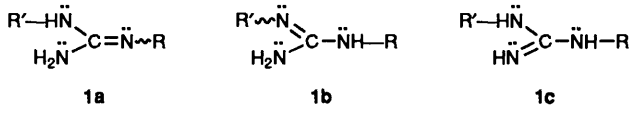
^1H and ^{15}N NMR Studies of *N*-Substituted-*N'*-cyanoguanidines

Ian D. Cunningham,*[a] Nan Chi Wan[a] and Brian G. Cox[b]
[a] *Department of Chemistry, University of Surrey, Guildford, UK GU2 5XH*
[b] *Zeneca Fine Chemicals Manufacturing Organisation, Huddersfield, UK HD2 1FF*

A series of *N*-aryl-*N'*-cyanoguanidines has been prepared and studied in $[^2H_6]Me_2SO$ by ^1H and ^{15}N NMR spectroscopy. The ^{15}N NMR coupling patterns for natural abundance and ^{15}N-enriched guanidines show unequivocally a structure with the C=N conjugated with the cyano group. The invariance of δ_H for the nitrogen bound protons with guanidine concentration, the temperature variation, the lack of water-induced change in δ_H, the linear free energy relationship (LFER) analysis and coupling patterns, all show that no prototropic tautomerisation is occurring on the NMR time-scale. The findings are considered in terms of possible dissociative and non-dissociative mechanisms.

The guanidine functional group [–N=C(–N⟨)$_2$] is an important one in organic and bioorganic chemistry and it has been the subject of a recent review.[1] Guanidine itself (**1**, R = R' = H) is a strong organic base owing to the stability of the guanidinium cation with its delocalised positive charge. Neutral monosubstituted guanidines **1** (R' = H) have possible tautomeric structures **1a** and the equivalent **1b** and **1c**. This class has been extensively studied,[1] in particular the biologically important molecule arginine {R' = H, R = $[CH_2]_3CH(NH_3^+)CO_2^-$}. Based on ^1H and ^{15}N NMR studies it has been proposed that arginine in Me_2SO exists as a rapidly (on the NMR time-scale) tautomerising mixture of the three forms **1a–c** with rapid rotation about the RN to C partial double bond in **1a**.[2] Compounds where R is an electron-withdrawing group such as nitro, cyano or *p*-aminobenzenesulfonyl, were in the past often written as **1c**, but in 1955 Kumler argued that the observed lack of acidity or basicity (among other chemical properties) was consistent only with structure **1a** for these compounds.[3] The predominance of structure **1a** was further supported by ^1H NMR, ^{15}N NMR and IR spectroscopy, as well as by X-ray crystallography in the solid state.[1] Similarly, where R is an aryl group ^{15}N NMR spectroscopy has shown structure **1a** to predominate.[4] *N,N'*-Disubstituted guanidines have three non-equivalent tautomeric forms **1a**, **1b** and **1c** and although in older literature they were often written as **1c**,[5] the relationship between basicity and σ_I suggests that **1b** predominates where R' is the more electronegative group.[6,7] However, even if one tautomer is favoured to a very large extent, this does not preclude rapid exchange of the protons within the molecule *via* trace amounts of less favoured tautomers, and such prototropic tautomerisations, fast for alkyl-substituted guanidines such as arginine, have not been extensively studied for guanidines bearing electron-withdrawing substituents. Of particular interest are the *N*-aryl-*N'*-cyanoguanidines **2** which have been used extensively as precursors to heterocyclic compounds,[8] polymers[8d,9] and biguanides;[10] the last often showing medicinal properties.[10c–g] We have therefore, undertaken a ^1H and ^{15}N NMR study of these cyanoguanidines in Me_2SO, the results of which are considered in this paper.



