^{13}C Nuclear Magnetic Resonance Study of Some Aliphatic Polyamines

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The ^{13}C n.m.r. spectra of the unprotonated and fully protonated forms of ethylenediame (en), *N*-(2-aminoethyl)propane-1,3-diamine (2,3-tri), 2,2′-ethylene di-iminobis(ethylamine) (trien), 2,2′-trimethylenedi-iminobis(ethylamine) (2,3,2-tet), and 3,3′-trimethylenedi-iminobis(propylamine) (3,3,3-tet) are reported, together with those of the unprotonated forms of 2,2′-iminobis(ethylamine) (dien), 3,3′-iminobis(propylamine) (dpt), 2,2′-iminodiethylenedi-iminobis(ethylamine) (tetren), and 2,2′,2″-nitrilotris(ethylamine) (tren). A full assignment of the chemical shifts is proposed, based on a two-term empirical relationship employing ' amine shift parameters ' π and π^+.

We have become interested in the possible use of ^{13}C n.m.r. spectroscopy to determine the co-ordination geometry of zinc in its complexes in solution. While it is generally agreed that the important role played by Zn^{II} in enzyme chemistry is associated with its ability to adopt a co-ordination number of 4, 5, or 6, and to change its co-ordination geometry comparatively easily, its d^{10} configuration has so far precluded the direct determination of its co-ordination number by spectroscopic techniques. There is thermodynamic [1] and other [2] evidence that this variability of co-ordination geometry is to be found in the complexes of Zn with a range of aliphatic polyamines, and we will discuss their ^{13}C n.m.r. spectra in future papers. A necessary requirement for such a discussion is a reasonably unambiguous assignment of the resonances in the free ligand, and it is with this problem that the present paper is concerned.

The ^{13}C chemical shifts are reported for the high-pH (unprotonated) and low-pH (fully-protonated) forms of ethylenediamine (en),† *N*-(2-aminoethyl)propane-1,3-diamine (2,3-tri), 2,2′-ethylenedi-iminobis(ethylamine) (trien), 2,2′-trimethylenedi-iminobis(ethylamine) (2,3,2-tet), and 3,3′-trimethylenedi-iminobis(propylamine) (3,3,3-tet), and for the high-pH (unprotonated) forms of 2,2′-iminobisethylamine (dien), 3,3′-iminobis(propylamine) (dpt), 2,2′-iminodiethylene-di-iminobis(ethylamine) (tetren), and 2,2′,2″-nitrilotris-(ethylamine) (tren). An attempt is made to assign the peaks by comparison with the spectra of simpler amines but, as has been the experience in other studies dealing with aliphatic polyamines (see, for example, refs. 3—5), it is possible to make only a few unambiguous assignments. An extension of the empirical method [6] of Sarneski *et al.* for ' predicting ' the ^{13}C shifts in aliphatic mono- and di-amines removes some of the ambiguities. However, by expressing the chemical shift of each C atom in the polyamines as the sum of two contributions from its two nearest amino groups, we are able to group the resonances so as to suggest an unambiguous assignment in each case. The use of this approach to investigate the nature of the partially protonated intermediates formed during the titration of several of the polyamines (*i.e.* their microscopic pK_a) will be reported in a future paper.

Experimental

Preparation of Solutions.—Commercial samples of the following amines were purified by distillation: en (B.D.H.; 116—117 °C at 760 Torr), dien (Aldrich; 82—83 °C at 2—3 Torr), 2,3-tri (Aldrich; 60—64 °C at 1 Torr), dpt (Aldrich; 72—76 °C at 0.15 Torr), 2,3,2-tet (Eastman; 100—102 °C at 0.05 Torr), 3,3,3-tet (Eastman; 104—105 °C at 0.1 Torr); tren was isolated from technical grade trien as the hydrochloride,[7] the regenerated amine being distilled under reduced pressure (127—128 °C at 0.15 Torr); trien (120—130 °C at 0.005—0.1 Torr) was obtained from the sulphate (Baker); tetren (B.D.H.) was precipitated as the nitrate [8] but purification proved difficult and solutions were made up by dissolving the salt in alkali at 0 °C. The purity of the amines was monitored by ^{13}C n.m.r. in conjunction with analytical g.l.c. 1,4-Dioxane (Fisons A.R.) was used without further purification. Solutions (0.2—0.4 mol dm^{-3}) were made up in D_2O (BOC Prochem; 99.8 atom %) with 0.2 mol dm^{-3} 1,4-dioxane. The pD (calculated using the empirical relationship [9] $pD = pH + 0.4$) was adjusted with concentrated HNO_3 and/or a saturated solution of KOH in D_2O: in all cases it was at least either 2 units above the highest or 2 units below the lowest known or estimated pK_a value of the amine.[10] For en, 2,3-tri, trien, 2,3,2-tet, and 3,3,3-tet this was confirmed by titration, details of which will be published elsewhere.

