Amidines. Part 34.[1] ^{15}N NMR Spectra of trisubstituted amidines. Substituent effects

Janusz Oszczapowicz, Iwona Wawer,[a] Manfred Dargatz[b] and Erich Kleinpeter[b]
[a] *Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warszawa, Poland*
[b] *Department of Chemistry, Martin-Luther University, Halle-Wittenberg, Germany*

^{15}N NMR spectra of four series of amidines (R^2R^3N–CR^1=NR^4; 24 compounds) in $CDCl_3$ solutions have been recorded and the chemical shifts of both nitrogen atoms assigned. The relation between substitution at the three sites of the amidino [>N–C(=N–)–] group and the ^{15}N NMR chemical shifts of both nitrogen atoms is discussed on the basis of the results and the data accessible in the literature for seven other non-tautomerizing open-chain amidines.

It is shown that, due to a strong conjugation in the amidino group, a substituent at either of the two nitrogen atoms exerts opposite effects on the shielding and thus on the chemical shifts of the amino and imino nitrogen atoms.

The effect of substitution at either of the two nitrogen atoms depends on substituents at the other two sites *i.e.* at the second nitrogen and the amidino carbon atom. For amidines containing a substituted phenyl ring at the imino (N^2) nitrogen atom the chemical shifts of both nitrogen atoms correlate with the Hammett type constants of substituents, but the slopes of the regression lines are opposite for both atoms, and depend on substituents at the amino (N^1) nitrogen atom.

The results indicate that calculation of the ^{15}N NMR chemical shifts in tautomerizing amidines (*i.e.* containing a hydrogen atom at the amino nitrogen) on the basis of the shifts in the corresponding methylated model compounds may yield incorrect results, and that this is the most probable source of discrepancies in estimations of the tautomeric equilibria by the nitrogen NMR method.

In the chemistry of amidines several structural problems are involved and still are the subject of extensive investigations.[2a] The two nitrogen atoms of the amidino group are formally differently bonded to the amidino carbon atom: the amino nitrogen (N^1) by a single bond and the imino nitrogen (N^2) by a double bond. In the literature these have been referred to as sp^3 and sp^2 nitrogens,[3–5] respectively. However, recently it was shown[1,6–8] that the electron distribution in the amidino group depends to a considerable degree on substituents at all three atoms and in certain cases both nitrogens may be sp^2 hybridized. The best way to estimate this distribution seems to be by ^{15}N NMR spectroscopy. However, papers on the ^{15}N NMR spectra of amidines are not numerous.[9]

Another important structural problem is tautomerism, which may occur in amidines containing at least one hydrogen atom at the amino nitrogen, *i.e.* in monosubstituted and *N,N'*-disubstituted ones.

$$R^1N{=}CR{-}NH_2 \rightleftharpoons R^1NH{-}CR{=}NH$$
Monosubstituted amidines

$$R^1N{=}CR{-}NHR^2 \rightleftharpoons R^1NH{-}CR{=}NR^2$$
N,N'-Disubstituted amidines

Individual tautomers are inseparable, because tautomerization in amidines is a very fast reaction, and the lifetime of each tautomer, as recently estimated by ^{1}H and ^{13}C NMR spectroscopy,[10a,11,12] is between 10^{-2} and 10^{-3} s. The question of tautomeric equilibria in amidines, and even the question which of the two tautomers predominates in the equilibrium mixture, was for a long time a matter of controversy.[10a]

The wide range displayed by the ^{15}N NMR chemical shifts and simplicity of the spectra makes them particularly valuable as a means of distinguishing between tautomeric structures and determination of tautomeric equilibria. However, tautomeric equilibria have been determined by ^{15}N NMR spectra only for just a few monosubstituted benzamidines.[13] At ambient temperature the averaged signal of both nitrogen atoms is observed in the ^{15}N NMR spectra. The chemical shifts of both nitrogen atoms in individual tautomers of amidines (and other tautomerizing compounds as well) are calculated on the basis of the chemical shifts in corresponding non-tautomerizing methylated model compounds. But the calculations of the ratio of the two tautomers, gave divergent results, depending on which of the two nitrogen atoms of the amidino group was taken for calculations.

