N-15 NMR Analysis of 1,2,3-Thiadiazoles

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The ^{15}N nmr spectra of a series of 1,2,3-thiadiazoles reveal the strong influence of substituents at C-5 on the N-2 resonance. Upon methylation, the two thiadiazole nitrogen resonances are shielded, but the most dramatic shift is observed for the methylated nitrogen, $\Delta\delta > 140$ ppm. The ^{15}N chemical shifts of some mesoionic thiadiazoles were also determined and explained by the dual effect of 5-substitution and salt formation. By disconnecting these effects, the ^{15}N chemical shifts of **10** and **11** were found to be unusual and to reflect a thiapentalene character.

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Nowadays structure analysis of organic compounds is essentially based on nmr spectroscopy. In the field of 1,2,3-thiadiazoles, substituent effects on the ^{13}C chemical shifts have been investigated [1], but no systematic study on the ^{15}N chemical shifts has been reported [2]. In this paper we shall fill this gap by first considering the effect of various C-4 or C-5 substituents on the ^{15}N chemical shifts of 1,2,3-thiadiazoles. Then, the influence of *N*-methylation on the nitrogen chemical shifts will be studied; and, finally, some mesoionic derivatives and thiadiazoles with thiapentalene character will be analyzed.

The ^{15}N nmr spectra of fifteen monosubstituted 1,2,3-thiadiazoles, prepared in our laboratory [1,3], were recorded on a Bruker WM spectrometer at 25.35 MHz, and the assignment of the nitrogen absorptions was based on the multiplicity patterns. The results, summarized in Table 1, indicate the strong dependence of the N-2 resonance on the R^5-substituent, due to the conjugation effect. For instance, the electron-withdrawing formyl group at the 5-position deshields N-2 by 17 ppm, whereas the 5-amine function shifts the N-2 resonance upfield by 56 ppm compared with the parent thiadiazole. Substituents at the 4-position have little effect on the nitrogen resonances.

Table 1

Nitrogen NMR Data of 1,2,3-Thiadiazoles **1** [a]

No.	R^4	R^5	Solvent	N-2	N-3
a	H	H	DMSO-d_6	409.9	436
b	H	Et	$CDCl_3$	403.7	434.5
c	H	SMe	$CDCl_3$	402	435
d	H	Cl	DMSO-d_6	414	443.5
e	H	NH_2 [b]	DMSO-d_6	353.6	433.8
f	H	COPh	$CDCl_3$	421.7	437.6
g	H	CHO	$CDCl_3$	427.2	438.4
h	H	CH=NOH (*Z*) [c]	DMSO-d_6	410.9	430
i	H	CH=NOMe (*Z*) [d]	$CDCl_3$	412.6	427.9
j	H	CH=N(O)Me (*Z*) [e]	DMSO-d_6	399.9	426.2
k	H	CH=NNHPh (*E*) [f]	DMSO-d_6	402.3	438.9
l	Ph	H	DMSO-d_6	411.2	433.3
m	*t*-Bu	H	DMSO-d_6	410.4	439.4
n	COOMe	H	DMSO-d_6	416.1	438.2
o	CHO	H	DMSO-d_6	417.0	438.95

[a] δ Values from liquid ammonia quoted, using nitromethane as external reference. The coupling constants are: $^2J_{N3\text{-}H4}$ = 9-11 Hz, $^3J_{N2\text{-}H4}$ = 2-3.5 Hz, $^3J_{N3\text{-}H5}$ = 2-3 Hz, $^3J_{N2\text{-}H5} \leq 1$ Hz. [b] NH_2 at δ 58.8. [c] NOH at δ 378.5 [d] NOMe at δ 389. [e] N(O)Me at δ 282.1. [f] N-NHPh at δ 343.3 and 153.8.

