Protonation Sequence of Linear Aliphatic Polyamines by ^{13}C NMR Spectroscopy

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The ^{13}C NMR spectra are reported as a function of pH for 4,7-diazadecane-1,10-diamine, 4,8-diazaundecane-1,11-diamine and 3,6,9-triazaundecane-1,11-diamine. The previously reported amine shift parameters π and π^+ are used to determine the protonation sites in the partially protonated intermediate forms of these and a further five polyamines whose ^{13}C–pH profiles have been published. The use of this simple method for determining protonation sequences is examined critically.

The protonation sequences of polybasic acids in solution are difficult to determine unless the intermediates can be characterised by some physical technique as, for example, with some aminopolycarboxylates.[1] The linear aliphatic polyamines $H_2N[CH_2]_kNH[CH_2]_l(NH[CH_2]_m)_nNH_2$ (where k–m = 2–4 and n = 0–3) are particularly difficult to analyse because the basicities of the N atoms in the component fragments $NH_x[CH_2]_zNH_y$ (where x, y = 1 or 2 and z = 2–4) can be very similar and the different parts of the molecules are so alike. These compounds are of considerable interest in coordination chemistry and some of the higher homologues have important physiological roles.

NMR spectroscopy provides the most promising approach to the problem since ^1H, ^{13}C and ^{15}N chemical shifts are all sensitive to the extent of protonation of the individual sites. The most direct of these, ^{15}N NMR spectroscopy, has been used[2] with thermospermine (k = l = 3; m = 4; n = 1) but the need for isotopic enrichment or very high sample concentration is likely to limit its further application. Of the other two, proton NMR spectroscopy should in principle be the more useful since the effect of protonation on ^1H chemical shifts falls off rapidly with distance while with ^{13}C chemical shifts it can extend to atoms as many as five centres distant,[3] though not monotonically. Unfortunately, the behaviour of the various α-methylene protons is so similar that the individual movements can only be resolved by ^1H–^{13}C two-dimensional correlation NMR spectroscopy.[4]

We recently found[5] that the ^{13}C chemical shifts of linear aliphatic polyamines can be analysed by means of a two-term empirical relationship employing 'amine shift parameters' π and π^+. The observed chemical shift δ is the sum of contributions associated with the two nearest amino groups, $[(\pi_1 \text{ or } \pi_1^+) + (\pi_2 \text{ or } \pi_2^+)]$, whose magnitudes depend on the type (primary or secondary) and distance along the chain from the C-atom in question. One series of parameters (π) has been determined[5] for the unprotonated polyamines and another (π^+) for the fully-protonated forms.

In another paper,[6] we explored the use of these amine shift parameters to determine the protonation sequences of the triamine *N*-(2-aminoethyl)propane-1,3-diamine [aepn; 2,3-tri] and the tetramines triethylenetetramine [trien] and 3,7-diazanonane-1,9-diamine [dadn; 2,3,2-tet]. The approach was to express the observed chemical shift for each C-atom and at various pH values in terms of the degrees of protonation f_i, f_j of the nearest N atoms (N_i, N_j) and the π,π^+ data. The simultaneous equations in f_i, f_j (*etc.*) generated in this way were solved by an iterative least-squares procedure to give numerical values of the charge-state (f_i, f_j *etc.*) of each N atom in the molecule (N_i, N_j *etc.*). The protonation sequences determined by this method agreed well with those predicted by application of Clark and Perrin's empirical method[7] for calculating the strengths of organic bases.

In the present paper we report the titrations of the ^{13}C NMR spectra of 4,7-diazadecane-1,10-diamine [dadd; 3,2,3-tet], 4,8-diazaundecane-1,11-diamine [daud; 3,3,3-tet] and 3,6,9-triazaundecane-1,11-diamine [tetraethylenepentamine; tetren], and the use of the π,π^+ parameters to determine the sites of protonation in the analytical intermediates HL, H_2L, *etc.* (For simplicity, the charges on ions are omitted and the predominantly deuteriated forms are referred to as protonated and represented by HL, H_2L, *etc.*) The analysis is based on the same assumptions as used previously[6] but differs in methodology. The observed chemical shift changes with added acid are generated empirically using standard equations linking individual chemical shifts and concentrations, and pK_a values. The δ_i values for C atoms in the individual partially-protonated intermediates are then analysed in terms of the π,π^+ parameters, as are the data from the previously-published ^{13}C chemical shift titrations of diethylenetriamine [dien],[8] dipropylenetriamine [dpt],[9] aepn,[9] trien[10] and dadn.[11] We consider the results critically in order to assess the possible wider use of the method for determining protonation sequences.