^{13}C *N.m.r. Spectra.*—The n.m.r. spectra were recorded at *ca.* 20 °C with a JEOL FT-100 spectrometer in the proton-noise decoupled mode at 25.15 MHz. Typically, 4 K data points were acumulated over a frequency range of 2 kHz with 500 scans. In most cases, the chemical shifts were measured relative to internal 1,4-dioxane but the data are quoted on the δ scale; for dpt and pn (trimethylenediamine),[6] external Me_4Si was used. In several experiments designed to confirm the lack of influence of typical solutes and pD on the signal of dioxane, both standards were used: the δ value of dioxane was always found to be 67.7 and we therefore used this value throughout. Although the spectra recorded with internal dioxane were generally reproducible to better than ± 0.1 p.p.m., those measured against Me_4Si alone sometimes showed discrepancies of a few tenths of a p.p.m. (usually to high δ) as compared with the spectrum of the same solute with internal dioxane. We attribute these differences to an experimental artefact (*e.g.* field inhomogeneity) associated with the use of the external standard.

Analysis of Spectra

The measured chemical shifts $\delta_C{}^m$ are listed in Table 1(a) and (b) for, respectively, the high-pD (unprotonated) and low-pD (fully protonated) forms of the amines. The terms C_1 to C_5 and $C_1{}'$ to $C_5{}'$ are used to identify the observed peaks, the numbering being determined by the relative positions in the spectrum. The terms C_a to C_e refer to the non-equivalent C

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† The abbreviations employed for the amines are those commonly used in co-ordination chemistry; in most cases they are based on the trivial name (*e.g.* dien for diethylenetriamine) but in 2,3-tri, 2,3,2-tet, and 3,3,3-tet the prefixed numbers represent the numbers of carbon atoms linking, respectively, the three (tri) and four (tet) nitrogen atoms.

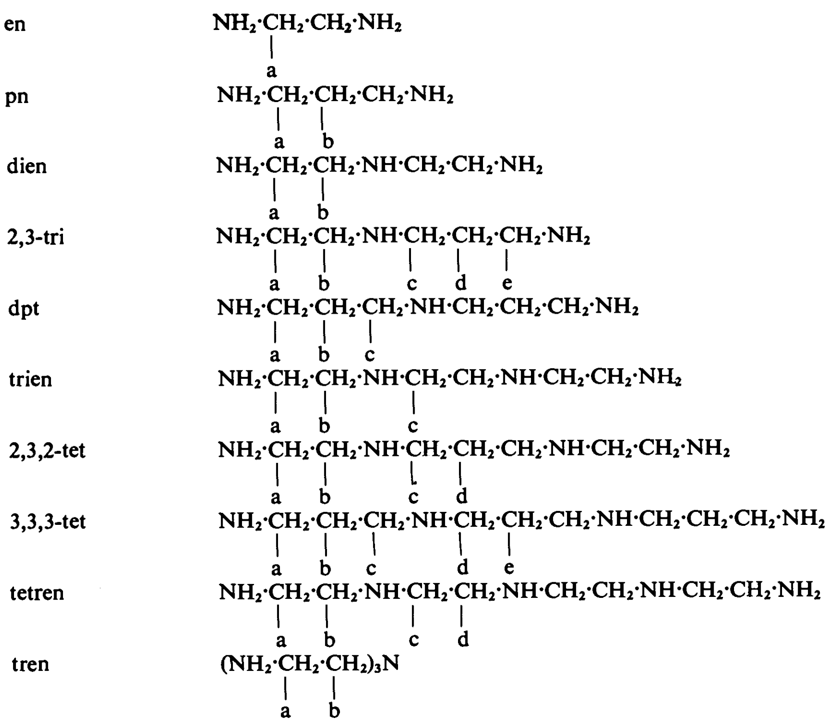
Table 1. Measured ^{13}C shifts (δ_C^m) for polyamines, and assignments based on amine shift parameters (see text)

