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Inter- and intramolecular hydrogen bonds in polyamines: variable-concentration ^{1}H-NMR studies

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Inter- and intramolecular hydrogen bonding play an important role in determining the arrangement, physical properties, and reactivity of a great diversity of structures in chemical and biological systems. Several aromatic nucleophilic substitutions (ANS) in nonpolar aprotic, (non-HBD), solvents recently studied in our laboratory have demonstrated the importance of self-association of amines by hydrogen-bond interactions. In this paper, we describe ^{1}H-NMR studies carried out at room temperature on bi- and polyfunctionalized amines, namely: *N*-(3-amino-1-propyl)morpholine (3-APMo), histamine, 2-guanidinobenzimidazole (2-GB), 1,2-diaminoethane (EDA), 3-dimethylamino-l-propylamine (DMPA), and 1-(2-aminoethyl)piperidine (2-AEPip). By ^{1}H-NMR measurements of amine solutions at variable concentrations we have shown that 3-APMo, histamine and 2-GB are able to form a six-membered ring by *intramolecular* hydrogen bonding, while EDA, DMPA, and 2-AEPip form dimers by *intermolecular* hydrogen bonds. Likewise, variable concentration ^{1}H-NMR studies allowed estimation of the corresponding equilibrium constants for the dimerization. These results are correlated with experimental kinetic results of ANS, confirming hereto the relevance of the "dimer mechanism" in reactions involving these amines. Copyright © 2011 John Wiley & Sons, Ltd.

Keywords: ^{1}H-NMR studies on amine solutions; ANS in non-HBD solvents; dimer nucleophile mechanism; dimerization equilibrium constants; hydrogen-bonding effects on ^{1}H-NMR; hydrogen-bonded nucleophiles

INTRODUCTION

NMR spectroscopy is a very useful tool for detecting non-bonding interactions, since it is extremely sensitive to molecular structure, conformational, solvent, and other environmental effects.[1] We have recently reported ^{1}H and ^{13}C-NMR studies on matters as diverse as identification of drug photo-degradation,[2–4] detection of intermediates,[5–9] and characterization of the natural attenuation of oil spills in Patagonian soils.[10,11] The role of inter- and intramolecular hydrogen bonding in determining the arrangement, physical properties, and reactivity of a great diversity of structures is a subject of experimental and theoretical research in chemical[12–15] and biological systems.[16] The sensitivity of aromatic nucleophilic substitution (ANS) with amines to solvent effects is very well recognized, although not fully understood yet.[17,18] The study of these effects contributes to the understanding of the molecular microscopic properties of the solvents interactions between the amine, the substrates, and/or the intermediates that occur involving the solvent molecules.[19–26] Interpretation of the influence of the solvents on the NMR parameters is relatively complex, since it is difficult to separate the bulk medium effect from more specific interactions.[27] Not only the H-bond effects, π interaction was also detected as an important factor in the NMR spectroscopy of aromatic compounds.[28] The position and intensity of signals in ^{1}H-NMR spectra is also solvent dependent.[17,29] Hydrogen bonding and dipolar interactions between different quinolines and organic solvents have been detected by using ^{1}H-NMR and UV-visible spectroscopy.[30] For example, in 8-hydroxyquinoline, the intramolecular hydrogen bond with the aza-aromatic nitrogen is slightly weakened by interaction with alkanols.[30]

Self-association of amines by hydrogen bond formation in nonpolar? Non-HBD solvents is a long known phenomena.[31] Intense research on the differential effects of mixed solvents is also carried out at present.[18,32–34] We have reported ANS reactions with amines in non-HBD solvents where "*atypical*" results can be consistently explained by the so called "*dimer nucleophile*" mechanism.[18] This mechanism has been recently confirmed by ANS reactions carried out in aprotic, (non-HBD), solvents using mono- and polyfunctionalized amines specially designed to form intra- or intermolecular hydrogen bonds.[19,35] In the present paper we report ^{1}H-NMR studies on several bi- and polyfunctionalized amines, namely: *N*-(3- amino-1- propyl)morpholine (3-APMo), histamine, 2-guanidinobenzimidazole (2-GB), 1,2-diaminoethane (EDA), 3-dimethylamino-l-propylamine (DMPA), and 1-(2-aminoethyl)piperidine (2-AEPip), at variable molar amine concentration, *c*(amine), in non-HBD solvents at room temperature, to determine the likely H-bonded structures of these amines.