Experimental

4,7-Diazadecane-1,10-diamine (Fluka; b.p. 103–107 °C 0.03 Torr*) and 4,8-diazaundecane-1,11-diamine (Eastman; b.p. 105 °C 0.05 Torr) were purified by distillation. 3,6,9-Triazaundecane-1,11-diamine (tetren) was isolated from the commercially available amine (Aldrich) as the nitrate; the regenerated amine[12] was purified by distillation (130–135 °C 0.05 Torr). The purity of the amines was monitored by ^{13}C NMR in conjunction with analytical GLC. 1,4-Dioxane (Fisons A.R.) was used without further purification. Solutions (0.2 mol dm^{-3}) were made up in D_2O as described previously;[5,13] the pD was calculated using the empirical[14] relationship pD = (meter reading) +0.40. The pD adjustments were made with concentrated HNO_3 and/or a saturated solution of NaOH in D_2O, except that in the case of tetren conc. $HClO_4$ was used in place of HNO_3 at low pD. The use of $HClO_4$ was necessitated by the precipitation of $[tetren(HNO_3)_5]$ at pD < 5 but, since NMR spectra recorded at 5 < pD < 7 using HNO_3 for the pD adjustment were not consistent with those obtained using $HClO_4$, the changeover was made at pD 7.

The NMR spectra were recorded[5,13] at 21 ± 1 °C with a

* 1 Torr ≈ 133 Pa.

JEOL FD-100 instrument, using air-conditioning and compressed air to achieve thermostatting. Chemical shifts were measured relative to internal 1,4-dioxane (δ 67.71) and are quoted on the δ scale; they are estimated to be reliable to ± 0.04 p.p.m. The spectral lines were consistently sharp and of the expected relative intensities.

Results

The N-atoms and non-equivalent C-atoms in the polyamines are identified as in Scheme 1. The measured chemical shifts, δ,

dien $NH_2.CH_2.CH_2.NH.CH_2.CH_2.NH_2$
a b
1 * * 2 3

aepn $NH_2.CH_2.CH_2.NH.CH_2.CH_2.CH_2.NH_2$
a b c d e
1 * * 2 * 3

dpt $NH_2.CH_2.CH_2.CH_2.NH.CH_2.CH_2.CH_2.NH_2$
a b c
1 * 2 3

trien $NH_2.CH_2.CH_2.NH.CH_2.CH_2.NH.CH_2.CH_2.NH_2$
a b c
1 * * 2 * 3 4

dadn $NH_2.CH_2.CH_2.NH.CH_2.CH_2.CH_2.NH.CH_2.CH_2.NH_2$
a b c d
1 * * 2 * 3 4

dadd $NH_2.CH_2.CH_2.CH_2.NH.CH_2.CH_2.NH.CH_2.CH_2.CH_2.NH_2$
a b c d
1 * 2 * 3 4

daud $NH_2.CH_2.CH_2.CH_2.NH.CH_2.CH_2.CH_2.NH.CH_2.CH_2.CH_2.NH_2$
a b c d e
1 * 2 * 3 4

tetren $NH_2.CH_2.CH_2.NH.CH_2.CH_2.NH.CH_2.CH_2.NH.CH_2.CH_2.NH_2$
a b c d
1 * * 2 * * 3 4 5

Scheme 1

of the C-atoms in dadd, daud and tetren at different pD are represented by the points in Fig. 1. The assignments[15] were made as described in ref. 5 and the titration curves were computed by the method described previously,[8,13] using the pK_a values (pK_D^c) and individual chemical shifts listed in Table 1.

The agreement between the derived pK_D^c values for dadd and daud (Table 1) and those predicted[13] on the basis of the literature values in H_2O (pK_H^c) and the application of a uniform deuterium isotope effect(ΔpK) of 0.63 is good (predicted values for dadd[16,17] are 11.24, 10.51, 9.07 and 6.36; and for daud[18] 11.24, 10.61, 9.32 and 7.98). With tetren the agreement is less good but this is not surprising in view of the variation between the literature values[19] of pK_H^c. (It might be noted that Cl^-, ClO_4^- and NO_3^- were all used as counterions in the literature reports—*cf.* Experimental section).