It has been pointed out[2b] that the most probable cause of this discrepancy is that the change of the chemical shift of the imino nitrogen atoms involved by methylation at the amino nitrogen, on account of strong conjugation in the amidino group, depends to a certain degree on substitution at the other two sites of the amidino group. Therefore the ^{15}N NMR chemical shift in a given tautomer may differ considerably from that calculated on the basis of corresponding methylated model derivatives.

Thus the question arose as to how far polar effects of substituents at the two nitrogen atoms have an influence on their ^{15}N NMR chemical shifts, and whether or not these effects depend on substitution at other sites of the amidino group. For this reason we have undertaken a study of the relationship between the structure of compounds containing the amidino group and their chemical shifts.

In this work the ^{15}N NMR chemical shifts of 24 amidines were determined in $CDCl_3$ solutions. The amidines **1–24** (substituents R^1, R^2, R^3 and R^4 are listed in the Table 1) were studied.

Table 1 ^{15}N NMR Chemical shifts[a] (δ) for nitrogen atoms of the amidino group in trisubstituted amidines $R^4N{=}CR^1{-}NR^2R^3$

	R^1	R^2	R^3	R^4	$\delta^{15}N$ N^1 (amino)	N^2 (imino)
1	H	Me	Me	4-$OMeC_6H_4$	−303.0	−149.6
2	H	Me	Me	4-MeC_6H_4	−302.0	−151.1
3	H	Me	Me	Ph	−301.7	−153.5
4	H	Me	Me	4-ClC_6H_4	−300.1	−158.7
5	H	Me	Me	4-BrC_6H_4	−299.7	−157.8
6	H	$-[CH_2]_5-$		4-$OMeC_6H_4$	−280.5	−158.7
7	H	$-[CH_2]_5-$		4-MeC_6H_4	−279.9	−157.9
8	H	$-[CH_2]_5-$		Ph	−279.0	−160.1
9	H	$-[CH_2]_5-$		4-ClC_6H_4	−277.0	−160.1
10	H	$-[CH_2]_5-$		4-BrC_6H_4	−277.4	−160.6
11	H	$-[CH_2]_5-$		3-$NO_2C_6H_4$	−274.1	−163.3
12	H	$-[CH_2]_5-$		4-$NO_2C_6H_4$	−269.2	−160.8
13	H	$-[CH_2]_6-$		Ph	−277.3	−159.0
14	H	$-[CH_2]_6-$		4-ClC_6H_4	−274.4	−159.5
15	H	$-[CH_2]_6-$		4-BrC_6H_4	−274.2	−159.5
16	H	$-[CH_2]_6-$		4-$NO_2C_6H_4$	−265.9	−158.4
17	H	$-[CH_2]_2O[CH_2]_2-$		4-$OMeC_6H_4$	−289.6	−152.1
18	H	$-[CH_2]_2O[CH_2]_2-$		4-MeC_6H_4	−288.9	−151.2
19	H	$-[CH_2]_2O[CH_2]_2-$		Ph	−287.7	−150.9
20	H	$-[CH_2]_2O[CH_2]_2-$		4-ClC_6H_4	−286.6	−154.6
21	H	$-[CH_2]_2O[CH_2]_2-$		4-BrC_6H_4	−284.5	156.5
22	Me	Me	Me	Ph	−306.0	−141.8
23	Ph	Me	Me	$PhCH_2$	−311.9	−163.6
24	Ph	Me	Me	4-$ClC_6H_4CH_2$	−310.0	−163.8

[a] $MeNO_2$ scale.

Table 2 Literature ^{15}N NMR chemical shifts for nitrogen atoms of the amidino group in trisubstituted amidines $R^4N{=}CR^1{-}NR^2R^3$

	R^1	R^2	R^3	R^4	$\delta^{15}N$ N^1 (amino)	N^2 (imino)	Ref.
25	Ph	Me	Me	Me	−310.5[a]	−161.4[a]	13
26	Ph	Me	Me	H	−309.5[a]	−158.7[a]	13
27	Ph	Me	Me	Ph	−302.4[a]	−138.1[a]	13
28	Ph	Ph	Me	Ph	−283.5[a]	−143.7[a]	13
3	H	Me	Me	Ph	−298.1[b]	−145.8[b]	23
29	$Me_2C{=}CH$	Me	Me	Ph	−299.3[b]	−135.5[b]	23
30	Me_2N	Me	Me	Ph	−321.7[b]	−171.7[b]	23

[a] Converted to $MeNO_2$ scale, correction factor[21] −381.9 used (liquid NH_3 external standard). [b] As reported by the authors (external standard NO_3^-, but cation, solvent and concentration are not given).