1a **1b** **1c**

Experimental

The *N*-substituted-*N'*-cyanoguanidines were prepared by refluxing the corresponding substituted amine (0.0112 mol) and sodium dicyanamide (0.0112 mol) in 0.5 mol dm^{-3} hydrochloric acid (20 cm^3) for 1–18 h; the crude products were isolated as precipitates from the cooled reaction solutions. The 4-nitro compound proved more difficult to prepare, requiring up to 76 h of refluxing in 2:3 1.0 mol dm^{-3} hydrochloric acid–acetone (25 cm^3), followed by filtration, concentration of the filtrate, and isolation by preparative TLC. All products were recrystallised from ethanol to purity by TLC and constant melting point; melting points agreed with literature values.[5,11] ^{15}N-Enriched aniline was prepared by nitration of benzene using potassium nitrate (14.4 atom% ^{15}N) in 70% H_2SO_4–H_2O followed by reduction with tin in hydrochloric acid. 4-Nitroaniline, ^{15}N-enriched at the amino group, was prepared from enriched aniline *via* acetanilide using standard methods.[12]

NMR spectra were obtained using a Bruker AC 300 MHz spectrophotometer. Samples were prepared for ^1H NMR spectroscopy by dissolving *ca.* 20 mg of the guanidine in 1 cm^3 of $[^2H_6]Me_2SO$. The amount of residual H_2O was determined by integration of the H_2O peak relative to that of the guanidine whose concentration was known; in some cases a further known quantity of H_2O was added by syringe. In all cases Me_4Si was used as internal reference. ^{15}N-Enriched samples for ^{15}N NMR spectroscopy were prepared similarly, but for natural abundance samples, concentrations were up to 200 mg cm^{-3}. For ^{15}N NMR analysis the operating frequency was 30.4 MHz and an external nitromethane reference was used.

Results

Preparation of Guanidines.—*N*-Substituted-*N'*-cyanoguanidines are normally prepared either by decomposition of azo precursors[5] or by attack of amine on dicyanamide.[13] The *para*- and *meta*-substituted *N'*-cyano-*N*-phenylguanidines **3–11** and *N'*-cyano-*N*-ethylguanidine **12** (Table 1) were prepared by a variation of the latter method.

^1H NMR Spectra.—^1H NMR spectra were obtained for guanidines **3–12** in $[^2H_6]Me_2SO$ at 25 °C; the assignments are given in Table 1. All spectra showed separate 1 H and 2 H signals due to hydrogens attached to nitrogen, as well as a separate water signal; a typical spectrum is shown in Fig. 1.

Most measurements were for the guanidines at a concentration of about 0.14 mol dm^{-3}, and no changes in values of δ_H for any signal were observed for small variations about this value. For the 4-methyl-substituted compound **4** ^1H NMR

Table 1 ^{1}H Chemical shifts (δ) for *N*-aryl-*N'*-cyanoguanidines[a]

Compound	Aryl substituent	NH[b]	Aryl–H	NH_2[b]	CH_3
3	4-CH_3O	8.84	7.04 (AA'XX')	6.84	3.73
4	4-CH_3	8.95	7.16 (AA'XX')	6.91	2.25
5	H	9.04	7.36–7.07 (m)	6.99	
6	4-Cl	9.18	7.37 (AA'XX')	7.09	
7	4-Br	9.17	7.41 (AA'XX')	7.09	
8	3-Cl	9.22	7.55 (s), 7.35–7.23 (m)	7.14	
9	3-NO_2	9.53	8.38 (d), 7.90 (d), 7.73 (d), 7.59 (t)	7.29	
10	4-CN	9.68	7.57 (AA'XX')	7.35	
11	4-NO_2	9.89	7.95 (AA'XX')	7.43	
12	*c*	6.80		6.65	1.01 (t)[d]

[a] In [$^2H_6$]Me_2SO relative to Me_4Si as internal standard. [b] All signals singlets. [c] Compound **12** is *N'*-cyano-*N*-ethylguanidine. [d] Quintet owing to CH_2 at δ 3.06.