(a) Unprotonated forms

Amine	pH	C_1			C_2			C_3			C_4			C_5		
		δ_C^m (p.p.m.)	Assignment	($\delta_C^m - \delta_C^x$) (p.p.m.)	δ_C^m (p.p.m.)	Assignment	($\delta_C^m - \delta_C^x$) (p.p.m.)	δ_C^m (p.p.m.)	Assignment	($\delta_C^m - \delta_C^x$) (p.p.m.)	δ_C^m (p.p.m.)	Assignment	($\delta_C^m - \delta_C^x$) (p.p.m.)	δ_C^m (p.p.m.)	Assignment	($\delta_C^m - \delta_C^x$) (p.p.m.)
en	13.2	43.9	C_a	−0.2												
pn [11]		36.7	C_b	0.7	40.1	C_a	0.6									
dien	11.9	41.0	C_a	0.0	51.7	C_b	−0.3									
2,3-tri	12.5	32.8	C_d	−0.1	39.9	C_e	0.0	41.1	C_a	0.1	47.4	C_c	0.0	52.0	C_b	0.0
dpt	12.5	33.2	C_b	0.3	40.3	C_a	0.4	47.9	C_c	0.5						
trien	12.0	41.0	C_a	0.0	48.8	C_c	−0.1	51.9	C_b	−0.1						
2,3,2-tet	12.7	29.7	C_d	−0.1	41.0	C_a	0.0	47.7	C_e	−0.1	51.9	C_b	−0.1			
3,3,3-tet	13.1	29.7	C_e	−0.1	32.9	C_b	0.0	39.9	C_a	0.0	47.4	C_c	0.0	47.9	C_d	0.1
tetren	12.5	41.0	C_a	0.0	48.7	C_c	−0.2	48.8	C_d	−0.1	51.9	C_b	−0.1			
tren	13.4	38.9	C_a	0.0	57.4	C_b	0.0									

(b) Fully protonated forms

Amine	pH	C_1'			C_2'			C_3'			C_4'			C_5'		
en	1.7	37.6	C_a	0.1												
2,3-tri	1.7	24.8	C_d	−0.1	36.7	C_a	0.3	37.7	C_e	0.0	45.5	C_c	0.0	46.3	C_b	1.0
trien	1.1	36.5	C_a	0.1	44.5	C_c	0.3	45.9	C_b	0.6						
2,3,2-tet	3.2	23.8	C_d	0.0	36.6	C_a	0.2	45.5	C_c	0.0	46.1	C_b	0.8			
3,3,3-tet	3.1	23.7	C_e	−0.1	24.9	C_b	0.0	37.9	C_a	0.2	45.9	C_c	0.4	45.9	C_d	0.4



en $NH_2\cdot\underset{a}{CH_2}\cdot CH_2\cdot NH_2$

pn $NH_2\cdot\underset{a}{CH_2}\cdot\underset{b}{CH_2}\cdot CH_2\cdot NH_2$

dien $NH_2\cdot\underset{a}{CH_2}\cdot\underset{b}{CH_2}\cdot NH\cdot CH_2\cdot CH_2\cdot NH_2$

2,3-tri $NH_2\cdot\underset{a}{CH_2}\cdot\underset{b}{CH_2}\cdot NH\cdot\underset{c}{CH_2}\cdot\underset{d}{CH_2}\cdot\underset{e}{CH_2}\cdot NH_2$

dpt $NH_2\cdot\underset{a}{CH_2}\cdot\underset{b}{CH_2}\cdot\underset{c}{CH_2}\cdot NH\cdot CH_2\cdot CH_2\cdot CH_2\cdot NH_2$

trien $NH_2\cdot\underset{a}{CH_2}\cdot\underset{b}{CH_2}\cdot NH\cdot\underset{c}{CH_2}\cdot CH_2\cdot NH\cdot CH_2\cdot CH_2\cdot NH_2$

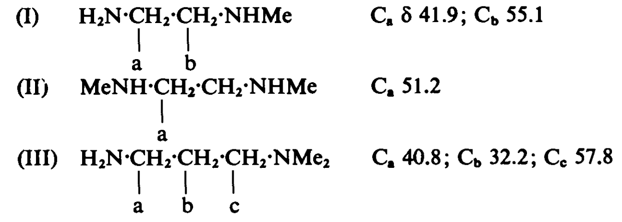
2,3,2-tet $NH_2\cdot\underset{a}{CH_2}\cdot\underset{b}{CH_2}\cdot NH\cdot\underset{c}{CH_2}\cdot\underset{d}{CH_2}\cdot CH_2\cdot NH\cdot CH_2\cdot CH_2\cdot NH_2$