With these data at hand we investigated the influence of *N*-methylation on the nitrogen chemical shifts. It is known that 1,2,3-thiadiazoles can be methylated at the N-2 and N-3 position [3-7]. We have selected five thiadiazoles **1a,d,l,m,n** for treatment with Meerweins's reagent in dichloromethane. The ratios of the methylated products **2** and **3** were determined by integration of the methyl singlets in the ^1H nmr spectra of the crude reaction mixtures;

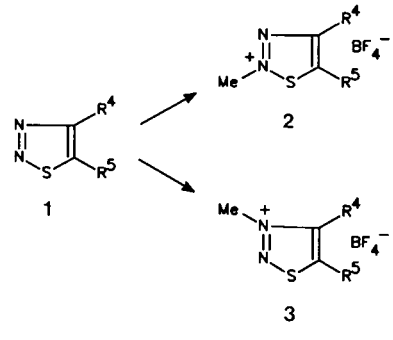


Table 2

Product Distribution during the Methylation of **1** with Meerwein's Reagent

No	R^4	R^5	**2** (%)	**3** (%)
a	H	H	4	96
d	H	Cl	–	100
l	Ph	H	81	19
m	*t*-Bu	H	86.5	13.5
n	COOMe	H	8	92

the results are shown in Table 2. Thus, methylation occurs preferentially at N-3 in the absence of a steric group at C-4. The influence of the ester function at C-4 in directing methylation at N-3 has already been discussed earlier [6]. The position of methylation was established by consideration of the coupled ^{13}C nmr spectra, and, in the cases of **2m** and **3l**, also by selective decoupling experiments (see Experimental).

Table 3 lists the ^{15}N nmr data of the thiadiazolium salts. All the nitrogen resonances are shielded compared with those of the corresponding thiadiazoles (Table 1). The most dramatic upfield shifts are found for the methyl-substituted nitrogen atoms, ranging from 142 to 145 ppm when the methyl is located at N-2, and from 158 to 167 ppm when N-3 is substituted. The average shielding of the β-nitrogen atom in the two cases is almost the same, 30-40 ppm. The observed large increase in shielding of the nitrogen resonance by removal of the lone electron pair is in consonance with other ^{15}N nmr studies on protonated or methylated *N*-heterocycles [8]; *e.g.* $\Delta\delta$ = 110 ppm for protonation of thiazole and 123 ppm for methylation of pyridine.

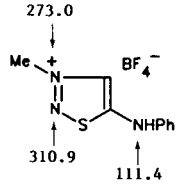
By treating **3d** with aniline, the salt **4** and the mesoionic compound **5** were prepared and analyzed by ^{15}N nmr spectroscopy. Since the negatively charged 5-substituent in mesoionic compounds displaces electron density towards the positively charged nucleus [9], the ring nitrogen shieldings are expected to be even larger than in the corresponding salts, with the largest effect on N-2. This is indeed the case as shown for the conversion of **4** into **5**, where the N-2 resonance is shifted upfield by 49 ppm and the N-3 resonance by only 9 ppm. Note also from the drawings that deprotonation of the anilino nitrogen causes a downfield shift of no less than 121.5 ppm. Similar but smaller effects have been reported for *N*-acetylsydnonimines [10].

Table 3

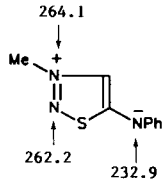
Nitrogen NMR Data of the 1,2,3-Thiadiazolium Salts **2** and **3** [a]

No	R^4	R^5	Compound **2**		Compound **3**	
			N-2	N-3	N-2	N-3
a	H	H			377.1	278
d	H	Cl			373.5	276.7
l	Ph	H	268.9	400.2	376.8	274.1
m	*t*-Bu	H	265.7	405.3	381.6	274.8
n	COOMe	H			387.1	277.7

[a] δ Values from liquid ammonia quoted, using nitromethane as external reference; solvent: dimethyl sulfoxide. The coupling constants are: for **2**: $^3J_{N3\text{-}H5}$ = 2 Hz, $^3J_{N2\text{-}H5}$ = 4-4.5 Hz, $^2J_{N2\text{-}Me}$ = $^3J_{N3\text{-}Me}$ = 1.5-2.5 Hz; for **3**: $^2J_{N3\text{-}H4}$ = 4-5 Hz, $^3J_{N2\text{-}H4} \leq$ 2 Hz, $^3J_{N3\text{-}H5}$ = 6 Hz, $^3J_{N2\text{-}H5} \leq$ 2 Hz, $^2J_{N3\text{-}Me}$ = $^3J_{N2\text{-}Me}$ = 1.5-2.5 Hz.

