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^{1}H, ^{13}C and ^{15}N nuclear magnetic resonance studies of polyamidines prepared from di(4,4′-aminophenyl) methane and different triethyl orthoesters—polymers with a prototropic tautomerism

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N^1,N^2-disubstituted polyform-, -acet- and -benzamidines containing the 4,4′-substituted diphenyl methane unit were studied by means of ^{1}H, ^{13}C and ^{15}N nuclear magnetic resonance (n.m.r.) in solution. The n.m.r. signals were assigned. For the polyacet- and -benzamidine slow tautomerism on the n.m.r. time scale resulted in separate signals for the amino and imino moiety due to preference for the *E*-anti configuration of the amidine group. This tautomerism was much faster for the polyformamidine due to cyclic dimerization of formamidine groups in the preferred *E*-syn configuration. In this case, the signals of the amino and imino moiety coalesced. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Previous papers reported on the synthesis and properties of aromatic polyformamidines[1,2], including the polyformamidine prepared from di(4,4′-aminophenyl) methane and triethyl orthoformate (**1**; *Scheme 1*). These investigations were extended to polyacetamidine and polybenzamidine containing the 4,4′-substituted diphenyl methane unit (**2**, **3**, *Scheme 1*)[3]. The degree of polymerization could be increased by melt polycondensation and variation of the catalytic acid.

The structure of N^1,N^2-disubstituted amidines $R^2HN^1C(R^1) = N^2R^3$ is characterized by three types of isomerism (*Scheme 2*)—geometrical isomerism (*Scheme 2a*), rotational isomerism (*Scheme 2b*) and prototropic tautomerism (*Scheme 2c*)[4,5].

It is well known[4,5] that these equilibria depend on the substituents R^1, R^2 and R^3 at the amidine group. In addition, solvent, concentration and temperature influence the equilibria in solution. The formation of intermolecular hydrogen bonds $-N^1-H\cdots N^2=$ is an important property of N^1,N^2-disubstituted amidines. It results in cyclic dimers for E-syn isomers. Molecules in E-anti configuration form linear dimers or polymeric chains. These effects are observed both in solid and solution state. Furthermore, intermolecular hydrogen bonds can be formed to the solvent.

In the solid state, *E* configuration is predominantly observed for formamidines (R^1 = H), acetamidines (R^1 = Me) and benzamidines (R^1 = Ph) with alkyl or aryl substituents at the imino nitrogen atom. The conformation at the C–N bond depends on R^1 and R^2. X-ray investigations on N^1,N^2-diphenylsubstituted amidines (R^2, R^3 = Ph) have shown that the formamidine exists as cyclic dimer of the *E*-syn isomer[6]. The acetamidine (R^2, R^3 = p-Tol) and benzamidine exist as *E*-anti isomers[7,8]. Intermolecular hydrogen bonds join the molecules into chains[7] and linear dimers[8], respectively.

There are many investigations on N^1,N^2-diarylsubstituted amidines in solution[4,5]. The extensive n.m.r. studies of Limbach *et al.*[9–11] on the tautomerism of N^1,N^2-diphenylformamidine and N^1,N^2-di-*p*-fluorophenylformamidine in tetrahydrofuran-d_8 (THF-d_8) are of particular interest. At low temperatures both the *E*-syn and *E*-anti isomers have been observed. Both isomers form hydrogen bonds to the solvent, but only the *E*-syn isomer is capable of forming a cyclic dimer in which a double proton exchange takes place. The *E*-anti isomer seems not to be involved in tautomeric processes directly. For proton exchange it has first to isomerize to the *E*-syn form and then associate in a cyclic dimer in which the proton could be transferred. Increase in concentration is accompanied by a decrease of the population of the *E*-anti, due to self-association of the *E*-syn isomer, and increase in the proton transfer rate. Above 250 K, the interconversion between the *E*-syn and *E*-anti isomer is fast on the n.m.r. time scale and intermediate signals have been observed. A similar mechanism was proposed by Borizov *et al.*[12]. A dipole moment study suggested that both rotamers of N^1,N^2-diphenylformamidine are populated approximately in the 1 : 1 ratio in benzene[13].