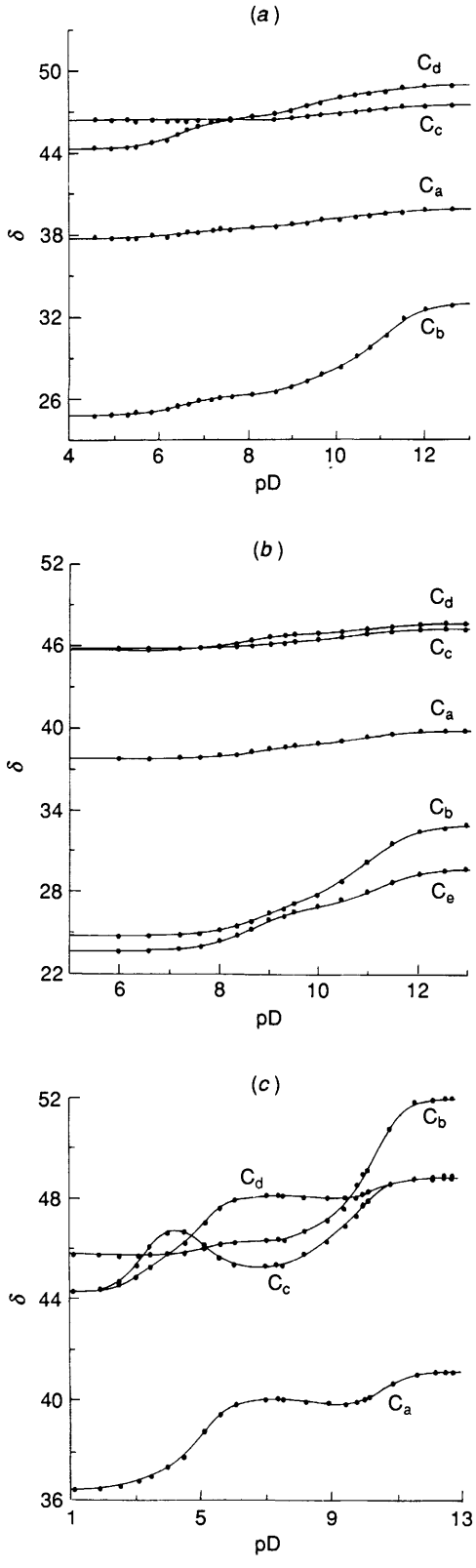

Fig. 1 ^{13}C NMR chemical shifts (δ) as a function of pD: (*a*) dadd (4,7-diazadecane-1,10-diamine); (*b*) daud (4,8-diazaundecane-1,11-diamine); (*c*) tetren (3,6,9-triazaundecane-1,11-diamine)

Analysis.—The ^{13}C chemical shifts for the starred atoms in the analytical species H_nL (n = 0–5) formed during the pD titration of the eight polyamines listed in Scheme 1 are given by horizontal lines in Fig. 2. The hollow circles represent the values δ_{calc} evaluated[5] by eqn. (1) for the intermediate microstates in

$$\delta_{calc} = \pi_i (\text{or } \pi_i^+) + \pi_j (\text{or } \pi_j^+) \quad (1)$$

Table 1 'Best' ^{13}C chemical shift (ppm) and pK_a values (pK_D[c]) for dadd, daud and tetren

Amine		δ(L)	δ(HL)	$\delta(H_2L)$	$\delta(H_3L)$	$\delta(H_4L)$	$\delta(H_5L)$	pK_D[c]
dadd[a]	C_a	39.83	39.40	39.20	38.45	37.70		11.30, 10.62, 9.35, 6.49
	C_b	33.00	29.90	28.20	26.25	24.72		
	C_c	47.41	47.05	46.80	46.30	46.35		
	C_d	48.85	48.25	48.10	46.50	44.20		
daud[a]	C_a	39.90	39.35	38.95	38.45	37.77		11.35, 10.60, 9.30, 8.40
	C_b	32.95	30.10	27.60	26.10	24.75		
	C_c	47.40	47.00	46.50	46.10	45.85		
	C_d	47.82	47.36	47.00	46.90	45.73		
	C_e	29.75	27.65	27.00	25.90	23.63		
tetren[a]	C_a	41.09	39.95	39.70	40.07	37.32	36.45	10.65,[b] 9.90,[b] 8.50,[b] 5.10,[c] 3.28[c]
	C_b	51.92	49.30	47.30	46.30	45.73	45.75	
	C_c	48.78	48.30	46.60	45.20	47.25	44.25	
	C_d	48.80	48.20	47.90	48.11	45.85	44.25	

[a] The 'best' values were determined from 24 (dadd, tetren) or 17 (daud) sets of data points. The standard deviations of the experimental chemical shifts from the values calculated on the basis of the parameters listed are as follows: dadd—C_a 0.059, C_b 0.079, C_c 0.026 and C_d 0.062; daud—C_a 0.029, C_b 0.060, C_c 0.023, C_d 0.034 and C_e 0.071; tetren—C_a 0.040, C_b 0.111, C_c 0.070 and C_d 0.038. The estimated errors in δ are ±0.1 ppm (dadd, daud) or ±0.2 ppm (tetren) and in pK_D[c], ±0.1. T = 21 ± 1 °C; I various. [b] HNO_3 used to adjust the pD. [c] $HClO_4$ used to adjust the pD.

Table 2 Individual ^{13}C 'amine shift' parameters for selected amino groups (in ppm)[a]

	α-Position	β-Position
NH_2	26.1	18.0
NH_3^+	24.5	13.0
NH	34.0	14.9
NH_2^+	32.3	11.9

[a] Data are from ref. 5. The estimated errors are generally ±0.1 ppm.

which protonation has occurred at the nitrogen(s) N_i, N_j identified by the number(s) alongside. The values π_i, π_i^+, π_j, π_j^+ are determined by the types of the two amino groups nearest to the C-atom in question and by their distance from it along the chain (Table 2).