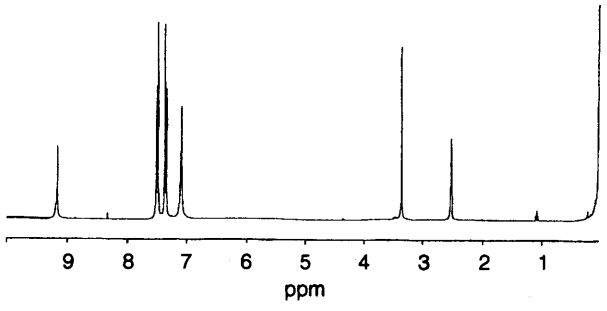


Fig. 1 ^{1}H NMR spectrum of *N*-(4-chlorophenyl)-*N'*-cyanoguanidine **6** in [$^2H_6$]Me_2SO. Peaks at δ 3.3 and 2.4 are due to water and residual protic Me_2SO, respectively.

spectra were obtained over a concentration range 0.056–0.280 mol dm^{-3} and no significant variations were observed for any signal.

Dependence of ^{1}H *NMR Spectra on Temperature and* H_2O *Concentration.*—The temperature variation of δ was determined for guanidines **4**, **7** and **10** over 25–125 °C (10 °C steps) in the presence of various amounts of H_2O. In all cases an upfield shift in the NH, NH_2 and H_2O signals was observed with increase in temperature along with a broadening of the NH and NH_2 signals, the extent of which broadening increased as the aryl substituent became more electron withdrawing. Plots of δ against *T* for the NH and the NH_2 of **4**, **7** and **10** are given in Fig. 2, showing a linear and parallel relationship within each set. Importantly, values of $\Delta\delta/\Delta T$ (Table 2) for **4**, **7** and **10** show little or no variation with solvent water content; this reflects the finding that at any constant temperature no variation in δ for either the NH or the NH_2 signal was observed in the presence of up to 0.42 mol dm^{-3} H_2O, a finding shown more explicitly for **4** in Table 3.

Linear Free Energy Relationships (*LFERs*).—Chemical shift values for the NH and the NH_2 signals were plotted against Hammett substituent constants,[14] (Figs. 3 and 4, respectively).* An excellent correlation is found between δ(NH) and the enhanced substituent constant σ^- (r = 0.997, n = 9). A good linear relationship is also found between the $\delta(NH_2)$ values

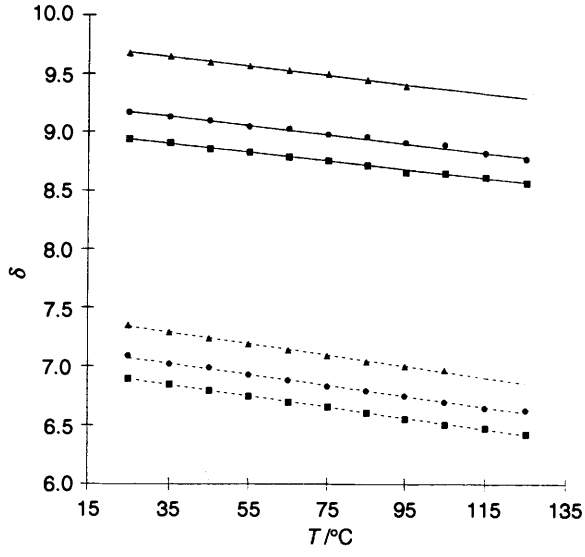


Fig. 2 Plots of δ against *T* (°C) for the NH (——) and NH_2 (– – – –) signals of compounds **4** (■), **7** (●) and **10** (▲)

and σ° for all substituents except 4-cyano and 4-nitro (r = 0.999, n = 7). Extrapolation shows that the points for the 4-cyano and the 4-nitro compounds can be fitted only if substituent constants of about 0.83 and 1.10, respectively are used; these lie between the σ° and the σ^- values for these substituents.

^{15}N *NMR Spectra.*—The ^{15}N NMR natural abundance spectrum of *N'*-cyano-*N*-phenylguanidine **5** showed a singlet at δ −184.6, a doublet at δ −277.5 [$^1J(^{15}N–H)$ = 89 Hz], a singlet at δ −282.9 and a triplet at δ −298.6 [$^1J(^{15}N–H)$ = 90 Hz] assigned to –CN, –NH–, =N– and $-NH_2$ nitrogens, respectively. The spectrum of **5** prepared from ^{15}N-enriched (about 14%) aniline, and therefore enriched only at the nitrogen adjacent to the phenyl group, showed enhancement of only the doublet at δ −277.5. It is estimated that the sensitivity was such that any other enhanced nitrogen peak could have been detected down to about 5% the intensity of that seen at δ −277.5. Owing to the small amount of material available it was not possible to obtain a natural abundance ^{15}N NMR spectrum of the 4-nitro compound **11**, but a sample enriched at the nitrogen adjacent to the aromatic ring showed only a doublet (which collapsed to a singlet on decoupling from the hydrogens) at δ −271.3 [$^1J(^{15}N–H)$ = 94 Hz].