For N^1,N^2-diphenylacetamidine in dimethylsulfoxide-d_6 (DMSO-d_6) and diluted chloroform-*d* ($CDCl_3$) solution,

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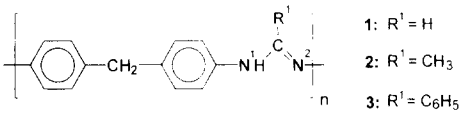
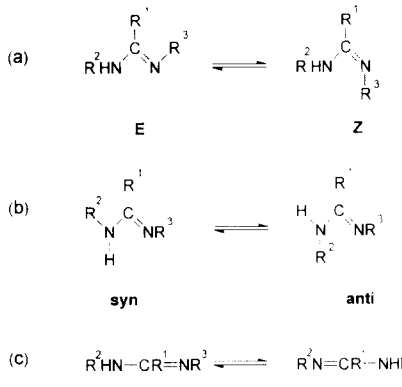


Scheme 1



Scheme 2

an equilibrium of *E*-syn and *Z*-anti isomers was suggested by Krechl *et al.*[14] which do not form cyclic dimers. This should explain the inequivalence of phenyl rings in the ^{13}C n.m.r. spectrum. For concentrated $CDCl_3$ solution and in the solid state, the formation of dimers has been proposed.

Moreover, i.r. studies[15,16] allowed the conclusion that N^1,N^2-diphenyl form-, acet- and benzamidine have *E*-configuration and display conformational isomerism on the C–N single bond. An equilibrium of both rotamers was stated. Whereas the *E*-syn form predominates for the formamide, the *E*-anti isomer prevails for the acet- and benzamidine. The *E*-anti isomer is also preferred in greater hydrogen-bonding acceptor solvents than carbon tetrachloride. The formation of the *E*-syn form is stimulated by hydrogen-bonding donors like $CHCl_3$ or phenols due to formation of cyclic structures.

The aim of this paper is to investigate the influence of the substituent R^1 on the different types of isomerism for the N^1,N^2-diarylsubstituted amidine unit in polyamidines **1–3** using ^1H, ^{13}C and ^{15}N n.m.r. spectroscopy in solution.

EXPERIMENTAL

Samples

Di(4,4′-aminophenyl) methane was melt polycondensed with a slight excess of triethyl orthoformate, triethyl orthoacetate and triethyl orthobenzoate, respectively, under nitrogen atmosphere by continuously removing the by-product ethanol by distillation[3]. Acetic and 2,4,6-trimethylbenzoic acid, respectively, were used as catalysts. Residual ethanol and low boiling catalyst acetic acid were removed by reducing pressure in the end. For the samples used for the n.m.r. studies the following degrees of polymerization (n) were determined by ^1H n.m.r. end-group analysis: **1**, $n = 6.4$; **2**, $n = 7.7$; and **3**, $n = 7.8$.

N.m.r. measurements

The n.m.r. measurements were carried out on a Bruker AMX 300 n.m.r. spectrometer operating at 300.13 MHz for ^1H, 75.47 MHz for ^{13}C and 30.41 MHz for ^{15}N. The deuterated solvents (DMSO-d_6 and THF-d_8, resp.) were used as lock. The ^1H and ^{13}C spectra were referenced on solvent signals—DMSO-d_6: $\delta(^1H) = 2.5$ ppm, $\delta(^{13}C) = 39.6$ ppm; THF-d_8: $\delta(^1H) = 3.57$ ppm (low-field signal). The ^{15}N spectra were referenced on external nitromethane ($\delta(^{15}N) = 0$ ppm). The Bruker B-VT 2000 temperature controlling unit was used to regulate the sample temperature.

The ^{15}N n.m.r. spectra were obtained using inverse gated decoupling and a relaxation delay of 20 s. ^1H–^1H correlated spectroscopy, ^1H–^{13}C correlated spectroscopy and ^1H exchange correlated spectroscopy (phase sensitive using time proportional phase incrementation) spectra were recorded using the standard pulse sequences included in the Bruker software package. A mixing time of 250 ms was applied for the ^1H exchange correlated spectra.