The solid circles in Fig. 2 represent the 'best' values of δ_{calc}, which may be either: (i) the value appropriate to a single microstate; or (ii) the average value for a combination of microstates. Case (i) applies to the unprotonated and fully protonated species; it also includes some of the partially-protonated intermediates, identified by reference to Fig. 3. Case (ii) applies where it is evident that no single microstate is appropriate, when the value of δ_{calc} is the average of those for the microstates identified in Fig. 3, weighted as indicated there. (It is clear from the appearance of the spectra that, as expected, proton exchange is rapid in all cases.) Preliminary inspection of Fig. 2 shows that the central atom in a partially-protonated fragment $N[CH_2]_3N$ often has a significantly lower chemical shift than expected. These cases are identified by 'X' in Fig. 2 and these cross-terms (*i.e.* terms involving both N atoms in a segment) are discussed further below.

Consider as an example the monoprotonated form HL of aepn. The observed chemical shifts[9] for C_a and C_b (39.7 and 49.9 ppm, respectively) agree well with the values predicted on the assumption that the single proton spends its time equally on each of the three N atoms (δ_{calc} for protonation at N_1, N_2 and N_3 = 39.4, 38.0, 41.0 and 47.0, 50.3, 52.0, respectively, which average at 39.5 and 49.8) but they are not consistent with either of these three microstates alone. However, the value of δ_{calc} for C_d determined on the same basis (30.2 from 32.9, 29.9 and 27.9) is significantly higher than the observed value (27.9) and a cross-term must be subtracted. C_c and C_e are not considered since they have no β-amino group and therefore only modest protonation shifts [$\delta(L) - \delta(H_3L)$ = 1.15 and 2.15 ppm, respectively].

Discussion

To assess the potential value of our method for determining the protonation sequence of a linear polyamine (which in principle can be extended to other polybasic organic molecules), it is necessary to answer the following questions. (i) How good is the agreement between observed and 'predicted' chemical shift? (ii) How well can we discriminate between different possible microstates for a given analytical intermediate? (iii) How well do the present results (shown in Fig. 3) agree with others in the literature? We shall consider each of these in turn.

Quality of Fit.—It is convenient to divide the 58 data sets for partially protonated species (Fig. 2) into four groups.

(*a*) By far the largest group of 37 resonances, for which the calculated value is within 0.4 ppm of the measured value and the average discrepancy is $\pm 0.2_0$ ppm. These figures compare with 0.5 and $\pm 0.1_2$ ppm, respectively, for the 40 resonances in the unprotonated and fully-protonated forms (Fig. 2). Bearing in mind that no attempt has been made to correct for varying ionic strength or solvent composition (amount of added H_2O) during the titration (*cf.* ref. 5), we consider that the level of agreement is good.

(*b*) The next largest group of 11 resonances indicated with 'X', for which the calculated value is on average 1.1 ppm higher than the measured. These are all associated with the central C atom in a partially-protonated $N[CH_2]_3N$ fragment, but a complicating factor is that not all C atoms of this type fall in this group. The five which do not are in dpt (H_2L), dadn (H_3L), dadd (H_2L and H_3L) and daud (C_b in H_3L).

Closer inspection of the 16 C_X resonances in partially-protonated N_i–CH_2–C_xH_2–CH_2–N_j fragments in the light of our conclusions on the states of protonation (Fig. 3) reveals an interesting feature. The 11 requiring the cross-term are all in fragments for which the combined charge on N_i and N_j is one or less, while for the five not needing a cross-term the combined charge is one or more. This is exemplified by the H_3L form of daud, where the terminal nitrogens N_1, N_4 are fully protonated but the inner nitrogens N_2, N_3 share a proton. The combined charge for C_b (N_1 + N_2) is therefore 1.5 but that for C_e (N_2 + N_3) is 1. [A possible origin of the cross-terms suggested by this result is steric compression at C_X (ref. 20) produced by partial hydrogen-bonding between the neighbouring N atoms, since it appears[21] that the geometry is favourable. We have no independent evidence for this, though.]

(*c*) The six C atoms in the H_2L form of dien and the H_3L form of tetren, for which the calculated value is about 0.7 ppm higher or lower than the measured value. The differences (δ –