$R^2R^3NC(R^1){=}NR^4$

1–5 N^1,N^1-dimethyl-N^2-arylformamidines
6–12 N^1,N^1-pentamethylene-N^2-arylformamidines
13–16 N^1,N^1-hexamethylene-N^2-arylformamidines
17–21 N^1,N^1-(3-oxapentamethylene)-N^2-arylformamidines
22 N^1,N^1-dimethyl-N^2-phenylacetamidine
23–24 N^1,N^1-dimethyl-N^2-arylbenzamidines

For comparative purposes literature ^{15}N NMR chemical shifts for other compounds (**3**, **25–30**) containing a non-tautomerizing open-chain amidino group are presented in Table 2.

Experimental

Compounds

All compounds were synthesized and purified in the Physical Organic Chemistry Laboratory at Warsaw University. The details of their synthesis have been given elsewhere (**1–5**,[14,15] **6–12**,[15,16] **13–16**,[16] **17–21**,[15,16] **22**,[17] and **23–24**[18]).

Spectra

The ^{15}N NMR spectra were recorded on Bruker FT spectrometers: on the WP 200 at 20.282 MHz and on the AM 500 at 50.698 MHz using nitromethane as an external reference and the INEPT[19] procedure for shortening the accumulation time. 1500–6000 scans were accumulated for 1 mol dm^{-3} solutions of amidine in $CDCl_3$. The INEPT experiment was optimized for the $^2J(^{15}N{-}C{-}H)$ value of $\approx$2.5 Hz.[20] Chemical shift values are summarized in Table 1. Chemical shifts of non-tautomerizing amidines reported in the literature are given in Table 2.

Chemical shifts' assignments

In the literature for the ^{15}N NMR chemical shifts two different scales are encountered.[21] In this work all chemical shifts are given in the frequency scale, preferred by organic chemists, and recommended by IUPAC,[21,22] *i.e.* in the δ ppm units with respect to nitromethane. Chemical shifts with respect to another standard (liquid NH_3) reported in the literature (Table 2, compounds **25–28**) were recalculated using the conversion factor given in the monograph of Martin, Martin and Gouesnard.[21] Chemical shifts with respect to NO_3^- (Table 2, compounds **3**, **29** and **30**) seem to be recalculated by the authors.

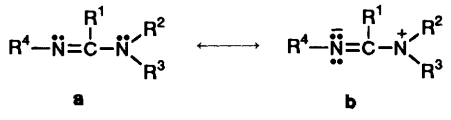
Results and discussion

For this study we have chosen amidines containing two identical substituents at the amino (N^1) nitrogen atom as in such case both conformers are identical and thus conformation has no influence on the chemical shifts. The chemical shifts of seven open chain trisubstituted amidines taken from the literature (Table 2) compared with the compounds from Table 1 enable us to draw more general conclusions. However, it has to be mentioned that the chemical shifts for compounds **25–28** are recalculated (liquid NH_3 as external standard). For **3**, **29** and **30** external standard NO_3^- was used, but neither cation, nor solvent and concentration of the standard were specified. The values of chemical shifts are close to those determined with respect to nitromethane, rather than to NO_3^- standards, thus it could be assumed that they are probably recalculated by the authors. However, there are considerable differences between the chemical shifts of **3** obtained in our study (Table 1) and those reported in the literature (Table 2).

All compounds considered can be divided into series depending on substituents at the amidino carbon atom (formamidines, R^1 = H; and benzamidines, R^1 = Ph) and at the amino nitrogen (**1–5**, **6–12**, **13–16**, **17–21**, **23–24** series).