RESULTS AND DISCUSSION

Figures 1 and *2* show the ^{13}C and ^1H n.m.r. spectra of poly(4,4′-diphenylmethane formamidine) (**1**)[1], poly-(4,4′-diphenylmethane acetamidine) (**2**) and poly(4,4′-diphenylmethane benzamidine) (**3**) in DMSO-d_6.

The polymerization of di(4,4′-aminophenyl) methane with different triethyl orthoesters[3] results in polyamidines with a degree of polymerization of up to 10. Therefore, besides the n.m.r. signals of the main chain atoms also end group signals were observed. Three types can be identified[1,3]—amino, imido ester and amide end groups. Whereas amino and imido ester end groups result from incomplete polymerization, hydrolysis of the different imido esters leads to the corresponding amide end groups.

^{13}C and ^{15}N n.m.r. spectra

The ^{13}C spectrum of **1** has already been published and discussed in ref. 1. Five signals are observed for the 4,4′-disubstituted diphenyl methane unit besides the carbon of the formamidine unit (*Figure 1a*) indicating equivalence of both phenyl rings.

The situation is quite different for the polyacetamidine **2** and polybenzamidine **3** (*Figures 1b* and *c*). The phenyl rings are non-equivalent and for almost each position two signals with equal intensity are observed. The carbons in 4 and 4′ position have the largest chemical shift difference. Only one signal appears for each carbon of the amidine moieties (*Table 1*). As the temperature is raised the ^{13}C n.m.r. signals of a 'doublet' become broader without changing the 1 : 1 ratio and, finally, coalesce.

In the ^{15}N n.m.r. spectra both for **2** and **3** two signals with equal intensity are observed (*Table 1*). In accordance with investigations on non-tautomerizing N^1,N^1,N^2-trisubstituted amidines[17,18] these signals can be assigned to the imino and amino nitrogen of the amidine group, respectively. For **1**, no ^{15}N n.m.r. signal could be observed.

The fact that both the amino and imino moiety of the diaryl substituted acet- and benzamidine unit can be observed in the ^{13}C and ^{15}N n.m.r. spectra of **2** and **3** and the ^{13}C n.m.r. signal coalescence at evaluated temperatures clearly indicate proton exchange according to *Scheme 2c* with a rate slow on the n.m.r. time scale at 298 K. A faster proton exchange at 298 K and, consequently, broader signals or the coalescence of signals are observed both by addition of a catalytic amount of acid