* Values for substituent constants are taken from ref. 14 where values from a range of cited sources are gathered. The constants given the symbol σ in ref. 14 appear to correspond to those defined elsewhere as σ° and the term σ° is used in this work.

Table 2 Variation of chemical shift with temperature for guanidines in [$^2H_6$]Me_2SO containing various amounts of H_2O

Compound	[H_2O]/ mol dm^{-1}	$-(\Delta\delta/\Delta T)/10^{-3}$ ppm K^{-1} [a] NH	NH_2
4	0.07	3.7	4.7
4	0.14	3.8	5.1
4	0.21	3.7	5.0
4	0.28	3.5	4.8
4	0.34	3.3	4.3
4	0.42	3.6	4.7
7	0.07	3.9	4.6
7	0.35	4.1	4.9
10	0.07	3.9[b]	4.8[c]
10	0.35	4.6[d,e]	4.6[c,d]

[a] All values ±0.01 except [d] ±0.02. [b] Peak disappeared above 95; [c] 105 and [e] 75 °C.

Table 3 Variation of chemical shift (δ) for guanidine **4** with concentration of H_2O in the [$^2H_6$]Me_2SO solvent at 25 and 125 °C;[a] [**4**] = 0.14 mol dm^{-3}

[H_2O]/ mol dm^{-3}	NH 25 °C	NH_2 25 °C	NH 125 °C	NH_2 125 °C
0.07	8.94	6.90	8.57	6.43
0.14	8.95	6.91	8.56	6.40
0.21	8.94	6.91	8.57	6.41
0.28	8.95	6.91	8.60	6.43
0.34	8.91	6.87	8.58	6.44
0.42	8.94	6.91	8.58	6.44

[a] All signals relative to Me_4Si as internal standard.

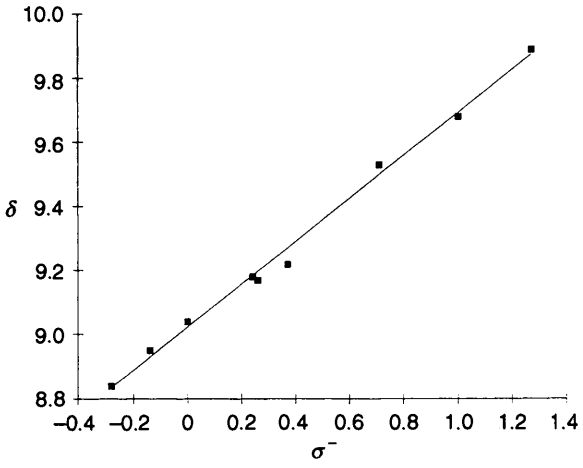


Fig. 3 Plot of δ(NH) (25 °C) against σ^- for guanidines **3** to **11**

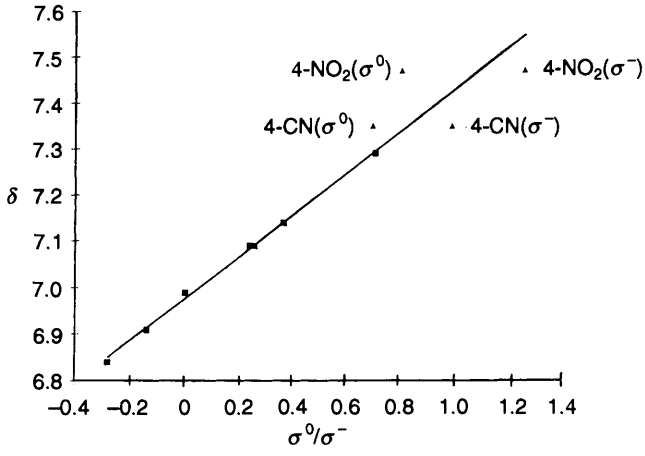
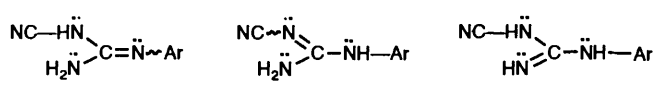