All amidines in our study contained a phenyl ring at the imino nitrogen atom and the structural changes occurred four or five bonds away from this atom (*meta*- or *para*-substitution) and six or seven bonds away from the amino nitrogen. Thus, in a series the chemical shifts of both nitrogen atoms can be attributed only to polar effects of substituents at the phenyl ring. The influence of substitution at the amino nitrogen atom or the amidino carbon atom is shown by comparison of the chemical shifts in corresponding compounds from different series.

According to classical organic chemistry the π-electron pair of the C=N double bond is conjugated with the lone pair of p-electrons on the amino nitrogen atom as indicated in Scheme 1.



a **b**

Scheme 1

There are three sites in the amidino group to which the substituents can be attached, the two nitrogen atoms and amidino carbon atom. Substituents at both nitrogen atoms have considerable influence on the extent of conjugation. Electron-withdrawing substituents at the imino nitrogen atom cause an increase of the conjugation favouring the mesomeric form (**b**), whereas at the amino nitrogen atom they cause a decrease of conjugation favouring form (**a**). Electron-donating substituents conversely, at the imino nitrogen will favour the mesomeric form (**a**) and at the amino nitrogen atom the form (**b**). If at both nitrogen atoms substituents are of the same kind, the result will depend on the difference in their polar effects.

In terms of ^{15}N NMR spectroscopy, predomination of the form (**b**) means shielding of the imino nitrogen atom and deshielding of amino nitrogen atom. Predomination of the form (**a**) means shielding of the amino nitrogen atom and deshielding of imino nitrogen atom.

The influence of substitution at the amidino carbon atom is not so obvious, but experimental data [10b,17,18,24] as well as the results of *ab initio* calculations [8] have shown that the polar effects of a substituent at either of the two nitrogen atoms depend on the substituent at the amidino carbon atom. In general, the effects of a substituent at any site of the amidino group depends on substitution at the other two sites.

Table 3 Parameters of regression of chemical ^{15}N shifts of the amino (N^1) nitrogen atom in the amidine group *vs.* σ° constants of substituents on the phenyl ring at the imino (N^2) nitrogen [eqn. (1)]

Series	a^a	b	r	n
1–5	6.18 ± 1.88	−301.5	0.986	5
6–12	9.39 ± 3.55	−279.0	0.950	7
17–21	7.34 ± 6.45	−287.5	0.900	5

[a] With confidence intervals at significance level of 0.95.

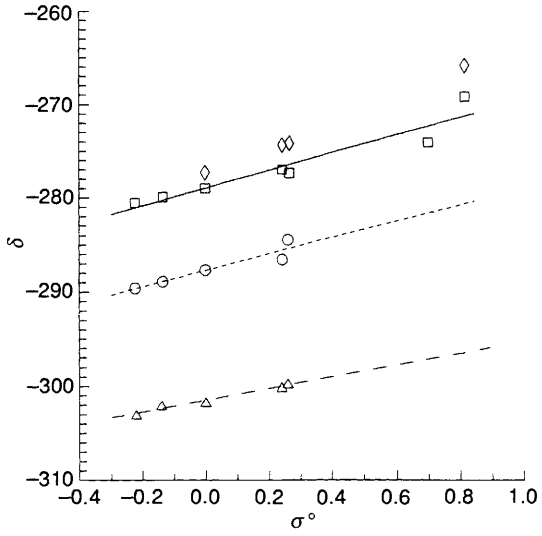


Fig. 1 Relation between the ^{15}N NMR chemical shift of the amino nitrogen atom and the σ° value of a substituent on the phenyl ring at the imino nitrogen atom: (△) series **1–5**; (□) series **6–12**; (◇) series **13–16**; (○) series **17–21**

Substitution at the imino (N^2) nitrogen atom

Results obtained indicate that substitution at the imino nitrogen atom has opposing effects on the chemical shifts. Electron-donating substituents such as *p*-Me or *p*-OMe (**1**, **2**, **6**, **7**, **17** and **18**) cause an upfield shift of 0.3–1.9 ppm of the amino nitrogen with respect to the corresponding compounds with an unsubstituted phenyl ring (**3**, **8**, **13** and **19**); and a downfield shift of 1.4–3.9 ppm of the imino nitrogen. Electron-withdrawing substituents such as Cl, Br and NO_2 (**4**, **5**, **9–12**, **14–16**, **20** and **21**) cause opposite effects: a downfield shift of the amino nitrogen of 1.1–11.4 ppm and an upfield shift of 0.5–5.2 of the imino nitrogen.