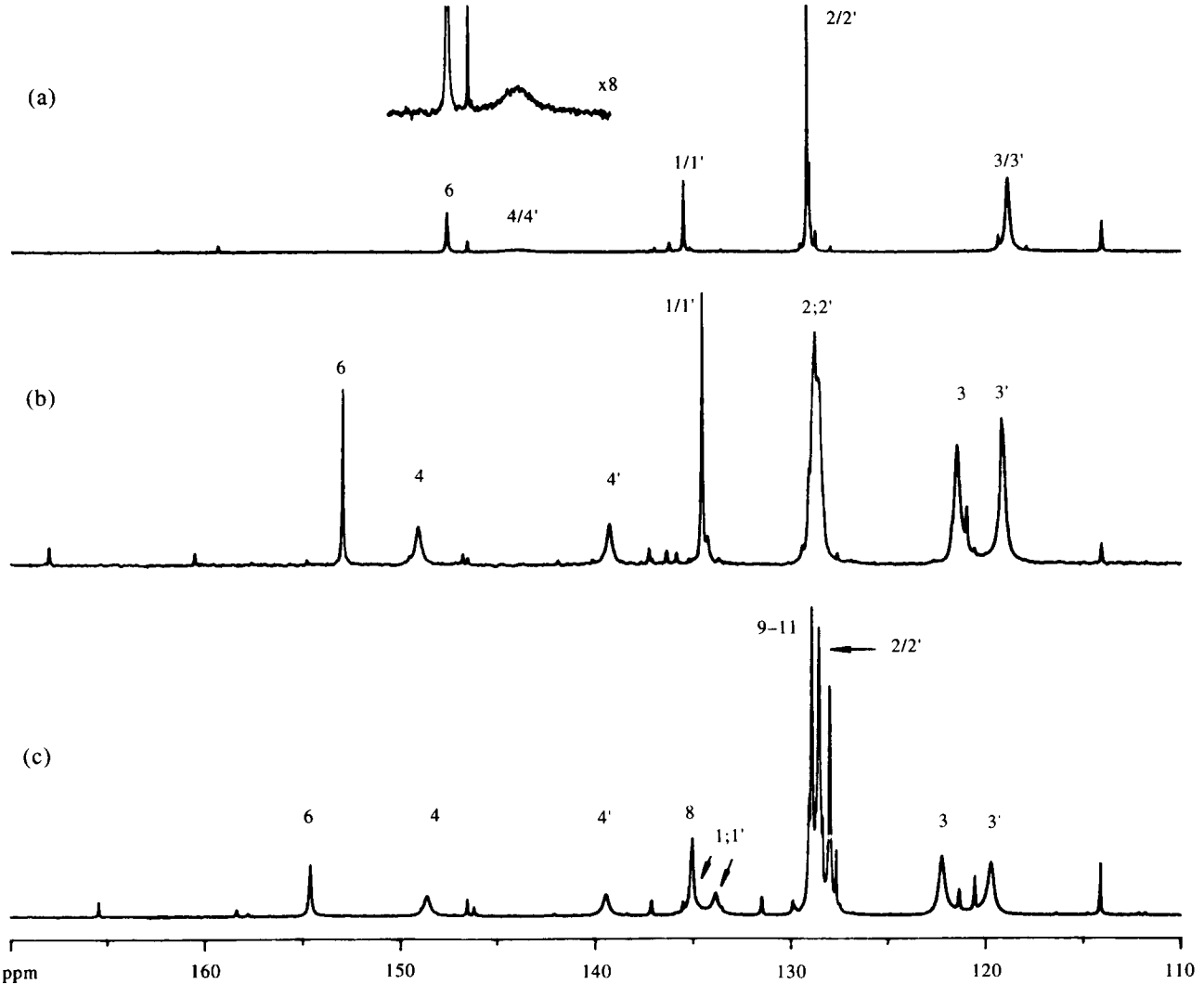


Figure 1 ^{13}C n.m.r. spectra of **1**–**3** (a–c) in DMSO-d_6 at 298 K (region of amidine and aromatic carbon signals). The signal numbering is as given in *Table 1*

and by application of hydrogen-bonding donor solvents or solvents with lower affinity to form hydrogen bonds as DMSO. The ^{13}C chemical shifts after coalescence are in the same region as those observed for **1** (*Table 1*).

For the polyformamidine **1**, the prototropic tautomerism is fast on the n.m.r. timescale and averaged signals are observed. However, the C-4/4′ and C-3/3′ signals of **1** show a residual broadening indicating the proton exchange (*Figure 1a*). The rate of proton exchange of **1** is in a region leading to a strongly broadened ^{15}N n.m.r. signal which could not be detected.

Different signals for the syn- and anti-rotamer are not observed for **1**–**3**. The reason may be both the existence of only one rotamer and a rotational isomerism (*Scheme 2b*) fast on the n.m.r. time scale. An equilibrium was proved by Raczynska *et al.*[15,16] for N^1,N^2-diarylsubstituted amidines. Their i.r. studies indicate that the *E*-antiform prevails in solution for acetamidines and benzamidines. In contrast, formamidines exist predominantly in the *E*-syn form. As only the *E*-syn isomer is capable of fast proton transfer in a cyclic dimer with a second amidine group the different exchange rates observed in our studies become understandable. A higher *E*-syn content of **1** results in the faster rate. For **2** and **3**, a predominating *E*-anti form must first isomerize to the *E*-syn form, which then can from cyclic dimers and exchange protons. However, the strong hydrogen-bonding acceptor solvent DMSO stabilize the *E*-anti form[16].