3,3,3-tet $NH_2\cdot\underset{a}{CH_2}\cdot\underset{b}{CH_2}\cdot\underset{c}{CH_2}\cdot NH\cdot\underset{d}{CH_2}\cdot\underset{e}{CH_2}\cdot CH_2\cdot NH\cdot CH_2\cdot CH_2\cdot CH_2\cdot NH_2$

tetren $NH_2\cdot\underset{a}{CH_2}\cdot\underset{b}{CH_2}\cdot NH\cdot\underset{c}{CH_2}\cdot\underset{d}{CH_2}\cdot NH\cdot CH_2\cdot CH_2\cdot NH\cdot CH_2\cdot CH_2\cdot NH_2$

tren $(NH_2\cdot\underset{a}{CH_2}\cdot\underset{b}{CH_2})_3N$

Scheme 1. Identification of the non-equivalent C atoms in the compounds studied



(I) $H_2N\cdot\underset{a}{CH_2}\cdot\underset{b}{CH_2}\cdot NHMe$ C_a δ 41.9; C_b 55.1

(II) $MeNH\cdot\underset{a}{CH_2}\cdot CH_2\cdot NHMe$ C_a 51.2

(III) $H_2N\cdot\underset{a}{CH_2}\cdot\underset{b}{CH_2}\cdot\underset{c}{CH_2}\cdot NMe_2$ C_a 40.8; C_b 32.2; C_c 57.8

Scheme 2.

atoms in each molecule, identified in Scheme 1. The assignments of C_1—C_5 and of C_1'—C_5' are not necessarily the same, since one or more ' crossovers ' between neighbouring peaks may occur during the titration. In cases where this appeared to happen, the shapes of the titration curves were of no help in making the assignment and so they have not been included in the present paper. In view of the problems [11,12] associated with the variable nuclear relaxation and nuclear Overhauser enhancements of different carbon atoms in a molecule, we have not used integrated peak areas to assist in making the assignments; neither have we been able to use evidence from single-frequency proton decoupling since in most cases the ^1H n.m.r. spectrum cannot be resolved.

The analysis of the chemical shifts $\delta_C{}^m$ will be described in three parts: comparison with published data for simpler amines, application of an empirical method based on that of Sarneski *et al.*,[6] and development of our own empirical two-term relationship using the ' amine-shift parameters ' π and π^+.

(a) *Comparison with Model Compounds.*—The three most appropriate models are *N*-methylethylenediamine (I), *N,N'*-dimethylethylene-1,2-diamine (II), and *N,N*-dimethyltrimethylenediamine (III), for which the assignments in Scheme 1 are accepted [12] (shifts, in p.p.m., refer to the unprotonated forms). In some cases the proximity of two peaks leads to uncertainty but inspection of Table 1(a) suggests a few definite assignments. For example, the C_1 peak of trien (δ 41.0) is close to the C_a resonances for compounds (I) (41.9) and (III) (40.8), both of which involve a C atom α to an NH_2 group, and we conclude that this is the case here also (*i.e.* C_1 is C_a). For the other two peaks of trien (δ 48.8 and 51.9) the situation is less clear and either could reasonably be attributed to the other C in the terminal ethylene group [C_b; *cf.* C_b in (I) at δ 55.1] or to the C in the central ethylene group [C_c; *cf.* C_a in (II) at δ 51.2].

,3-tri: C_1 is C_d; C_2 and C_3 are C_a and C_e; C_4 and C_5 are C_b and C_c
trien: C_1 is C_a; C_2 and C_3 are C_b and C_c
2,3,2-tet: C_1 is C_d; C_2 is C_a; C_3 and C_4 are C_b and C_c
3,3,3-tet: C_1 and C_2 are C_b and C_e (although comparison with 2,3-tri and 2,3,2-tet suggests that C_1 is C_e and C_2 is C_b); C_3 is C_a; C_4 and C_5 are C_c and C_d

Scheme 3.

This approach indicates the assignments in Scheme 3. Consideration of the shifts of the fully protonated amines [Table 1(b)] and of the remaining data in Table 1(a) produces assignments with a similar degree of uncertainty.

