolium-2-thiolates. In order to get enriched ^{15}N at positions N-3 and/or N-4 in both heterocyclic systems phenylhydrazine was prepared by the diazotization of aniline (enriched or otherwise) with either Na^{15}NO$_2$ (MSD

Table 4 ^{13}C CPMAS for 1,3,4-triazolium-2-thiolates, **II.1** and **II.2**[a]

Atom no.	TOSS[b] (δ)	
	II.1	**II.2**
2	170.6	169.2
5	149.8	148.9
6	136.3	135.2
7,7'	129.8	117.4
8,8'	129.8	128.1
9	127.4	128.1
10	137.7	136.9
11,11'	129.8	128.1
12,12'	129.8	128.1
13	133.1	131.5
14	123.9	116.0
15,15'	129.8	117.4
16,16'	129.8	117.4
17	133.1	162.1
—	—	55.2

[a] See Scheme 3 for structures. [b] The CPMAS–NQSTOSS (non-quaternary suppression–total suppression side bonds) technique was used to obtain quaternary carbon resonance signals: C-2, C-5, C-6, C-10, C-14; the chemical shift magnitudes are essentially the same.

Isotopes) or NaNO$_2$ followed by heating at 90 °C (1 h), with Na$_2$SO$_3$–Na$_2$S$_2$O$_3$.[12]

General Procedure for Carrying out the Transformations Shown in Fig. 4.—1,3,4-Thiadiazolium-2-aminides, **IA**, *as conjugate acids.* A solution of the appropriate thiosemicarbazide (0.7 mmol dm^{-3}) in 1,4-dioxane was refluxed with the corresponding aroyl chloride (0.7 mmol dm^{-3}) for 2 h to give a solid which was filtered off and purified, when possible, by recrystallization from CHCl$_3$–acetone (1:1). **IA.1**, Ar = C$_6$H$_5$, m.p. 258.5–260 °C (Found: C, 65.2; H, 4.4; N, 11.5. Calc. for C$_{20}$H$_{16}$ClN$_3$S: C, 65.7; H, 4.4; N, 11.5%); δ_C 118.4 (C-7), 129.9 (C-8), 124.0 (C-9), 126.2 (C-11), 129.4 (C-12), 133.2 (C-13), 123.3 (C-14), 130.2 (C-15), 129.6 (C-16) and 131.5 (C-17). **IA.2**, Ar = 4-MeOC$_6$H$_4$, m.p. 243.5–244 °C (Found: C, 63.8; H, 4.7; N, 10.2. Calc. for C$_{21}$H$_{18}$ClN$_3$OS: C, 63.7; H, 4.7; N, 10.6%); δ_C 119.5 (C-7), 130.4 (C-8), 125.3 (C-9), 126.7 (C-11), 130.9 (C-12), 132.3 (C-13), 115.4 (C-14), 132.9 (C-15), 115.7 (C-16), 163.9 (C-17) and 56.5 (OCH$_3$). **IA.D**, Ar = 4-O$_2$NC$_6$H$_4$, m.p. 238.5–239 °C (Found: C, 58.1; H, 3.6; N, 13.8. Calc. for C$_{20}$H$_{15}$ClN$_4$O$_2$S: C, 58.5; H, 3.6; N, 13.6%); δ_C 118.9 (C-7), 129.9 (C-8), 124.8 (C-9), 126.4 (C-11), 130.3 (C-12), 132.1 (C-13), 129.4 (C-14), 132.4 (C-15), 124.4 (C-16) and 149.9 (C-17). Some data comes from unlabelled compounds.