A fast interconversion between *Z*-anti and *E*-syn form by rapid tautomerism and slower rotation about the C–N bond was proposed by Perrin[19] to explain the non-equivalence of nitrogen substituents observed for N^1,N^2-disubstituted amidines[14,20,21]. However, this would result in equivalent C–N amidine bonds. This can be ruled out for **2** and **3** due to the appearance of an amino and imino signal in the ^{15}N n.m.r. spectra. Our results on polyacetamidine suggest to explain the inequivalence of the phenyl rings in the ^{13}C n.m.r. spectrum of N^1,N^2-diphenylacetamide in DMSO-d_6 solution observed by Krechl *et al.*[14] by a slow proton exchange due to predominating *E*-anti in the *E*-syn/*E*-anti equilibrium.

A detailed lineshape analysis of the signals of **2** and **3** to determine the activation parameters for the prototropic tautomerism was beyond the scope of this study. These parameters would be valid only for the specific sample because the end group concentration, residual water in DMSO-d_6 and the content of acid used in synthesis also should influence the proton exchange rate.

Table 1 summarizes the ^{13}C signal assignments. The signals of C-1(1′) to C-4(4′) of **2** and **3** are assigned based on the ^{13}C chemical shifts of N^1-methyl-N^1,N^2-diphenylformamidine (**4**) and -acetamidine (**5**)[22] and