Fig. 4 Plot of $\delta(NH_2)$ (25 °C) against σ^0/σ^- for guanidines **3** to **9** (■). The points (▲) are for the 4-cyano and 4-nitro compounds, **10** and **11**, respectively, for showing the deviations upon use of either σ^0 or σ^-.

Discussion

With respect to structure, the observation for all compounds of one and two proton N–H signals, along with the ^{15}N coupling patterns (singlet, doublet, triplet) rules out structure **2c**. The correlation of δ(NH) with σ^- is consistent with either structure **2a** or **2b**, and while the correlation of $\delta(NH_2)$ for the key 4-CN and 4-NO_2 compounds with a substituent constant lying between σ^- and σ^0 might suggest a mixture of **2a** (direct resonance of the NH_2 lone pair with the Ar substituent is possible) and **2b** (direct resonance is not possible), the ^{15}N NMR is unequivocal in favouring **2b**. The ^{15}N NMR spectrum shows a doublet, indicative of an NH, for the nitrogen bearing the Ar group, both for **5** (Ar = phenyl) a compound lying in the linearly correlated portion of the $\delta(NH_2)$ plot, and for **11** (Ar = 4-nitrophenyl), a compound lying in the 'deviant' region. *N*-Ethyl-*N'*-cyanoguanidine **12** also exists as a tautomer analogous to **2b**; separate broad peaks due to NH and NH_2 are seen in its ^1H NMR spectrum, and coupling of the CH_2 to the NH results in a quintet for this signal.



2a **2b** **2c**

Proton transfer between X–H and X', X and X' being two C, N, S or O sites in a molecule (prototropic tautomerism) is an important and much studied phenomenon in chemistry; in particular transfers involving the N–H • • • N' system are slower than those of O, faster than those of C, and are suitable for NMR analysis.[15] In the present case the observed ^{15}N–H couplings with $^1J(^{15}N–H)$ values close to those expected (89–94 Hz), indicate negligible prototropic tautomerization, either inter- or intra-molecular, on the 'coupling' time-scale for those compounds and conditions where these data are available. However, the following discussion will consider all the cyanoguanidines **3**–**11** over a wider range of conditions.

Proton transfers are either dissociative or non-dissociative; the former type involves stepwise pre-protonation *via* solvent of X' followed by de-protonation of X–H to solvent or *vice versa* and is typically found when water is present as or in the solvent.[16] In general, increasing chemical exchange of protons between different groups is reflected in the NMR spectrum as a broadening and moving together, with eventual coalescence, of the signals for the protons[17] and the groups X and X' involved,[18] along with the collapse of any coupling; if exchange is dissociative *via* water the water signal will also be involved in the coalescence. In the present case the observation for guanidines **3**–**11** of separate ^1H signals for NH, NH_2 and H_2O corresponds to either no significant exchange by this mechanism, or to the onset of exchange where broadening and moving together has just commenced. If the latter is the case, the addition of further water would be expected to enhance significantly any coalescence, but the results of Tables 2 and 3 show that this is not the case; no significant change in peak broadening or chemical shift is seen at any given temperature when the water concentration is increased up to sixfold. A temperature-induced broadening and movement is seen for these three signals for compounds **4**, **7** and **10**. We attribute the

change in δ to a general upfield shift consistent with a decrease in hydrogen bonding to solvent ($[^2H_6]Me_2SO$) rather than a coalescence; addition of H_2O has no effect and the $\Delta\delta/\Delta T$ values are of a magnitude (*ca.* 4×10^{-3} ppm K^{-1}) appropriate to a solvation effect, with no additional factor which could be attributed to chemical exchange. With chemical exchange ruled out the temperature-induced broadening must be due to the attached ^{14}N quadrupolar nucleus; a similar broadening effect was noted by Hammond and Neumann in spectra of amidinium salts.[19] It can be attributed to the electric field of the ^{14}N nucleus becoming more symmetric as temperature is increased and as the aryl substituent becomes more electron withdrawing, resulting in slower ^{14}N relaxation and incipient coupling of H to N.[20]