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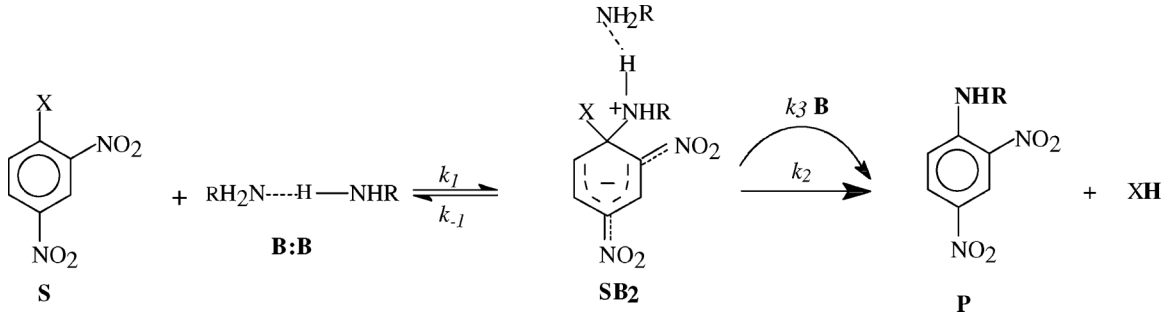


Scheme 1. The dimer nucleophile mechanism of ANS reactions

RESULTS AND DISCUSSION

In this paper, we examine the type of hydrogen bond likely present in amines involved in ANS reactions in non-HBD solvents. In the "*dimer nucleophile*" mechanism the inter- or intramolecular hydrogen-bonded homo-dimer as well as mixed dimers of the amine with other H-bond acceptors (HBA) act as the true nucleophile.[18] The simplified reaction scheme is depicted below (Scheme 1).

Hydrogen-bonded amines (with inter- or intramolecular homo-aggregates) are better nucleophiles than those in which no hydrogen-bond interactions are possible, due to the higher electron density on the hydrogen-bond donor nitrogen. The intermediate SB_2 is highly zwitterionic and the extra amine molecule should help to stabilize the developing charge in non-HBD solvents.

^{1}H-NMR spectroscopic determinations

^{1}H-NMR chemical shifts and signal strengths are very sensitive to hydrogen-bond formation. In almost all cases, formation of a hydrogen bonds shifts the ^{1}H-NMR signal downfield.[36] Hydrogen bonds and the concurrent fast proton exchange contribute to widening of the resonance signal.[37] ^{1}H-NMR allows a differentiation between inter-and intramolecular hydrogen bond, since the chemical shift of N—H signal is in the first case dependent on amine concentration, while the N—H signals of species with intramolecular hydrogen bonds are not affected by variation in the amine concentration, *c* (amine).[38]

The N—**H** chemical shifts, δ(N—**H**), of six amines, measured at different concentrations in dimethylsulfoxide-d_6 or chloroform-d_1 solutions using TMS as an internal standard are reported in Table 1. The signal assignment was carried out according to known methods.[39] The chemical shifts were recorded in the concentration range of 0.001–0.3 M: it has been observed that there is no change in δ(N—**H**) of 2-GB, histamine, and 3-APMo over the range of concentrations studied. Because of the ability of these amines to form a six-membered ring by intramolecular hydrogen-bonds, the formation of intermolecular self-aggregates is prevented. On the other hand, δ(N—**H**) of EDA, DMPA, and 2-AEPip shows an appreciable concentration dependence and the signals are broad for high concentration, indicating the presence of variable inter-molecular H-bonded aggregates.