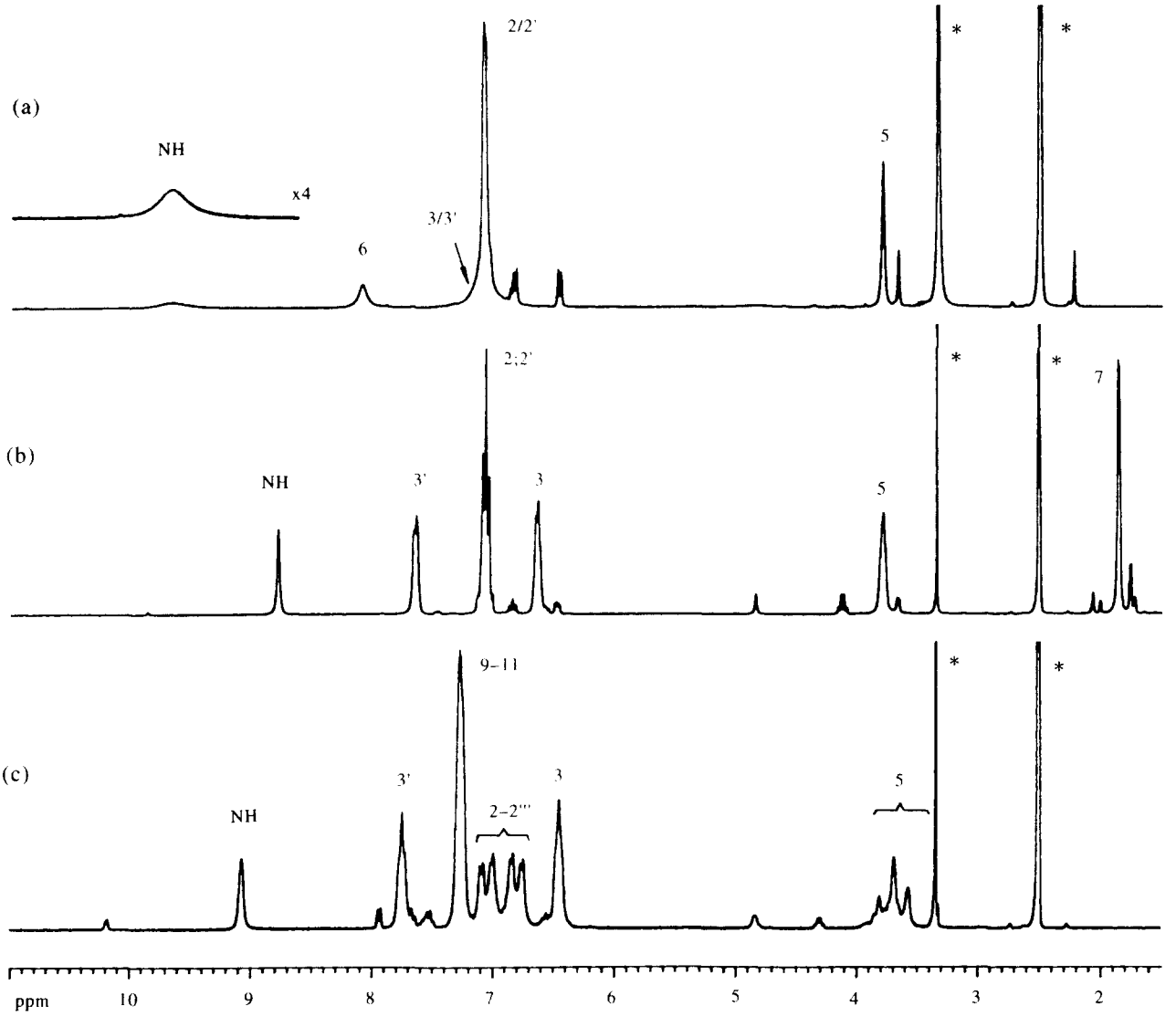


Figure 2 ^{1}H n.m.r. spectra of **1**–**3** (a–c) in DMSO-d_6 at 298 K. The signal numbering is as given in *Table 1* (*HDO and DMSO-d_5)

the chemical shift increment of the C_6H_5–CH_2 group[23]. It may surprise that the experimental amino phenyl carbons chemical shifts only correlate with calculations basing on the data of **4**. The data of **5** result in a significant deviation for the *ortho*-position (C-3). However, this can be explained by a different rotamer equilibrium for **4** and **5**. Whereas for **2** and **3**, and obviously **4**, the anti-position of the N^1-bonded phenyl ring is preferred, this ring seems to be predominately in syn-position for **5** as can be concluded from X-ray data of similar compounds[24,25]. The *ortho*-position is most sensitive to different steric interactions with the amidine-carbon substituent as observed. In addition, ^{1}H–^{13}C shift correlated spectra prove the assignments.

^{1}H n.m.r. spectra

The effect of different proton exchange rates can also be established in the ^{1}H spectra of **1**–**3** (*Figure 2*). Whereas the H-3/3′ signal of **1** is significantly exchange broadened, for **2** and **3** well separated signals are observed for these *ortho*-protons due to the amino and imino moiety. The signal assignment was done using additivity parameters for N^1,$N^{1'}$-disubstituted amidines[26].

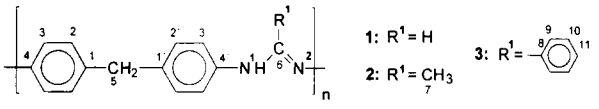
The ^{1}H shift values (*Table 1*) show that the chemical shift effects of the amidine group strongly depend on the substituent at the amidine carbon. In contrast to **2**, an additional splitting of the *meta*-protons signal is observed for **3**. Four signals H-2 to H-2‴ appear with equal intensity. They are caused by three substructures **I**–**III** (*Scheme 3*).

The signal intensities indicate a statistical appearance of these substructures. The ^{1}H–^{1}H shift correlated spectrum of **3** in THF-d_8 at 203 K (*Figure 3a*) illustrates the correlation between *ortho*- and *meta*-protons. It is assumed that the inner two *meta*-proton signals H-2′ and H-2″ are due to the mixed substructure **II**. A splitting due to these three substructures is also observed for the methylene protons (*Table 1*) and, to minor extent, for the H-3 and H-3′ signals.

Figure 3b shows a ^{1}H exchange correlated spectrum of **3**. Cross peaks appear in the aromatic region between positions which are exchanged due to tautomerism. The cross peak pattern between the *meta*-protons proves the equilibrium between substructures **I**–**III**. The more intense cross peaks result from a single –NH– to =N– (or reverse) change due to tautomerism (*Scheme 3*). Peaks of lower intensity are caused by two probably successive changes.