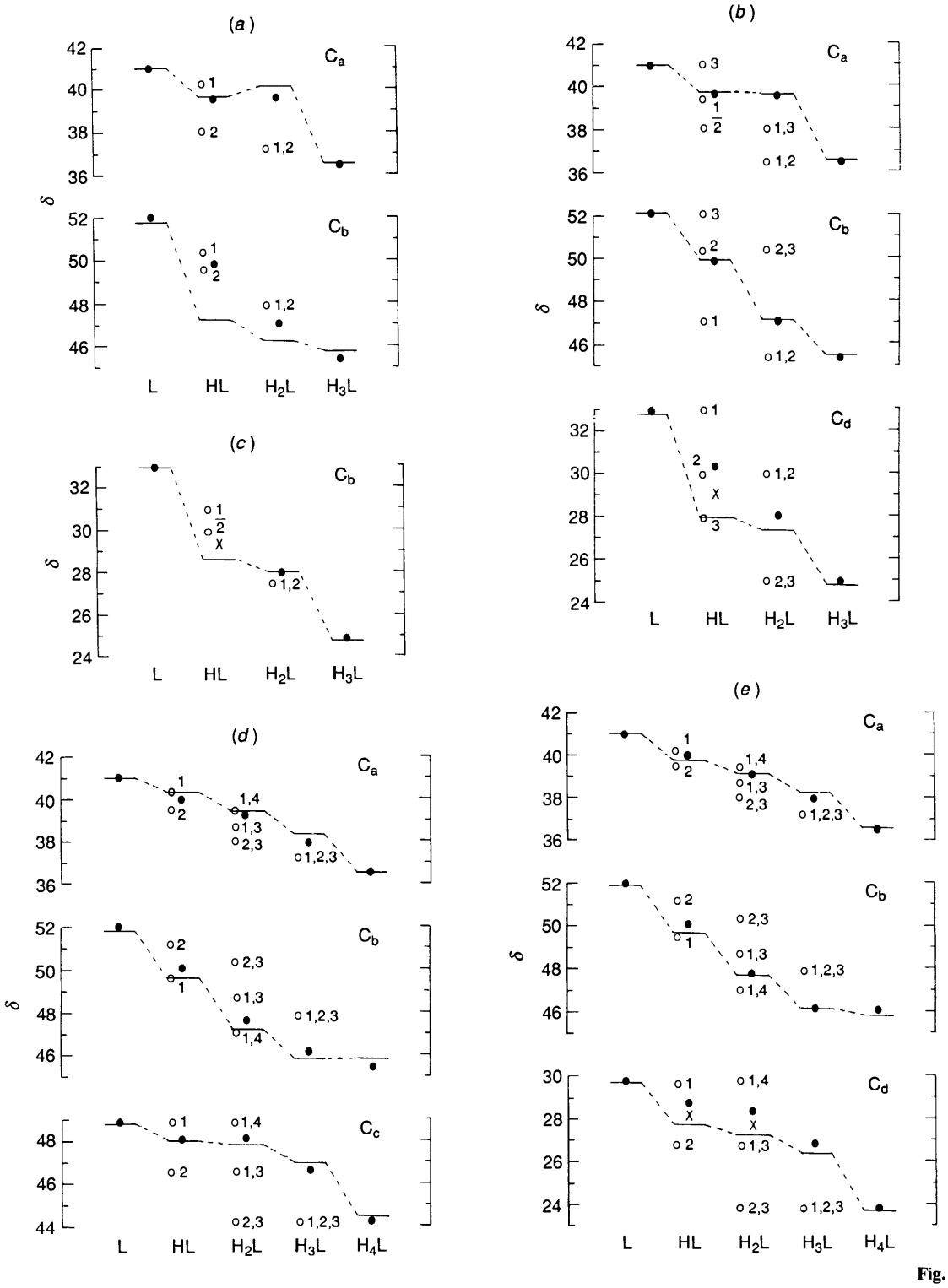

Fig. 2 (Contd.)

δ_{calc}) have similar patterns, being respectively +0.7 and −0.8 ppm for C_a, C_b in dien(H_2L), and +0.7, −0.7, −0.7, +0.9 ppm for C_a, C_b, C_c, C_d in tetren(H_3L). We offer no explanation for this but note that the highly-symmetrical structure tetren(H_3L) can be regarded as comprising two dien(H_2L) moieties placed end-to-end (Fig. 3). Interestingly, there is theoretical evidence[22] to suggest that both ions have unusually stable hydration structures.

(*d*) A residual group of four resonances, where the discrepancy between measured and calculated values is large. These are also in dien [C_b of HL (−2.6)] and tetren [C_b of HL (−0.8) and H_2L (−1.4), and C_a of H_4L (+0.9)] and again we offer no rationalisation.

Despite this last result, our conclusion is that on the whole the ^{13}C chemical shifts for the atoms marked with a star in Scheme 1 behave in a regular and predictable fashion.

Discrimination between Microstates.—The values of the C_a, C_b resonances in aepn(HL) were used above to explain our conclusion that the proton spends its time equally on the three N atoms in this analytical species. The C_d resonance confirms this if a cross-term is included. The H_2L form of aepn presents a similarly clear-cut picture [Fig. 2(*b*)]: (N_1,N_3) protonation is the only possibility for C_a, C_b and this is confirmed by the C_d resonance (again, if allowance is made for a cross-term).