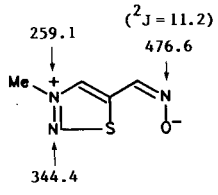


4 (DMSO)

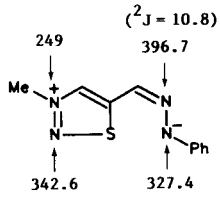


5 (DMSO)

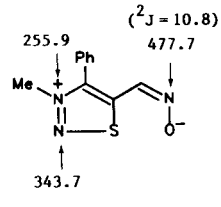
Two other illustrations of the dual role of salt formation and electron delocalization of the R^5-substituent are found when the oxime **1h** and the hydrazone **1k** (Table 1) are transformed into the mesoionic compounds **6** and **7**; the N-2 and N-3 resonances then experience a shielding of 66.5/60 and 171/190 ppm respectively. The contribution of the R^5-substituent in these cases can be calculated by comparison of the ^{15}N chemical shifts with those of **3a**, giving the results shown in Table 4.



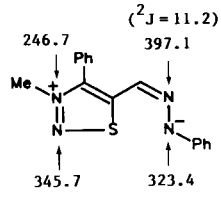
6 (DMSO)



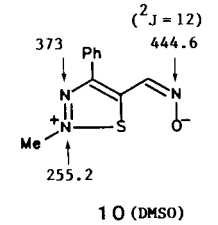
7 ($CDCl_3$)



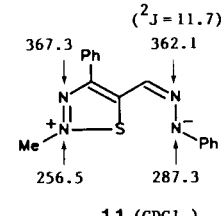
8 (DMSO)



9 ($CDCl_3$)



10 (DMSO)



11 ($CDCl_3$)

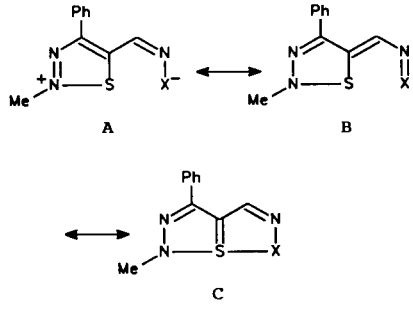
Table 4

Incremental Substituent Effects [a]

Compound	Z_{52}	Z_{53}
6	-33	-19
7	-34.5	-29
8	-33	-18
9	-31	-27
10	-14	-27
11	-12	-33

[a] Z_{ij} denotes the influence of a substituent in position i on the nitrogen resonance of position j; negative values correspond to upfield shifts.

Finallly, let us consider the following two series: **8** and **9** *versus* **10** and **11** which are the 5-substituted derivatives of **3l** and **2l**. The incremental R^5-substituent effects are given in Table 4. Whereas the calculated increments for **8** and **9** are similar to those for **6** and **7** respectively, the values for **10** and **11** deviate from expectation. Indeed, the fully conjugative interaction of the side-chain substituent, represented by canonical form **B**, should result in stronger shielding of the N-2 atom, which is not the case. In fact, the side-chain nitroso and azo functions of resonance form **B** are also not in compliance with the observed ^{15}N chemical shifts; for instance nitrosobenzene resonates at δ 913 and azobenzene at δ 509 ppm [11]. We believe that this anomaly reflects the thiapentalene character of the molecules **10** and **11**, represented by canonical form **C**. Thiapentalenes have a hypervalent sulfur atom and a three-center four-electron bonding system with a high electron density at the terminal heteroatoms, compensated by weakening of their σ-bonds with sulfur [12]. This extra electron density decreases the shielding effect of the R^5-substituent on N-2 and explains the smaller values for **10** and **11**. X-ray crystal structure analyses of these compounds support this conclusion [5,13].



10/11 : X = O or NPh

EXPERIMENTAL

The ^1H and ^{13}C nmr spectra were recorded on a Bruker WM-250 or AMX-400 spectrometer. The chemical shifts are reported in ppm relative to TMS as an internal reference.

Natural abundance ^{15}N nmr spectra were recorded on a Bruker WM-250 spectrometer, operating at 25.35 MHz, and equipped with a selective ^{15}N 10 mm probe. The chemical shifts were determined with respect to external nitromethane contained in a 4 mm capillary held centrally in the sample tube. This reference was given a δ value of 380.2 ppm, thus converting the N chemical shifts to the liquid ammonia shielding scale.

The DEPT pulse sequence based on polarization transfer through long range coupling (^2J and $^3J_{N\text{-}H}$) was used to detect the nitrogens two or three bonds away from aromatic or methyl protons. In most cases the ^1H coupled spectra were recorded to help assignment of the various nitrogens, and to measure the values of ^2J and $^3J_{N\text{-}H}$.