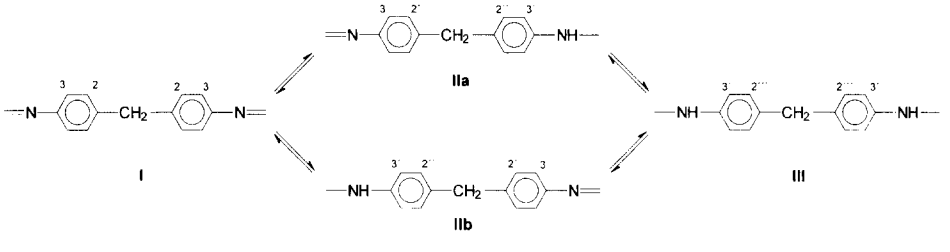
The ^{1}H chemical shift and line width of the NH signals support the discussion of different exchange rates of **1**

Table 1 ^{13}C, ^{15}N and ^{1}H chemical shifts of **1**–**3** in DMSO-d_6 at 298 K



Position[a]	^{13}C and ^{15}N chemical shifts (in ppm)			Position[a,d]	^{1}H chemical shifts (in ppm)		
	1	**2**	**3**		**1**	**2**	**3**
1			134.9[b]	2		7.05[b]	6.75
	134.4	134.5			7.09		
1′			133.8[b]	2′		7.08[b]	6.84
2		128.8[b]		2″	—	—	7.00
	129.1		128.5				
2′		128.6[b]		2‴	—	—	7.09
3		121.4	122.2	3		6.64	6.46/6.43[f]
	118.8				7.13[e]		
3′		119.1	119.7	3′		7.66	7.66/7.73[f]
4		149.0	148.6	5	3.79	3.79	3.81/3.69/
	143.9						3.57[f]
4′		139.2	139.4	6	8.09	—	—
5	39.9	40.1	39.9	7	—	1.86	—
6	147.6	153.0	154.6	9–11	—	—	7.27/7.25
7	—	17.8	—	NH	9.66	8.78	9.07
8	—	—	135.0				
9–11	—	—	128.9; 128.0				
N^1	[c]	−264.5	−261.8				
N^2		−134.0	−135.8				

[a] Only one chemical shift is given for the amino and imino moiety if the signals coalesce
[b] The assignment of corresponding signals to the amino and imino moiety is uncertain
[c] Signal not obtained due to too much exchange broadening
[d] The assignment of positions 2–2‴ (only for **3**) corresponds with *Scheme 3*
[e] Signal strongly exchange broadened. $\delta(^1H)$ determined from the ^1H–^{13}C shift correlated spectrum
[f] Splittings due to substructures **I**–**III** (*Scheme 3*), for H-5 intensity ratio 1 : 2 : 1



Scheme 3

and **2**/**3**. According to refs. 9–11, this signal appears for **1** at lower field and broadened due to self-association and proton exchange indicating preference for the syn-rotamer. The narrower NH signals of **2** and **3** are in accordance with lower exchange rate due to preference for the anti-rotamer. Proton exchange can also occur with other hydrogen-bonding groups in cyclic complexes.

In our case, such an exchange occurs with the protons of the end group and with residual water in the solvent. This may be proved by exchange peaks between the amidine-NH protons of **1**–**3** and the NH_2 end group protons and the HDO signal as observed in the corresponding ^1H exchange correlated spectra.

Our investigations benefit from the slow-down effect of DMSO on the proton exchange rate due to the formation of intermolecular hydrogen bonds in solvent–amidine complexes. In THF-d_8 the same effects are observed for **2** and **3** at lower temperatures. However, separate signals due to the *E*-syn and *E*-anti rotamers are not observed even at 193 K. A reduced proton exchange was observed for **1** at low temperatures but neither a splitting of the H-3/3′ signal nor different rotamers are stated.