(b) *Application of the Empirical Method of Sarneski* et al.[6]—A linear regression analysis of a large number of data on aqueous aliphatic monoamines led Sarneski *et al.* to propose two two-term empirical equations which express, respectively, the chemical shift δ_C of each carbon in an unprotonated amine in terms of δ^{alk}, and the change in chemical shift experienced when the amino group is protonated, the ' protonation shift ' Δ_C. Values of δ^{alk}, the shift of the corresponding C atom in the hydrocarbon obtained by replacing the N atom by CH, may be taken from the literature or calculated by means of an eleven-parameter empirical equation due to Lindeman and Adams.[13] Although these empirical equations for calculating δ_C and Δ_C relate to the monoamines, Sarneski *et al.* suggest how they can be modified for diamines.

We have used this approach to calculate δ_C in the unproton-

Table 2. Preliminary assignments based on calculated [11] ^{13}C shifts (δ_C) and protonation shifts (Δ_C) (in p.p.m.)

2,3-tri					
	C_1/C_1'	C_2/C_3'	C_3/C_2'	C_4/C_4'	C_5/C_5'
δ_C/Δ_C (meas.)	32.8/−8.0	39.9/−2.2	41.1/−4.4	47.4/−1.9	52.0/−5.7
δ_C/Δ_C (calc.)	30.3/−8.6	[41.1/−2.3]	[42.6/−4.3]	[48.5/−3.1]	[50.8/−6.1]
	C_d	[C_e]	[C_a]	[C_c]	[C_b]
trien					
	C_1/C_1'	C_2/C_2'	C_3/C_3'		
δ_C/Δ_C (meas.)	41.0/−4.5	48.8/−4.3	51.9/−6.0		
δ_C/Δ_C (calc.)	41.7/−4.3	[48.7/−4.2]	[50.7/−6.1]		
	C_a	[C_c]	[C_b]		
2,3,2-tet					
	C_1/C_1'	C_2/C_2'	C_3/C_3'	C_4/C_4'	
δ_C/Δ_C (meas.)	29.7/−5.9	41.0/−4.4	47.7/−2.2	51.9/−5.8	
δ_C/Δ_C (calc.)	26.7/−6.4	41.7/−4.3	[46.8/−2.2]	[49.1/−6.1]	
	C_d	C_a	[C_c]	[C_b]	
3,3,3-tet					
	C_1/C_1'	C_2/C_2'	C_3/C_3'	C_4/C_4'	C_5/C_5'
δ_C/Δ_C (meas.)	29.7/−6.0	32.9/−8.0	39.9/−2.0	47.4/−1.5	47.9/−2.0
δ_C/Δ_C (calc.)	[26.7/−6.4]	[28.5/−8.3]	39.9/−2.3	[45.5/−2.2]	[47.2/−3.1]
	[C_e]	[C_b]	C_a	[C_d]	[C_c]

ated form and Δ_C for each carbon atom in 2,3-tri, trien, 2,3,2-tet, and 3,3,3-tet. In the case of Δ_C, we have assumed that each C is influenced only by the two amino groups nearest to it; in other words, we have treated each polyamine as a diamine with movable N atoms. The results of these calculations, which were based on the parameter values of Sarneski *et al.*[6] and Lindeman and Adams,[13] are shown in Table 2, together with the measured values. Square brackets have been used to indicate the uncertain assignments identified in section (a) above and in some cases the agreement between measured and calculated values is sufficiently good to remove the ambiguity. For example, there is little doubt that the two high-shift peaks in the spectrum of trien (δ 48.8 and 51.9) are due, respectively, to C_c and C_b (calc. δ 48.7 and 50.7). Moreover, it is probable that the two peaks in the low-pH form (C_2' δ 44.5, C_3' 45.9) correspond to C_c and C_b also, giving protonation shifts of −4.3 and −6.0 p.p.m. (*cf.* calculated values of −4.2 and −6.1 p.p.m.). In particular, it is unlikely that there is a single 'crossover' between the two peaks during the titration since taking C_2 with C_3' and C_3 with C_2' would give calculated values for Δ_C of −2.9 and −7.4 p.p.m. In fact, the only pair of peaks for which the calculations suggest that there is a single 'crossover' during the titration is C_2/C_3 and C_2'/C_3' for 2,3-tri.