Clearly dissociative prototropic tautomerisation *via* water is slow on the NMR time-scale. This might appear surprising considering that several N–H···N′ dissociative transfer mechanisms are known for the related amidine (N=C–NH)[1] and imidazole systems; for example tautomerisation within the imidazole ring of adenine occurs *via* four water catalysed mechanisms: initial protonation of the imino N by H_2O, or by H_3O^+, and initial de-protonation of the amino N–H by HO^-, or by N^- from another adenine.[21] However, although guanidine **1** (R = R′ = H) and many of its derivatives are strongly basic (the pK_a of guanidinium sulfate is 13.6) and tautomerise readily,[2] the lack of H_2O or H_3O^+ catalysed tautomerisation for guanidines **3–11** is understandable; replacement of a hydrogen of guanidine by a strongly electron-withdrawing group such as cyano or nitro results in a dramatic reduction of basicity and the pK_a values for the conjugate acids of *N*-cyano- and *N*-nitro-guanidine are −0.85 and −0.98, respectively.[7] Perhaps more surprising is the lack of catalysis by HO^-; nitroguanidines are weakly acidic, with *N*-nitro-*N*′-phenylguanidine having a pK_a(water) of 10.5,[6] and although no data are available for cyanoguanidines the pK_a values for compounds **3–11** are unlikely to be more than a few units higher. Possibly, the Me_2SO solvent reduces the acidity in the present case to the extent that prototropic tautomerisation by HO^- is negligible.

Three non-dissociative mechanisms have been proposed for the X–H···X′ transfer system:[16] intramolecular proton transfer, mutual transfer within a dimer, and concerted transfer *via* a cyclic structure of associated water molecules. Given structure **2b** it is difficult to envisage intramolecular hydrogen bonding or proton transfer, and the linear temperature dependencies of δ(NH) and $\delta(NH_2)$ (Table 2) are similar to those observed for amide protons involved in solvent ($[^2H_6]Me_2SO$) rather than intramolecular hydrogen bonding.[22] For guanidine **4**, the lack of variation of δ(NH) or $\delta(NH_2)$ with concentration (see for example ref. 23 for the effect of amide–amide interactions), although over a relatively limited range, shows that the second non-dissociative mechanism is not important and that **4** exists in one form over this range. Evidence for more general associative homogeneity across the range of guanidines **3–11** is the linearity of the LFER for the NH signal, and overall, it seems reasonable to suggest a monomeric form in $[^2H_6]Me_2SO$. The lack of transfer within a dimer is in contrast to the situation for amidines where prototropic tautomerisation through a cyclic dimer is important.[24] Transfer *via* the last mechanism would be expected to result in increasing coalescence of the NH and NH_2 peaks on addition of water and can be discounted here. Again it seems reasonable to relate the lack of non-dissociative proton transfer to the low basicity and acidity of the cyanoguanidines; additionally, the Me_2SO–cyanoguanidine hydrogen bonding may be important in preventing dimer formation and tautomerisation *via* this mechanism.

For **2b** there is the possibility of *E*–*Z* isomerism about the C=N, and the potential for restricted rotation about the partial double bonds, C to NH–Ar and C to NH_2. However, no NMR effects attributable to these factors were noted in the present work. Presumably, the *E*-isomer is the more stable, and the rotational barriers are lower than in the related amidines.[25]

Conclusions

The NMR study has shown that in Me_2SO solvent the *N*-aryl-*N*′-cyanoguanidines have the **2b** structure. There is no evidence for prototropic tautomerisation or general exchange of the NH hydrogens even at elevated temperature. This can be attributed to the very low basicity and acidity of the cyanoguanidines compared to other N–H···N′ compounds such as amidines,[26] 'normal' guanidines and even imidazoles. It appears that the strongly electron-withdrawing cyano group, which reduces guanidine basicity and favours tautomer **2b**, also reduces the rate of prototropic tautomerisation.

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