Most of the resonances considered in this paper provide a

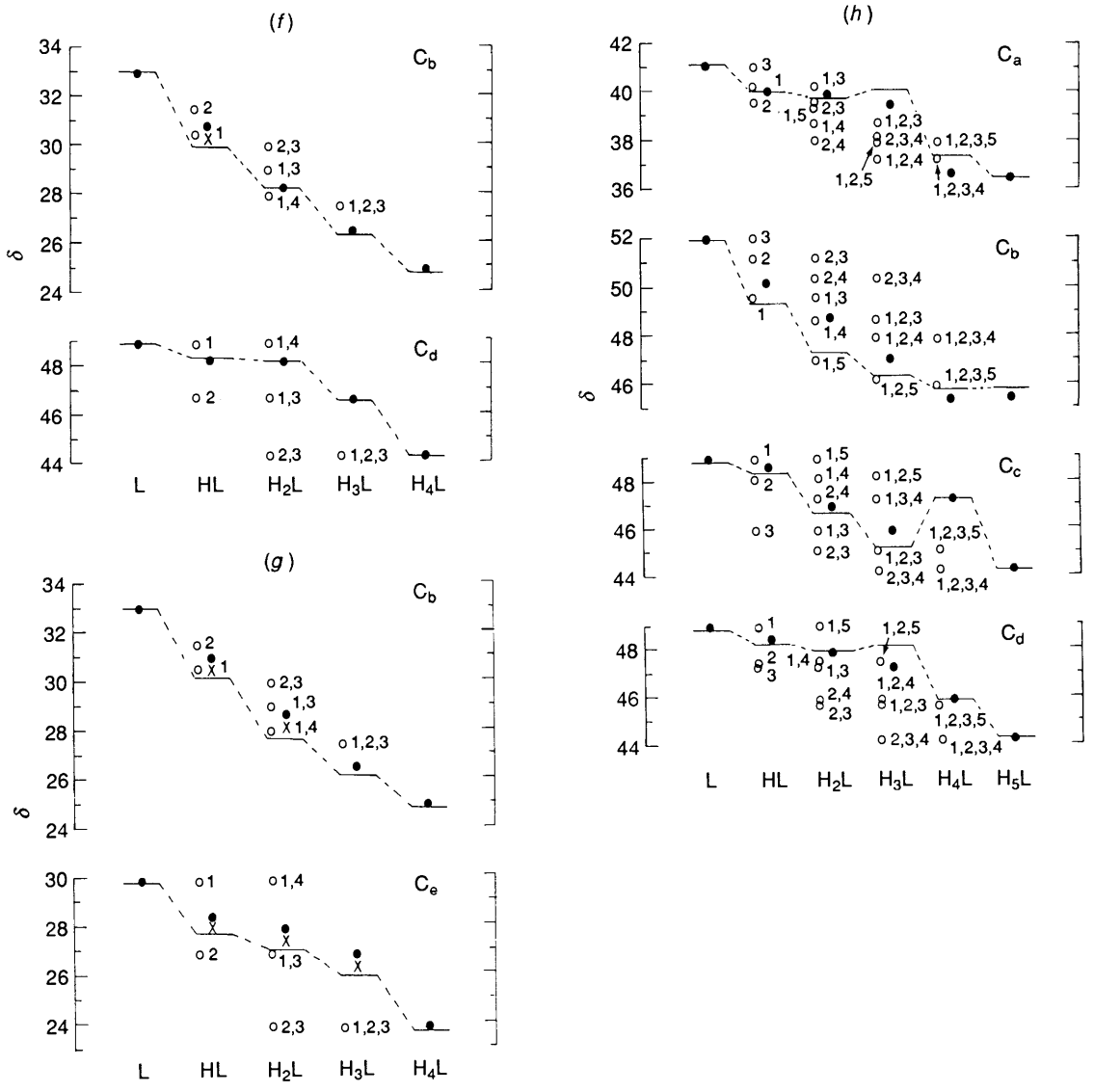

Fig. 2 Summary of ^{13}C chemical shifts (δ) for polyamines: (*a*) dien (diethylenetriamine); (*b*) aepn [*N*-(2-aminoethyl)propane-1,3-diamine]; (*c*) dpt (dipropylenetriamine); (*d*) trien (triethylenetetramine); (*e*) dadn (3,7-diazanonane-1,9-diamine); (*f*) dadd (3,7-diazadecane-1,10-diamine); (*g*) daud (4,8-diazaundecane-1,11-diamine); (*h*) tetren (3,6,9-triazaundecane-1,11-diamine)

similarly unequivocal choice between the possible microstates or their combinations but a few cannot. Dpt is unique among these polyamines in having only one usable C atom. The relationship between the observed and calculated δ values of this, coupled with uncertainty about the size of the cross-term, make it impossible to decide between N_1 and N_2 protonation in HL. (Although from the behaviour of the other triamines we would expect a 2:1 statistical mixture.) Other examples where a degree of uncertainty remains include dien(HL) (where C_b cannot be used) and dadn(H_2L), where there is little to choose in quality of fit between a 1:1 mixture of the (N_1,N_4) and (N_1,N_3) protonated forms and a 2:1 mixture of the same microstates.