Estimation of the dimerization constants

Figures 1–3 show the —N—**H** chemical shifts, δ(N—**H**), for EDA, DMPA, and 2-AEPip in $CDCl_3$ as a function of the logarithm of the amine concentration. Each NMR spectrum was determined in triplicate from independent amine solutions. As can be seen, at low concentrations the N—**H** signal appears at higher field, probably indicating a fully solvated (non-hydrogen bonded) amine H-atom. At high concentrations the δ(N—**H**) values appear at lower fields, which presumably correspond to the amine–amine hydrogen-bonded intermolecular aggregates. The NMR data for the amines that showed concentration dependence of the N—**H** signals can be treated as follows to estimate the dimerization constant. In the equilibrium:

$$\mathrm{B} + \mathrm{B} \rightleftarrows \mathrm{Dim} \tag{1}$$

where B is the amine and Dim the dimeric form, the dimerization constant, *K*, is given by Eqn (2):

$$K = \frac{c(\mathrm{Dim})}{c(\mathrm{B})^2} \tag{2}$$

the mass balance is:

$$c(\mathrm{Bt}) = c(\mathrm{B}) + 2c(\mathrm{Dim}) \tag{3}$$

where *c*(Bt) is the analytical concentration of B, which is partially dimerized.

By applying several rearrangements, Eqns (4)–(6) can be derived

$$c(\mathrm{B}) = \frac{-1 + \sqrt{1 + 8Kc(\mathrm{Bt})}}{4K} \tag{4}$$

$$K \times \left(\frac{-1 + \sqrt{1 + 8Kc(\mathrm{Bt})}}{4K}\right)^2 = c(\mathrm{Dim}) \tag{5}$$

$$\frac{c(\mathrm{Bt})}{2} + \frac{1}{8K} - \frac{\sqrt{1 + 8Kc(\mathrm{Bt})}}{8K} = c(\mathrm{Dim}) \tag{6}$$

If the "dimerizing fraction" (% *D*) is defined as *c*[Dim]/*c*[Bt], it is easy to demonstrate that:

$$1 + \frac{\sqrt{1 + 8Kc(\mathrm{Bt})}}{4Kc(\mathrm{Bt})} = (\%D) \tag{7}$$

Likewise, when $c(\mathrm{Bt}) = 1/K$, the dimerizing fraction is 0.5

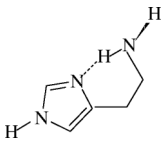
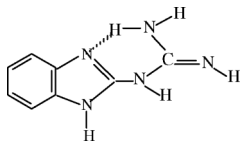
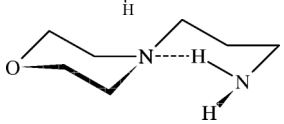
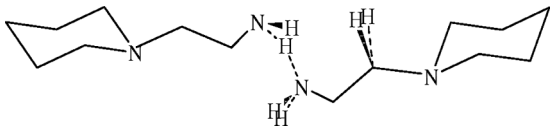
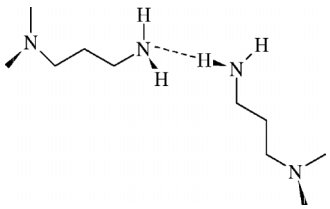
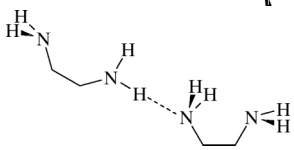
$$[\%D]_{1/K} = 1 + \frac{1 - \sqrt{1 + 8K(1/K)}}{4K(1/K)} = 0.5 \tag{8}$$