It has to be mentioned that the changes of chemical shifts of the imino as well as the amino nitrogen atom with the same structural change, *i.e.* substitution of the hydrogen atom in the phenyl ring by any substituent, are not identical for amidines of various series. This provides support for the assumption that the changes in the chemical shifts of nitrogen atoms caused by substitution at one site depend on substituents at the other two sites of the amidino group.

We have found that the chemical shifts of the amino nitrogen atom in N^1,N^1-dialkyl-N^2-phenylformamidines (**1–5**, **6–12**, **13–16** and **17–21** series) are related to the Hammett type constants of the substituents on the phenyl ring at the imino nitrogen atom. As has been shown already [10c,17,18] for substituents at both nitrogen atoms the most appropriate are σ° values. Parameters of linear regressions (1) for the **1–5**, **6–12** and **17–21** series are summarized in Table 3.

$$\delta(N^i) = a\sigma^\circ + b \qquad (1)$$

In the series **1–5** the number of compounds is insufficient to obtain reliable results, however the experimental points on the

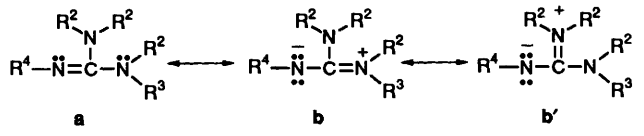
Fig. 1 indicate that the relation for these compounds is similar to the ones observed for other studied series.

The difference between the slopes of regression lines for various series of amidines provides further evidence that the sensitivity of the chemical shifts of both nitrogen atoms to the effects of substituent depend to a considerable degree on substitution at another nitrogen atom.

Substitution at the functional carbon atom

The influence of substitution at the carbon atom of the amidino group can be shown by the example of the compounds **3**, **22**, **27** and **30**. Exchange of hydrogen at the amidino carbon atom in N^1,N^1-dimethyl-N^2-phenylformamidine (**3**) for a methyl (acetamidine, **22**), phenyl (benzamidine, **27**), or 2,2-dimethylvinyl group (β-methylcrotonamidine, **29**) cause a considerable downfield shift of the imino nitrogen atom (+11.7 ppm for **22**, +15.4 ppm for **27** and +18.0 ppm for **29**) and a comparatively very small upfield shift (−4.3 ppm for **22**, −0.7 ppm for **27** and +2.4 ppm for **29**) of the imino nitrogen atom.

Guanidines can be considered as amidines substituted by an amino group at the functional carbon atom. However, it has to be kept in mind that the electron distribution in guanidines is somewhat different from that in amidines. In guanidines there are three mesomeric forms as shown by Scheme 2. Two of



a **b** **b′**

Scheme 2

them (**b**) and (**b′**) cause shielding of the imino nitrogen atom. The exchange of a hydrogen atom in N^1,N^1-dimethylformamidine (**3**) for a dimethylamino group (tetramethylguanidine, **30**) causes considerable changes in the conjugation. As a result an upfield shift (−18.2 ppm) for the imino nitrogen atom is observed. Positive charge (deshielding) in guanidines is distributed between two amino nitrogens in mesomeric forms (**b**) and (**b′**). Thus each of the two amino nitrogens is deshielded to a much smaller extent than in amidines, and in consequence for these atoms an upfield shift (−20.0 ppm) is observed.

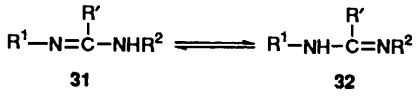
Note that the difference between chemical shifts of imino and amino nitrogen atoms for amidines containing a carbon atom bonded to a functional carbon atom is almost the same; 164.2 ppm for **22**, 164.3 ppm for **27** and 163.8 ppm for **29**. If hydrogen is bonded to the central atom of the amidine group this difference is much smaller, 148.2 ppm for **3**, whereas in the case of the nitrogen atom (**30**) the difference is higher and amounts to 150.0 ppm.