[Strictly speaking, our analysis is also ambiguous in that, for the H_2L forms of the tetramines, it is impossible to distinguish between (N_1,N_3) and (N_1,N_2) protonation. However, knowledge[23] of the general behaviour of multiple charges together with our observation that (N_2,N_3) protonation does not occur in the tetramines nor (N_1,N_2) protonation in the triamines, leads us to discount the latter possibility.]

Comparison with the Literature.—Until recently, the evidence about successive protonation sites in linear aliphatic polyamines has come entirely from thermodynamic measurements. In their 1964 review[7] and following an analysis of the existing literature, Clark and Perrin proposed an empirical formulation which can be used to estimate the pK_a value of each individual site during protonation.

Although an isolated secondary amino group is more basic than an isolated NH_2, the presence of the other groups in L leads to the prediction that, in the monoprotonated forms of all the compounds shown in Scheme 1 except tetren, the proton is shared by all the nitrogens. Support for such tautomerism in HL has been obtained (initially for dien[24] but subsequently for all the other polyamines except aepn[16,17,25-28]) from measurements of $\Delta H°$ and $\Delta S°$. More recently, Delfini *et al.* have argued[12] on the basis of ^{13}C and ^{1}H NMR evidence that initial protonation of dien, aepn, dpt and two higher homologues occurs only at the primary amino groups. Our own ^{13}C NMR results (Fig. 3) fully support the earlier proposal for a tautomeric equilibrium involving both primary and secondary N atoms.

Prue and Schwarzenbach proposed[23,29] that the electrostatic repulsion between the two charges in H_2L would result in their moving as far from one another as possible, to the ends of the molecule. Enthalpy and entropy measurements support this for the triamines[24,26] but for the tetramines there have been conflicting interpretations[16,17,25,27,28] of the data (which are

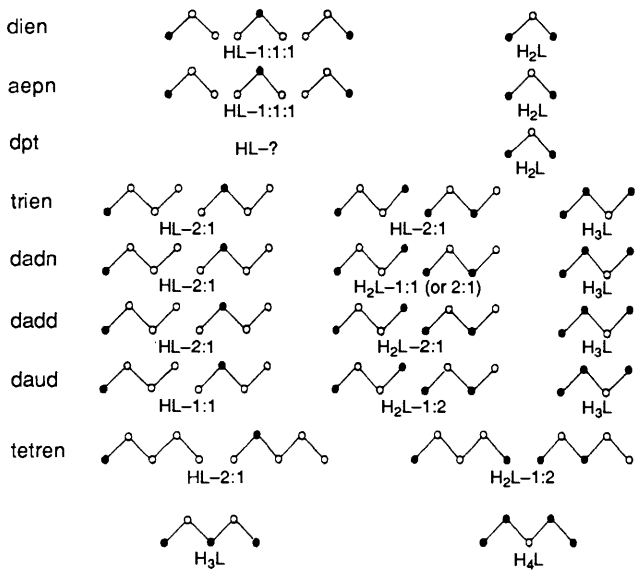

Fig. 3 Schematic representation of the principal micro-states formed during the protonation of linear polyamines: (○) unprotonated amino group; (●) protonated amino group

not, in fact, linked to the identities of the molecules). The alternative interpretation to (N_1,N_4) protonation is of a tautomeric mixture of (N_1,N_3) and (N_1,N_4) protonated forms, which was initially proposed by Hedwig and Powell[17] and is in line with the Clark–Perrin analysis. Our ^{13}C NMR results confirm the predominance of (N_1,N_3) protonation for the triamines and provide evidence for the existence of the proposed tautomeric mixtures in the tetramines.

Triprotonation of the tetramines can in principle occur at positions N_1, N_2, N_3 or at positions N_1, N_2, N_4. The thermodynamic data and Clark–Perrin analyses unequivocally favour the latter arrangement and our own results are in full agreement.

The thermodynamic results for tetren indicate[30] only that the first proton divides its time between primary and secondary amine groups and that the primary nitrogens tend to be favoured as the second and third protons are added. The Clark–Perrin analysis is in broad agreement but also suggests that there will be little or no protonation of N_3 in HL; that H_2L will involve principally (N_1,N_4) and (N_1,N_5) protonation; that H_3L will involve protonation at N_1, N_3 and N_5 only; and that H_4L will comprise a mixture of (N_1,N_2,N_3,N_5) and (N_1,N_2,N_4,N_5) protonated forms. Our own conclusions (Fig. 3) are in line with the thermodynamic interpretation and the first and third indications of the Clark–Perrin analysis but only partly with the other two. Thus we find that in H_2L the protons are at N_1 and N_3 rather than N_1 and N_4 (in addition to N_1 and N_5), and that H_4L involves protonation at N_1, N_2, N_4 and N_5 only. The unusual maximum in the pD plot of the C_c chemical shift in moderately strong acid [Fig. 1(*c*)] is a clear indication that N_3 (β to C_c) is protonated in H_3L and H_5L but not in H_4L. The relatively large discrepancies between the observed and calculated values of δ for several of the resonances (mentioned above) suggest, however, that there are still some aspects of the ^{13}C NMR behaviour of tetren to be resolved.