If the dimer formation is fast, the observed ^{1}H chemical shifts are an average of monomer and dimer N—H atoms:

$$\delta_{\mathrm{obs}} = \frac{c(\mathrm{Bt}) - 2c(\mathrm{Dim})\delta_{\mathrm{monomer}}}{c(\mathrm{Bt})} + \frac{2c(\mathrm{Dim})\delta_{\mathrm{dimer}}}{c(\mathrm{Bt})} \tag{9}$$

Each NMR spectrum was determined in triplicate from independent amine solutions. The δ(N—**H**) values shown in

Table 1. ^{1}H chemical shifts, δ, of the signals for the N**H**— atoms at various amine concentrations (in ppm from TMS as internal standard)

Amine	Solvent	c (amine).10^3, M	δ(N—**H**)/ppm
Histamine 	$CDCl_3$	1.0	4.90
		8.0	4.90
		50.0	4.90
2-GB 	CD_3SOCD_3 (DMSO-d_6)	1.0	7.10
		8.0	7.10
		50.0	7.10
3-APMo 	$CDCl_3$	1.0	1.37
		8.0	1.37
		50	1.37
		100	1.37 (broad)
		300	1.37 (broad)
2-AEPip 	$CDCl_3$	1.0	1.89
		8.0	2.10
		50	2.50
		100	2.80 (broad)
		300	3.00 (broad)
DMPA 	$CDCl_3$	1.0	1.30
		8.0	2.10
		50	2.80
		100	3.20 (broad)
		300	3.40 (broad)
EDA 	$CDCl_3$	1.0	0.85
		8.0	1.25
		50	2.07
		100	2.40 (broad)
		300	2.58 (broad)

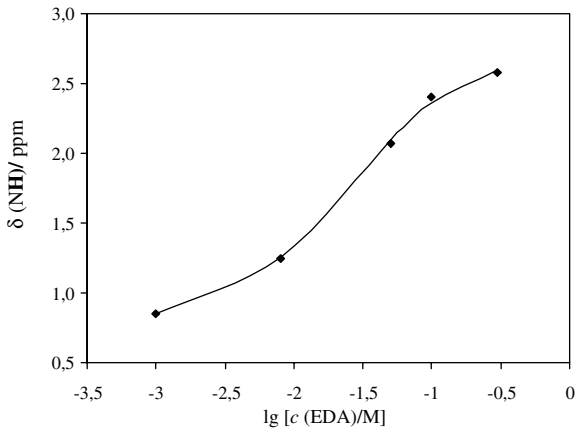


Figure 1. —N**H** NMR chemical shift of 1,2-diaminoethane as a function of the logarithm of amine concentration, measured in $CDCl_3$ at room temperature

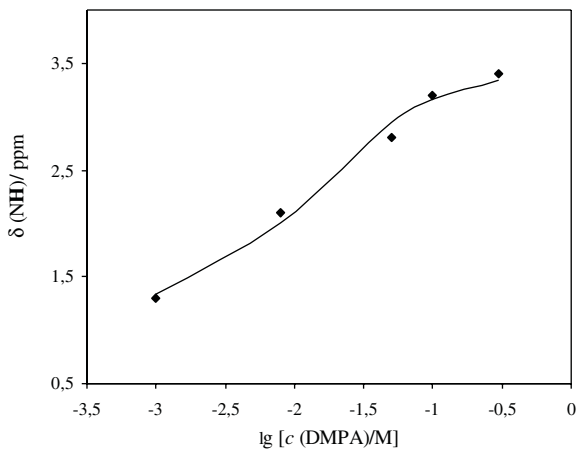


Figure 2. —N**H** NMR chemical shift of 3-dimethylamino-l-propylamine as a function of the logarithm of amine concentration, measured in $CDCl_3$ at room temperature