To detect the N-2 and N-3 atoms in 4,5-disubstituted thiadiazoles, and N-2 in 4-substituted thiadiazoles ($^3J_{N2\text{-}H5} < 1$ Hz), the ^{15}N nmr spectra were taken by the inverse gated heteronuclear decoupling technique.

Typical acquisitation parameters for the DEPT sequence are: spectral width 9000 Hz (δ 550 → 200 ppm), pulse angle 45°, delay time .05 sec (^nJ = 10 Hz), number of scans ~10000 for ^1H coupled spectra. Typical acquisition parameters for the inverse gated sequence are: spectral width 9000 Hz, pulse angle 45°, relaxation delay 10 sec, number of scans ~10000.

The compounds **1, 6, 7, 8, 10** and **11** have been synthesized previously [3,5,13].

Methylation of **1a**.

To a solution of **1a** (0.86 g, 10 mmoles) in dichloromethane (30 ml) was added trimethyloxonium tetrafluoroborate (1.63 g, 11 mmoles), and the reaction mixture was stirred at room temperature for 15 hours. After evaporation of the solvent, the residual oil was crystallized from methanol to give crystals in 42% yield (800 mg), composed of **2a** and **3a** in a ratio of 3:97%. They were not further purified.

2-Methyl-1,2,3-thiadiazolium Tetrafluoroborate (**2a**).

This compound had ^1H nmr (400 MHz, dimethyl sulfoxide-d_6): δ 4.70 (s, 3H, NMe), 9.23 and 9.86 (two d, 2H, C_4-H and C_5-H, ^3J = 3 Hz); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 46.2 (q, NMe, $^1J_{CH}$ = 146 Hz), 147.1 (d x d, C-4, $^1J_{CH}$ = 205 Hz, $^2J_{CH}$ = 5 Hz), 149.9 (d x d, C-5, $^1J_{CH}$ = 206 Hz, $^2J_{CH}$ = 13 Hz).

3-Methyl-1,2,3-thiadiazolium Tetrafluoroborate (**3a**).

This compound had ^1H nmr (400 MHz, dimethyl sulfoxide-d_6): δ 4.62 (s, 3H, NMe), 9.67 and 9.80 (two d, 2H, C_4-H and C_5-H, ^3J = 3 Hz); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 46.8 (q x d, NMe, $^1J_{CH}$ = 146.6 Hz, $^3J_{CH}$ = 0.8 Hz), 145.8 (d x d x q, C-4, $^1J_{CH}$ = 207 Hz, $^2J_{CH}$ = 9 Hz, $^3J_{CH}$ = 3 Hz), 150.6 (d x d, $^1J_{CH}$ = 208 Hz, $^2J_{CH}$ = 12 Hz; ^{15}N nmr: see Table 3.

Anal. Calcd. for $C_3H_5BF_4N_2S$ (mol wt 188, mixture of **2a** and **3a** in 3:97%): C, 19.17; H, 2.68. Found: C, 19.31; H, 2.67.

5-Chloro-3-methyl-1,2,3-thiadiazolium Tetrafluoroborate (**3d**).

To a solution of **1d** (5 g, 41.5 mmoles) in dichloromethane (100 ml) was added 1.1 equivalents of trimethyloxonium tetrafluoroborate (6.75 g) and the mixture was stirred at room temperature for 15 hours. The solvent was removed and the residue was washed with diethyl ether to give **3d** in 93% yield (8.6 g), mp 90-93°; ^1H nmr (250 MHz, dimethyl sulfoxide-d_6): δ 4.6 (s, 3H, NMe), 9.95 (s, 1H, C_4-H); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 47.8 (q, NMe, $^1J_{CH}$ = 147 Hz), 145.7 (d x q, C-4, $^1J_{CH}$ = 208 Hz, $^3J_{CH}$ = 3 Hz); 154.7 (d, C-5, $^2J_{CH}$ = 7.5 Hz); ^{15}N nmr: see Table 3.

Anal. Calcd. for $C_3H_4BClF_4N_2S$ (mol wt 222): C, 16.20; H, 1.81. Found: C, 16.26; H, 1.71.

Methylation of **1l**.

To a solution of **1l** (1.62 g, 10 mmoles) in dry dichloromethane (30 ml) was added 1.1 equivalents of trimethyloxonium tetrafluoroborate (1.63 g) and the mixture was stirred at room temperature for 15 hours. The precipitate was collected and shown by ^1H nmr to consist of a mixture of **2l** and **3l** in a ratio of 63:37%; overall yield 82% (2.155 g). The isomers were not separated.