Conclusions.—The method described here for locating protons by an analysis of the terms used in the computer-generated pD profiles of ^{13}C chemical shifts appears promising. The quality of fit between observed and 'predicted' values, and the degree of discrimination between possible tautomers are both generally high, while the results obtained for 21 partially-protonated linear polyamines accord well with current knowledge. The method represents a considerable improvement on our previous method[6] in being simpler to use and providing a more reliable fit with the experimental data, especially where cross-terms are involved. It provides similar information in a somewhat more transparent form to that reported for some higher homologues using two-dimensional ^1H–^{13}C correlation[4] and ^{15}N (ref. 2) NMR spectroscopy. It also appears to have potential use with other organic molecules containing multiple acid/base functionalities, once the necessary individual 'shift parameters' have been determined.

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References

1 K. Nakamoto, Y. Morimoto and A. E. Martell, *J. Am. Chem. Soc.*, 1963, **85**, 309.
2 Y. Takeda, K. Samejima, K. Nagano, M. Watanabe, H. Sugeta and Y. Kyogoku, *Eur. J. Biochem.*, 1983, **130**, 383.
3 D. L. Rabenstein and T. L. Sayer, *J. Magn. Reson.*, 1976, **24**, 27.
4 F. Onasch, D. Aikens, S. Bunce, H. Schwartz, D. Nairn and C. Hurwitz, *Biophys. Chem.*, 184, **19**, 245.
5 S. P. Dagnall, D. N. Hague and M. E. McAdam, *J. Chem. Soc., Perkin Trans. 2*, 1984, 435.
6 S. P. Dagnall, D. N. Hague and M. E. McAdam, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1111.
7 J. Clark and D. D. Perrin, *Quart. Rev.*, 1964, **18**, 295.
8 D. N. Hague and A. D. Moreton, *J. Chem. Soc., Dalton Trans.*, 1987, 2889.
9 S. P. Dagnall, D. N. Hague and A. D. Moreton, *J. Chem. Soc., Dalton Trans.*, 1988, 1989.
10 S. P. Dagnall, D. N. Hague, M. E. McAdam and A. D. Moreton, *J. Chem. Soc., Dalton Trans.*, 1985, 2381.
11 S. P. Dagnall, D. N. Hague and A. D. Moreton, *J. Chem. Soc., Dalton Trans.*, 1987, 2897.
12 M. Delfini, A. L. Segre, F. Conti, R. Barbucci, V. Barone and P. Ferrute, *J. Chem. Soc., Perkin Trans. 2*, 1980, 900.
13 S. P. Dagnall, D. N. Hague, M. E. McAdam and A. D. Moreton, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 1483.
14 R. G. Bates, *Determination of* pH, *Theory and Practice*, Wiley, New York, 1964.
15 D. N. Hague and A. D. Moreton, *J. Chem. Soc., Dalton Trans.*, 1989, 1171.
16 R. Barbucci, L. Fabbrizzi, P. Paoletti and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1973, 1763.
17 G. R. Hedwig and H. K. J. Powell, *J. Chem. Soc., Dalton Trans.*, 1973, 793.
18 P. Teyssié, G. Anderegg and G. Schwarzenbach, *Bull. Soc. Chim. Belg.*, 1962, **71**, 177.
19 L. G. Sillén and A. E. Martell, *Stability Constants of Metal-Ion Complexes*, Chem. Soc., London, 1964; suppl. 1, 1971.
20 D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.*, 1972, **94**, 5318.
21 *cf.* M. Micheloni, A. Sabatini and P. Paoletti, *J. Chem. Soc., Perkin Trans. 2*, 1978, 828.
22 R. Barbucci and V. Barone, *J. Solution Chem.*, 1979, **8**, 427.
23 G. Schwarzenbach, *Pure Appl. Chem.*, 1970, **24**, 307.
24 M. Ciampolini and P. Paoletti, *J. Phys. Chem.*, 1961, **65**, 1224.
25 R. Barbucci, L. Fabbrizzi and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, 1972, 745.
26 P. Paoletti, F. Nuzzi and A. Vacca, *J. Chem. Soc. A*, 1966, 1385.
27 P. Paoletti, M. Ciampolini and A. Vacca, *J. Phys. Chem.*, 1963, **67**, 1065.
28 L. Fabbrizzi, R. Barbucci and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, 1972, 1529.
29 J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, 1950, **33**, 985.
30 P. Paoletti and A. Vacca, *J. Chem. Soc.*, 1964, 5051.

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