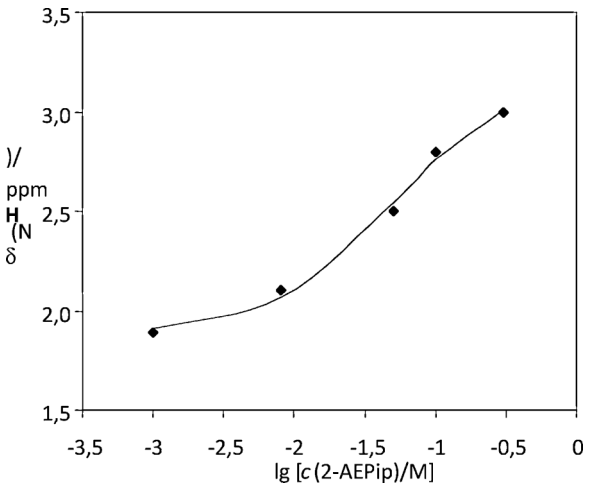


Figure 3. —N**H** NMR chemical shift of 1-(2-aminoethyl)piperidine as a function of the logarithm of amine concentration, measured in $CDCl_3$ at room temperature

Figures 1–3 are the average of three NMR determinations from independent amine solutions. For the calculations of the dimerization constants, the middle wave point of Figures 1–3 (Eqn (8)) was estimated from an hyperbole calculated by least squares analysis, extrapolating the data to the δ_0 intercept, that corresponds to infinite dilution, and the limit value δ_∞ consistent with an amine–amine fully hydrogen-bonded chemical shift (Eqn (10)).

$$\delta_{obs} = \delta_0 + \frac{(\delta_\infty - \delta_0)c(Bt)}{1/(K_{dim} + c(Bt))} \quad (10)$$

The dimerization constants thus obtained are gathered in Table 2. It can be observed that dimerization is important for the three amines under the conditions chosen, and the three dimerization constants are of the same magnitude; these results are consistent with kinetic determinations of ANS reactions of these amines with fluoro-2,4-dinitrobenzene and chloro-2,4-dinitrobenzene, recently reported; they showed a fourth-order kinetics typical for the "*dimer nucleophile*" mechanism.[19,35] These specially designed systems exhibit a peculiar kinetic behavior in a amine concentration range that allows a further refined treatment of the kinetics results, that has been recently reported.[40] On the other hand, reactions with 2-guanidinobenzimidazole (2-GB) studied in dimethylsulphoxide show a typical behavior, while in toluene and in binary toluene-DMSO mixtures, evidence for both intramolecular and mixed-aggregates was determined. Likewise, the reactions of the same substrates with histamine and *N*-(3- amino-1- propyl)morpholine (3-APMo) in toluene are second-order in amine.[19] We have recently reported theoretical molecular orbital calculations on the structures of 2-GB by *ab initio* and density functional theory carried out with the specific purpose of examining the likely hydrogen-bonding interactions in vacuum and in DMSO solution. It was found that 2-GB exhibits intra- and intermolecular H-bonds, forming homo- and mixed solute-solvent dimers.[41] Though, in principle, it could be expected that the molecular structure of DMPA could be considered similar to that of ·3-APMo it is worthwhile to note that in DMPA the N is approximately planar while the sp^3 N in the chair conformation of morpholine is more basic. Thus, the N is forced to adopt a more rigid sp^3 structure that more easily contributes to the formation of an H-bonded structure; 3-APMo is also too sterically hindered for another molecule to approach at the distance needed to form an intermolecular H-bonded structure.[41] The reported results afford additional evidence concerning the critical role that hydrogen-bonding bond interactions and formation of *homo-* and *"mixed aggregates"* play in the kinetics of these reactions.

Table 2. Amine dimerization equilibrium constants, K_{dim}, (M^{-1}) calculated from the ^{1}H-NMR data determined in $CDCl_3$ (see text for the derived equations)[a]

Amine [B]	K_{dim} (M^{-1})
EDA	26.0 ± 3
DMPA	56.4 ± 6
2-AEPip	11.7 ± 1

[a] Each NMR spectrum was determined in triplicate from independent amine solutions.