CONCLUSIONS

Polyamidines show tautomerism in solution as their low-molecular weight model compounds. However, the rate depends on the substituent R^1 at the amidine carbon. Whereas for polyformamidine ($R^1 = H$) a fast rate on the n.m.r. time scale is observed in DMSO-d_6, the proton exchange is significantly slower for polyacet- (R^1 = methyl) and -benzamidine (R^1 = phenyl). The different behaviour can be explained by the preference

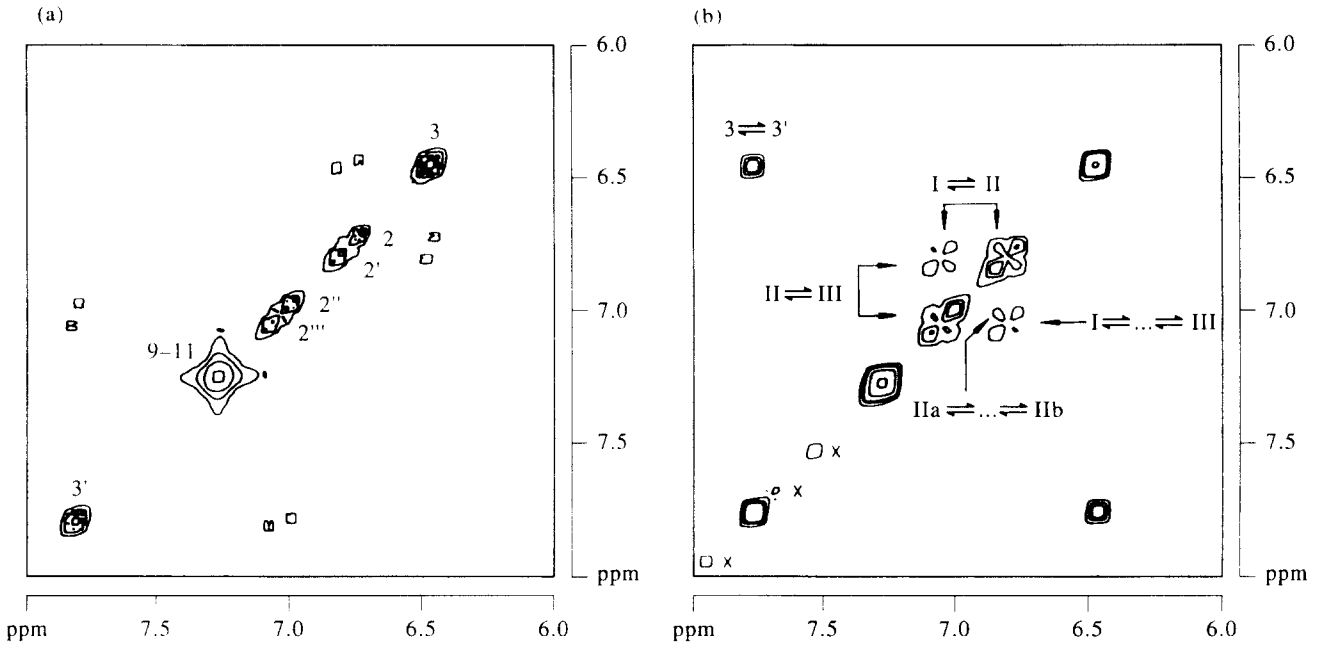


Figure 3 (a) ^{1}H-^{1}H shift correlated spectrum of **3** in THF-d_8 at 203 K (region of aromatic protons) indicating the $^{3}J_{H,H}$ couplings. (b) ^{1}H exchange correlated spectrum of **3** in DMSO-d_6 at 298 K (region of aromatic protons) indicating positions connected by exchange processes. For both spectra, the signal numbering is as given in *Table 1* and *Scheme 3* (x, end group signals)

of different configurations by the amidine unit. Formamidines prefer the *E*-syn configuration which can form cyclic dimers with fast cyclic proton transfer. The *E*-anti isomer which is not able to form cyclic dimers is preferred by the acet- and benzamidine group. In solution, proton exchange takes place after isomerization to the *E*-syn isomer.

We observed the effects described here for polyamidines also in the ^{1}H, ^{13}C and ^{15}N n.m.r. spectra of several N^{1},N^{2}-diarylform-, -acet- and -benzamidines used as model compounds. Furthermore, also in the solid-state ^{13}C and ^{15}N n.m.r. spectra of these polymers and model compounds different rates of proton exchange can be observed. This will be the subject of a forthcoming paper[27].

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