(c) *Development of Empirical Two-term Relationship using 'Amine-shift Parameters' π and π⁺*.—Whilst the agreement between calculated and observed values of δ_C and Δ_C in Table 2 is fair, the internal self-consistency between the measured shifts of analogous C atoms is significantly better. This encouraged us to reanalyse the data on the assumption that each ^{13}C shift is determined principally by the types of the two nearest amino groups and their distance along the chain. For example, C_a in trien is α to a primary amino-group and β to a secondary, and may therefore be designated $\alpha_1\beta_2$; C_b is α to a secondary and β to a primary amino-group ($\alpha_2\beta_1$); and C_c is α to one secondary amino-group and β to another ($\alpha_2\beta_2$). Grouping the shifts and assuming that the two amino groups influencing each C atom act independently (and therefore additively), we have evaluated empirical individual 'amine shift parameters' which we have designated π and π⁺; these are listed in Table 3.

In Table 1 are listed the differences between the observed chemical shifts ($\delta_C{}^m$) and the values calculated from the π and π⁺ parameters ($\delta_C{}^x$) for all the compounds studied, together with our final assignments. With the exception of the protonated form of $\alpha_2\beta_1$ (C_b in 2,3-tri, trien, and 2,3,2-tet), where the calculated value is consistently lower than that measured, these differences are very small.

Discussion

The general approach to the problem of 'predicting' the ^{13}C shifts of polysubstituted alkanes, typified by the method of Sarneski *et al.*,[6] is to start with the shift of the relevant C atom in the corresponding unsubstituted hydrocarbon and to add contributions from each group using empirical relationships derived from a study of monosubstituted compounds. Since the substitution effects are rapidly attenuated as the distance from the group increases, only groups which are α, β, γ, or δ to the carbon in question are generally considered to influence the shift. In some cases it is necessary to add cross-terms which reflect the interactions between the substituent groups. In the polyamines under discussion, each amino group is separated from its neighbour(s) by at least two methylene groups and therefore it is reasonable to assume that the only amino groups to influence the shielding experienced by each C atom are the two nearest to it. Thus, the actual shift δ_C can be considered to comprise three components [Figure, (a)]: an 'initial' value (δ^{alk}) associated with the corresponding unsubstituted hydrocarbon, and two increments (AB + BC) which represent the effects of the two nearest amino groups. For the fully protonated form of the amine both AB and BC are modified, but not δ^{alk}.

The approach we have taken is to express the shift δ_C as the sum of two terms [Figure, (b)], the first π_1 (or $\pi_1{}^+$ if the N atom is protonated) associated with one of the two nearest amino groups and the second (π_2 or $\pi_2{}^+$) with the other. This is tantamount to treating each C atom as a disubstituted methane CH_2XY and, it is therefore not altogether surprising

Table 3. Individual ^{13}C ' amine shift ' parameters for unprotonated (π) and protonated (π^+) amino groups (in p.p.m.)

		Primary		Secondary		Tertiary	
α-Position	π	26.1 (11) *	α_1	34.0 (12)	α_2	39.4 (1)	α_3
	π^+	24.5 (6) *		32.3 (8)			
β-Position	π	18.0 (11)	β_1	14.9 (12)	β_2	12.8 (1)	β_3
	π^+	13.0 (6)		11.9 (8)			
γ-Position	π	13.4 (4)	γ_1	13.8 (5)	γ_2		
	π^+	13.2 (2)		13.2 (4)			

* The numbers in parentheses represent the numbers of resonances used to derive the value of π or π^+. The estimated errors are generally ± 0.1 p.p.m. (but see text).

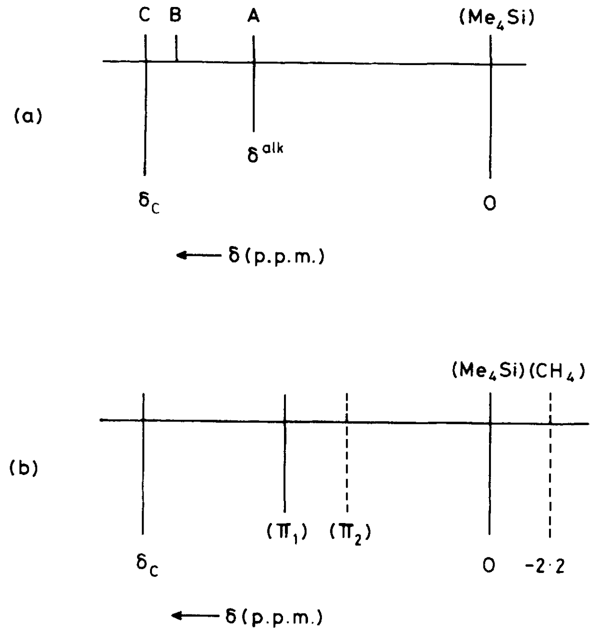


Figure. ^{13}C Shifts for the polyamines (see text for further explanation)