CONCLUSIONS

The present ^{1}H-NMR studies show that in diamines with an appropriate rigid molecular geometry an intramolecular hydrogen bond is easily established, which prevents or significantly reduces the formation of intermolecular H-bonded aggregates. On the other hand, in flexible structure diamines with two and three methylene groups in a lateral chain to the alicyclic nitrogen, the ability to form a six-membered ring is crucial. An intramolecular hydrogen-bond is established, which prevents the formation of intermolecular dimers. In contrast, aliphatic amines with two and three methylene groups easily establish intermolecular hydrogen-bond dimers. All these results afford additional evidence in favor of the "*dimer nucleophile*" mechanism observed in ANS reactions with amines in non-HBD solvents.

EXPERIMENTAL

General procedures

^{1}H-NMR spectra were recorded with a Bruker ARX-300 spectrometer using TMS as a reference standard and were determined in DMSO-d_6 or $CDCl_3$ as solvents. *J* values are given in Hertz. Thin-layer chromatography was performed on Merck Kiesegel 60 F254. Melting points were determined on a Kofler hot stage and are uncorrected.

Reagents and solvents

All solvents and reagents used were analytical reagent grade and the solvents were freshly distilled and dried before use according to established procedures. DMSO-d_6 (99%) deuterated (Fluka) and $CDCl_3$ deuterated (Fluka) were used directly without any further purification. The solvents were stored in a special vessel protected from light which allowed delivery without air contamination.

2-Guanidinobenzimidazole (2-GB, Aldrich) was recrystallized twice from ethyl acetate. To assure full removal of the solvent, the crystals were dissolved in chloroform and held *in vacuo* was

applied until a dried residue was obtained; it was reduced to powder in a mortar and the procedure was repeated until no impurities were detected by thin-layer chromatography. Finally, it was kept in a desiccator protected from light under dry nitrogen atmosphere (mp 242–244 °C, lit. 242.8–244.5 °C).[42]

3-Dimethylamino-1-propylamine (DMPA) was prepared from dimethylamine and acrylonitrile adapting a known technique.[43] After two days, the excess of dimethylamine was distilled off under reduced pressure at 75–77 °C/11 mmHg Torr). The *N*,*N*-dimethylpropanenitrile obtained was reduced with Na/EtOH. Distillation of the resulting product gave DMPA as a liquid, which was stored under a nitrogen atmosphere at 5 °C (bp. 133–135 °C). [^{1}H-NMR ($CDCl_3$): $\delta = 1.30$ (s, 2H, broad, —NH_2), 1.70 (m, 2H, —CH_2—), 2.31 (s, 6H, CH_3), 2.41 (t, 2H, —CH_2—), 2.84 (t, 2H, —CH_2—)].

1,2-Diaminoethane: (EDA, Fluka) was kept overnight over potassium hydroxide, distilled over zinc powder and then over sodium; both distillations were carried out at normal pressure, and the fraction of bp. 116–118 °C was collected (lit. 116.5 °C).[44] It was kept in a desiccator protected from light.

4(5)-2′-Aminoethylimidazole (Histamine Base) (Fluka) was used without any purification and was kept in a desiccator protected from light.

1-(2-Aminoethyl)piperidine (2-AEPip, Aldrich): the commercial product was kept over sodium strings during several days, distilled by reduced pressure fractional distillation over zinc powder and then twice over sodium strings under reduced pressure. The fraction of 78–80 °C at 20 mmHg Torr was collected. It was kept in a desiccator under dry nitrogen atmosphere, protected from light, and it was re-distilled immediately before use.

N-(3-amino-1-propyl)morpholine (3-APMo, Aldrich): the commercial product was kept over sodium strings during several days, distilled by reduced pressure fractional distillation over zinc powder and then twice over sodium strings under reduced pressure. The fraction 96–97 °C at 20 mmHg Torr was collected. It was kept in a desiccator under dry nitrogen atmosphere, protected from light, and was re-distilled immediately before using.

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