2-Methyl-4-phenyl-1,2,3-thiadiazolium tetrafluoroborate (**2l**).

This compound had ^{1}H nmr (400 MHz, dimethylsulfoxide-d_6): δ 4.75 (s, 3H, NMe), 7.55-7.65 (m, 3 Ph protons), 8.12 (d x d, 2 Ph *ortho* protons), 10.16 (s, 1H, C_5-H); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 46.5 (q, NMe, $^1J_{CH}$ = 146.5 Hz), 127.3, 127.6, 129.4 and 131.1 (Ph C-atoms), 143.7 (d, C-5, $^1J_{CH}$ = 202 Hz), 158.1 (q, C-4, $^2J_{CH}$ = $^3J_{CH}$ = 4.2 Hz); ^{15}N nmr: see Table 3.

3-Methyl-4-phenyl-1,2,3-thiadiazolium Tetrafluoroborate (**3l**).

This compound had ^{1}H nmr (400 MHz, dimethyl sulfoxide-d_6): δ 4.45 (s, 3H, NMe), 7.6-7.75 (m, 3 Ph protons), 7.78 (d x d, 2 Ph *ortho* protons), 9.9 (s, 1H, C_5-H); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 46.1 (q, NMe, $^1J_{CH}$ = 146.5 Hz), 124.7, 129.1, 130.0 and 131.6 (Ph C-atoms), 148.6 (d, C-5, $^1J_{CH}$ = 205 Hz), 156.2 (m, C-4, becomes d x t upon irradiation of the NMe protons, $^2J_{CH}$ = 8.3 Hz); ^{15}N nmr: see Table 3.

Anal. Calcd. for $C_9H_9BF_4N_2S$ (mol wt 264, mixture of **2l** and **3l** in 63:37%): C, 40.94; H, 3.44. Found: C, 40.71; H, 3.32.

Methylation of **1m**.

To a solution of **1m** (2 g, 14 mmoles) in dry dichloromethane (60 ml) was added 1.1 equivalents of trimethyloxonium tetrafluoroborate (2.3 g) and the mixture was stirred at room temperature for 15 hours. After removal of the solvent, the residual oil was crystallized from methanol/diethyl ether to give crystals in 77% yield (1.7 g), composed of **2m** and **3m** in a ratio of 88:12%. The isomers were not separated.

4-*t*-Butyl-2-methyl-1,2,3-thiadiazolium Tetrafluoroborate (**2m**).

The compound had ^{1}H nmr (400 MHz, dimethyl sulfoxide-d_6): δ 1.44 (s, 9H, *t*-Bu), 4.65 (s, 3H, NMe), 9.55 (s, 1H, C_5-H); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 29.6 and 34.1 (*t*-Bu), 46.2 (q, NMe, $^1J_{CH}$ = 146.9 Hz), 143.7 (C-5, $^1J_{CH}$ = 202 Hz, $^4J_{CH}$ = 1 Hz), 169.4 (d x decet, C-4, becomes d upon irradiation of *t*-Bu protons, $^2J_{CH}$ = 4.5 Hz, $^3J_{CH}$ = 4.5 Hz); ^{15}N nmr: see Table 3.

4-*t*-Butyl-3-methyl-1,2,3-thiadiazolium Tetrafluoroborate (**3m**).

This compound had ^{1}H nmr (400 MHz, dimethyl sulfoxide-d_6): δ 1.53 (s, 9H, *t*-Bu), 4.69 (s, 3H, NMe), 9.31 (s, 1H, C_5-H); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 28.4 and 33.6 (*t*-Bu), 48.1 (q, NMe, $^1J_{CH}$ = 146 Hz), 146.7 (d, C-5, $^1J_{CH}$ = 204 Hz), 164.9 (C-4); ^{15}N nmr: see Table 3.

Anal. Calcd. for $C_7H_{13}BF_4N_2S$ (mol wt 244, mixture of **2m** and **3m** in 88:12%): C, 34.45; H, 5.37. Found: C, 34.58; H, 5.24.

4-Methoxycarbonyl-3-methyl-1,2,3-thiadiazolium Tetrafluoroborate (**3n**).