that the effects are found to be additive. Lauterbur noted [14] at an early stage that the effects of successive substitution of H by the halogens and other groups in CH_4 and other simple molecules are approximately additive, and this result has been confirmed (see, for example, ref. 15). Again, it is sometimes necessary [16] to involve cross-terms; in fact, the need for such a term may well be the reason for the comparatively poor agreement between δ_C^m and δ_C^x for the $\alpha_2\beta_1$ carbons (C_b for 2,3-tri, trien, and 2,3,2-tet) seen in Table 1(b).

It is not possible to compare directly the application of the two approaches to the polyamines since the one involves the parent hydrocarbon, and this varies along the series. We have already seen that our π and π^+ parameters are consistent with those derived by Sarneski *et al.*;[6] there is a similar degree of consistency between the π values and the empirical parameters of Eggert and Djerassi, which are based [17] on a rather larger sample of monoamines. (The latter authors did not consider protonation shifts.) It is interesting to compare the π and π^+ values for the primary and secondary amino-groups (Table 3) since the latter are related to one another rather like the alcohols are to the ethers. As pointed out by Stothers,[11] the α-carbon resonance for a typical ether is shifted by +9.5 p.p.m. and that for a β-carbon by −1.7 p.p.m. with respect to the signals from the parent alcohol, and both changes are approximately those to be expected for replacement of a hydrogen by a carbon along the alkyl chain. Similar changes in shift are found here, namely, +7.9 and +7.8 p.p.m. for the α-carbon, and −3.1 and −1.1 p.p.m. for the β. Not surprisingly, the changes in the γ-position (+0.4, 0.0 p.p.m.) are negligible.

It will be interesting to see how widely the amine shift parameters listed in Table 3 (and, more generally, the method of analysis based on CH_2XY) may be applied to polydentate ligands. The agreement between calculated and observed shifts for the bridging methylenes in $EtNH\cdot CH_2\cdot CH_2\cdot NH_2$ (calc. 52.0, 41.0; obs.[6] 52.4, 41.7 p.p.m.), $EtNH\cdot CH_2\cdot CH_2\cdot NHEt$ (calc. 48.9; obs.[6] 49.1 p.p.m.), $Et_2N\cdot CH_2\cdot CH_2\cdot NH_2$ (calc. 57.4, 38.9; obs.[6] 56.0, 39.5 p.p.m.), and $[CH_2\cdot N(CH_2CO_2^-)_2]_2$ (edta^{4-}: calc. 52.2; obs.[18] 52.8 p.p.m.) is encouraging, as it is for both non-equivalent C atoms in the fully protonated form of dien (calc. 45.3, 36.4; obs.[19] 45.9, 36.8 p.p.m.). Recently, Brubaker and Johnson have reported [5] the spectra of 3,3′-ethylenedi-iminobis(propylamine) (3,2,3-tet) and *N*-(2-aminoethyl)-*N*′-(3-aminopropyl)ethylenediamine (2,2,3-tet), and there is reasonable agreement between the observed resonances and those calculated from our π parameters: for 3,2,3-tet, calc. 32.9, 39.9, 47.4, 48.9; obs. 33.8, 40.0, 47.3, 49.3 p.p.m.; and for 2,2,3-tet calc. 32.9, 39.9, 41.0, 47.4, 48.9, 48.9, 52.0; obs. 32.1, 38.7, 40.0, 45.8, 47.5, 47.9, 51.1 p.p.m. The case of 2,2,3-tet does, however, illustrate the need for empirical relationships of the type developed here. Comparison with other spectra leads the authors to ascribe the resonances at δ 47.9 and 51.1 to C_b and C_e, respectively ($NH_2\cdot CH_2\cdot C_bH_2\cdot NH\cdot C_eH_2\cdot CH_2\cdot NH[CH_2]_3NH_2$); on our analysis the assignment is reversed.

Acknowledgements

We are grateful to I.C.I. for a Research Fellowship (for M. E. M.) and to the S.R.C. for a studentship (for S. P. D.).

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Received 18*th August* 1983; *Paper* 3/1464