Substitution at the amino (N^1) nitrogen atom

Substitution at the amino nitrogen atom has a strong influence on the chemical shift of this atom and a discernible influence on the chemical shift of the imino nitrogen. Exchange of the two methyl groups in N^1,N^1-dimethylformamidines for the pentamethylene group (**6**–**10** *vs.* **1**–**5**, respectively) causes a downfield shift of 22.1–23.1 ppm of the amino nitrogen and an upfield shift of 1.4–9.1 ppm of the imino nitrogen. Exchange for the hexamethylene groups (**13**–**15** *vs.* **3**–**5**) causes a downfield shift of the amino nitrogen of 24.4–25.5 ppm and an upfield shift of 1.7–5.5 ppm of the imino nitrogen. Exchange for the 3-oxapentamethylene group (**17**–**21** *vs.* **1**–**5**) causes a downfield shift of the amino nitrogen of 13.1–15.2 ppm and an upfield shift of 1.3–2.6 ppm of the imino nitrogen for the phenyl, *p*-bromophenyl and *p*-chlorophenyl derivatives (**19**–**21**). For *p*-methoxyphenyl derivative **17**, however, an upfield shift of −2.5 ppm for the imino nitrogen is observed.

^{15}N NMR spectra and tautomeric equilibria of the amidine system

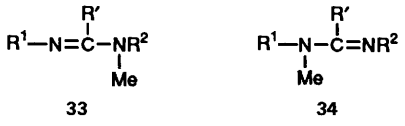
Comparison of the data in Table 2 sheds some light on the discrepancies in tautomeric equilibria determined by the ^{15}N NMR spectra. For monosubstituted and N,N′-disubstituted amidines displaying prototropic tautomerism as shown by the Scheme 3 chemical shifts of nitrogen atoms in individual



31 **32**

Scheme 3

tautomers of amidines **31** and **32** were calculated on the basis of the chemical shifts in the corresponding non-tautomerizing methylated model compounds **33** and **34**, respectively.[10a]



33 **34**

These calculations were on the assumption that the change of chemical shift of the amino nitrogen atom caused by methylation is always the same and that the ^{15}N NMR chemical shift of the imino nitrogen atom in tautomerizing amidine is identical to that in the corresponding methylated compound, which in our opinion is rather seldom true. Suffice is to mention that methylation of the imino nitrogen in **25** causes a downfield shift of the second (amino) nitrogen in **26** of 1.0 ppm, which shows, evidently, that the chemical shift of the imino nitrogen in tautomerizing amidine may differ from that in the methylated model compound.

The influence of the same structural changes at both nitrogen atoms on the chemical shifts is more evident in the example of the benzamidines **25**–**28**. Exchange of a methyl group at the amino nitrogen atom for a phenyl group, **28** *vs.* **27**, causes an upfield shift of the second (imino) nitrogen atom of 5.6 ppm whereas the same exchange at the imino nitrogen atom (**25** *vs.* **27**) causes a downfield shift of the second (amino) nitrogen atom of 8.1 ppm.

These changes provide further support for an earlier conclusion[1,8,10a,b,17,18,24] that substitution at one site influences the sensitivity to the effect of a substituent at other sites. Thus, it seems obvious that calculation of the nitrogen chemical shifts of methylated model compounds, at least in some cases, may lead to incorrect results and that another method, *e.g.* low temperature spectra would be more appropriate for the purpose.

Conclusions

Polar effects of substituents at either of the two nitrogen atoms in amidines on the ^{15}N NMR chemical shifts of the amino nitrogen (N^1) atom are opposite to those on the imino (N^2) nitrogen. The values of the changes in the ^{15}N NMR chemical shifts caused by a certain substituent at one site of the amidino group depend to a considerable degree on substituents at the other two sites. The ^{15}N NMR chemical shifts in tautomerizing amidines may considerably differ from those calculated on the basis of corresponding methylated derivatives. Thus, determination of tautomeric equilibria may yield incorrect results.

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