To a solution of **1n** (1.44 g, 10 mmoles) in dry dichloromethane (30 ml) was added 1.1 equivalents of trimethyloxonium tetrafluoroborate (1.63 g) and the mixture was stirred at room temperature for 15 hours. After removal of the solvent, the residual oil was crystallized from methanol to give **3n** in 46% yield (1.13 g), mp 103°; ^{1}H nmr (400 MHz, dimethyl sulfoxide-d_6): δ 4.02 (s, 3H, OMe), 4.75 (s, 3H, NMe), 10.07 (s, 1H, C_5-H); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 48.8 (q, NMe, $^1J_{CH}$ = 148 Hz), 54.3 (q, OMe, $^1J_{CH}$ = 150 Hz), 145.7 (d x q, C-4, $^2J_{CH}$ = 7.4 Hz, $^3J_{CH}$ = 2 Hz), 154.2 (d, C-5, $^1J_{CH}$ = 208 Hz), 156.0 (q x d, CO); ^{15}N nm: see Table 3.

Anal. Calcd. for $C_5H_7BF_4N_2O_2S$ (mol wt 246): C, 24.41; H, 2.87. Found: C, 24.52; H, 2.77.

3-Methyl-1,2,3-thiadiazolium-5-anilide (**5**).

A solution of **3d** (1.11 g, 5 mmoles) and three equivalents of aniline (1.395 g) in acetonitrile (30 ml) was stirred overnight at room temperature. The reaction mixture was poured in aqueous sodium hydrogen carbonate (1.5 g in 150 ml) and extracted three times with dichloromethane (100 ml). The organic extracts were dried over magnesium sulfate, evaporated and chromatographed on silica gel with chloroform/methanol (20:1) as the eluent to give **5** in 94% yield (0.9 g), mp 99-104° (lit [4e] 94-96°); ^{1}H nmr (400 MHz, dimethyl sulfoxide-d_6): δ 4.1 (s, 3H, NMe), 6.95 (m, 3H, Ph *ortho* and *para* protons), 7.35 (t, 2H, Ph *meta* protons), 8.27 (s, 1H, C_4-H); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 45 (NMe, $^1J_{CH}$ = 144 Hz, $^3J_{CH}$ = 1.7 Hz), 119.7, 122, 129.2 and 151.1 (Ph C-atoms), 128.1 (C-4, $^1J_{CH}$ = 199 Hz, $^3J_{CH}$ = 3 Hz), 163.1 (C-5, $^2J_{CH}$ = 9 Hz); ^{15} N nmr: see structure **5**.

Methylation of 4-Phenyl-1,2,3-thiadiazole-5-carbaldehyde Phenylhydrazone.

To a solution of the hydrazone [5] (0.56 g, 2 mmoles) in dry dichloromethane (20 ml) was added 1.5 equivalents of trimethyloxonium tetrafluoroborate (450 mg) and the whole was stirred overnight at room temperature. The reaction mixture was poured into ice-cooled water (100 ml) containing 1 g of potassium carbonate. The organic layer was collected and the aqueous phase was extracted three times with dichloromethane (50 ml). The organic extracts were washed with water (3 x 50 ml), dried over magnesium sulfate and evaporated to give a mixture of **9** and **11** in 97% yield (573 mg, ratio by nmr 3:1). This mixture was separated by column chromatography on silica gel with dichloromethane/petroleum ether (1:1) as the eluent.

3-Methyl-4-phenyl-1,2,3-thiadiazolium-5-phenylazomethylide (**9**).

This compound was obtained as dark red crystals in 43% yield (254 mg), mp 148-150°; ^{1}H nmr (250 MHz, deuteriochloroform): δ 4.0 (s, 3H, NMe), 7.0-7.8 (five m, 2 Ph), 8.0 (s, 1H, CH=N); ^{13}C nmr (deuteriochloroform): δ 43.2 (NMe, $^1J_{CH}$ = 143.6 Hz), 118.3-130.4 and 151.1 (Ph C-atoms), 123.0 (CH=N, $^1J_{CH}$ = 190 Hz), 139.1 (C-5, $^2J_{CH}$ = 14 Hz), 141.0 (C-4); ^{15}N nmr: see structure **9**.

Anal. Calcd. for $C_{16}H_{14}N_4S$ (mol wt 294): C, 65.28; H, 4.79. Found: C, 65.10; H, 4.86.

2-Methyl-4-phenyl-5-phenylazomethylene-1,2,3-thiadiazole (**11**).

This compound was obtained in 18% yield (106 mg) and was found to be identical with a previously prepared sample [5].

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