1,3,4-Thiadiazolium-2-aminides, **I**, *as free bases.* Dry ammonia gas was passed through a solution of compounds **IA** in chloroform to afford deeply-coloured viscous oils, after filtering off ammonium chloride and rotoevaporating the solution. The oils may be solidified by drying *in vacuo* for 3 h. **I.1**, Ar = C$_6$H$_5$, red, δ_C 120.2 (C-7), 128.5 (C-8), 124.5 (C-9), 125.0 (C-11), 128.7 (C-12), 130.7 (C-13), 125.9 (C-14), 129.1 (C-15), 128.9 (C-16) and 130.1 (C-17). **I.2**, Ar = 4-MeOC$_6$H$_4$, red, δ_C 121.0 (C-7), 129.3 (C-8), 121.9 (C-9), 125.2 (C-11), 130.3 (C-12), 130.1 (C-13), 112.6 (C-14), 118.2 (C-15), 114.2 (C-16), 161.1 (C-17) and 55.3 (OCH$_3$). **I.3**, Ar = 4-O$_2$NC$_6$H$_4$, violet, δ_C 120.8 (C-7), 129.7 (C-8), 122.2 (C-9), 125.9 (C-11), 129.7 (C-12), 130.8 (C-13), 116.9 (C-14), 129.8 (C-15), 123.9 (C-16) and 148.0 (C-17).

1,3,4-Triazolium-2-thiolates, **II**, *as free bases.* Compounds **IA** were refluxed for 3 h in pyridine. The red colour faded giving rise to yellowish solids which were filtered off. After recrystallizing from methanol the isomeric products were obtained. **II.1**, Ar = C$_6$H$_5$, m.p. 316–317 °C (lit.,[2a] 325 °C, lit.,[5] 319 °C); δ_C 128.9 (C-7), 129.0 (C-8), 128.8 (C-9), 125.6 (C-11),

128.6 (C-12), 131.6 (C-13), 122.4 (C-14), 129.4 (C-15), 129.8 (C-16) and 130.5 (C-17). **II.2**, Ar = 4-MeOC$_6$H$_4$, m.p. 283–284 °C; δ_C 130.1 (C-7), 129.4 (C-8), 130.3 (C-9), 126.2 (C-11), 129.7 (C-12), 130.6 (C-13), 114.1 (C-14), 132.8 (C-15), 114.8 (C-16), 161.2 (C-17) and 55.9 (OCH$_3$). **II.3**, Ar = 4-O$_2$NC$_6$H$_4$, m.p. 309–310 °C; δ_C 129.6 (C-7), 129.6 (C-8), 128.7 (C-9), 123.7 (C-11), 129.1 (C-12), 130.1 (C-13), 128.4 (C-14), 132.4 (C-15), 126.6 (C-16) and 149.0 (C-17).

NMR Spectra.—The NMR spectra were recorded on a Bruker WH400 (for ^{1}H) spectrometer; 40.6 MHz for ^{15}N and 100.6 MHz for ^{13}C. ^{15}NH$_4$NO$_3$ 5 mol dm^{-3} in 2 mol dm^{-3} HNO$_3$ was used as the external standard for the ^{15}N spectra taken either in CDCl$_3$ (compounds **I**) or [^{2}H$_6$]DMSO (compounds **IA** and **II**) on 0.03 mol dm^{-3} solutions. TMS was the reference for the ^{13}C NMR spectra. The ^{15}N NMR spectra were obtained with wideband proton decoupling where the resonance signals are observed as singlets; inverse gated decoupling was used to suppress the NOE (nuclear Overhauser effect), and with proton coupling, where ^{15}N signals are observed as doublets. Here, the resulting loss in signal-to-noise ratio is compensated by the nitrogen enrichment. Wideband proton decoupling (NOISE modulation) was used to measure ^{13}C NMR signals either for natural abundance work, where a singlet is observed or with enriched nitrogen, where a doublet due to split between ^{13}C–^{15}N is observed. DEPT (distortionless enhancement by polarization transfer) was used to distinguish between CH and quaternary carbon atoms. ^{15}N CPMAS (cross polarization magic angle spin) high-resolution solid-state NMR spectra were obtained using a Bruker 300 MHz (for ^{1}H proton) solid state spectrometer, operating at 30.42 MHz (for ^{15}N).

The chemical shifts in Table 3 were referred originally to neat nitromethane (external primary reference used in this work) but reported relative to 5 mol dm^{-3} NH$_4$NO$_3$ in 2 mol dm^{-3}, +359.0 from neat nitromethane. External TMS was used for the ^{13}C CPMAS NMR data.

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