

## Correlation of x-ray photoelectron spectroscopic core level binding energies with melting point for a series of diamine dihydrochlorides

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MS received 10 April 1985

**Abstract.** X-ray photoelectron spectroscopic (XPS) and differential thermal analysis (DTA) studies of a series of diamine dihydrochlorides have shown that a linear relationship exists between the N(1s) and Cl(2p<sub>3/2</sub>) binding energy shifts and the melting points of these salts. A theoretical model is presented to verify this empirical correlation. It is apparent that such binding energy shifts and melting points are also dependent upon intrinsic electronic and bonding features of these salts such as quaternary nitrogen substituent inductive effects, charge delocalisation within the cation, cation-anion interaction and salt hydration.

**Keywords.** Diamine dihydrochloride; x-ray photoelectron spectrum; differential thermal analysis; melting point; inductive effect; hydration effect.

### 1. Introduction

With the development of x-ray photoelectron spectroscopy (XPS), there have been many applications of this technique to the study of the nitrogen environment in a wide variety of nitrogen compounds. Notable publications in this field have been by Baker and Betteridge (1972), Bakke *et al* (1980), Barber and Clark (1970), Basch and Snyder (1969), Davis *et al* (1970), Fahlman *et al* (1966), Finn *et al* (1971), Hedman *et al* (1969), Hendrickson *et al* (1969), Hollander *et al* (1968), Hollander and Jolly (1970), Jack and Hercules (1971), Jolly and Hendrickson (1970), Nordberg *et al* (1968) and Siegbahn *et al* (1969). A significant aspect of these various studies has been an investigation of correlations of core electron binding energies with: calculated atomic charges, thermodynamic data based on the approximation that the energy of core electron capture by a nucleus is independent of chemical environment, empirical parameters characteristic of directly bonded groups and molecular-orbital-calculated binding energies.

The data of Finn *et al* (1971) and Jack and Hercules (1971) are most relevant to the present study. Finn *et al* (1971) have investigated correlations of empirical N(1s) binding energy shifts for gaseous ammonia, methylamine, dimethylamine and trimethylamine, (i) with nitrogen atomic charges as calculated by the Pauling and CNDO methods, (ii) with thermodynamically estimated N(1s) binding energy shifts and (iii) with N(1s) binding energy shifts derived by the empirical parameter method. Apart from these correlations, a further significant feature of their study is that the N(1s)

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binding energies for these compounds, relative to dinitrogen, decrease as the hydrogen atoms of ammonia are successively replaced by methyl groups, which reflects the progressively increasing inductive effect of these substituents. Jack and Hercules (1971) have reported N(1s) binding energy data for a series of tetra-alkylammonium salts  $R_4N^+X^-$ ; R = alkyl or aryl, X = halide. N(1s) binding energies for these quaternary nitrogen compounds were found to be dependent on the nature and size of the R-substituents and on the nature of the halide counter-ion. For salts involving the same R-groups but different  $X^-$  anions, a direct correlation exists between the N(1s) binding energy and the electronegativity of X (Jolly 1970, Pauling 1960).

The present study involves the determination of N(1s) and Cl(2p) binding energy shifts for a series of diamine dihydrochlorides and an investigation of a correlation of these shifts with the melting point of these salts.

A melting point broadly represents the temperature at which a crystal lattice converts to a less-ordered or disordered liquid lattice and for a series of structurally related compounds, the variation in melting point reflects the variation in lattice energy within the series. The lattice energy of these diamine dihydrochlorides is primarily determined by the strength of the intrinsic ionic bonding which is in turn dependent on the quaternary nitrogen atomic charge and the degree of interaction of the cation and chloride. The net quaternary nitrogen atomic charge is essentially determined by the nature and number of attached R-substituents and the length of the relevant alkyl chain. R-group steric effects complicate this direct dependency. The net anionic charge depends also on the net quaternary nitrogen atomic charge by virtue of cation-anion interaction. Hence the core level binding energies  $E_b^f(N\ 1s)$ ,  $E_b^f(Cl\ 2p)$  and melting point are all related to the magnitude of net atomic charges existing in these compounds. A thermodynamic model is presented to quantify these correlations.

## 2. Experimental

The diamine dihydrochlorides studied are abbreviated as:

- |  |                           |
|--|---------------------------|
| 1. ethylenediamine dihydrochloride                 | (en)2HCl                  |
| 2. N,N'-dimethylethylenediamine dihydrochloride    | (Me <sub>2</sub> en)2HCl  |
| 3. N,N'-diethylethylenediamine dihydrochloride     | (Et <sub>2</sub> en)2HCl  |
| 4. N,N'-diphenylethylenediamine dihydrochloride    | ( $\phi_2$ en)2HCl        |
| 5. 1,3-diaminopropane dihydrochloride              | (DAP)2HCl                 |
| 6. 1,3-diacetyl-1,3-diaminopropane dihydrochloride | (Ac <sub>2</sub> DAP)2HCl |
| 7. 1,4-diaminobutane dihydrochloride               | (DAB)2HCl                 |
| 8. o-phenylenediamine dihydrochloride              | (o-Ph)2HCl                |

These salts were prepared according to a procedure previously reported for ethylenediamine dihydrochloride by Roe *et al* (1982) and are characterised by their infrared spectra (table 1) and DTA thermograms (table 2). Infrared spectra in the range 4000–250  $cm^{-1}$  were obtained on a Perkin-Elmer 457 spectrophotometer, using the KBr disc method with band calibration relative to polystyrene. DTA thermograms were obtained on a Rigaku-Denki, Type 8085 Thermal Analysis System, using platinum sample pans, a 10 mg sample mass, a heating rate of 10°C  $min^{-1}$  and an atmosphere of static air. Alumina was used as the thermally inert reference.

xps spectra were recorded on a spectrometer previously described by Kemeny *et al*





Table 2. Differential thermal analysis (DTA) data for some diamine dihydrochlorides.

Diamine dihydrochloride	Dehydration endotherm (°C)	Melting endotherm $T_m$ (°C)	Decomposition endotherms (°C)
(en) 2HCl	143 b	339 sh	348 sh, 351 sh, 360 sh, 371 sh
(Me <sub>2</sub> en)2HCl		246 sh	306 b, 322 sh, 327 sh, 334 sh, 340 sh
(Et <sub>2</sub> en)2HCl		276 sh	340 sh
( $\phi_2$ en)2HCl	72 b	153 sh	200 b
(DAP)2HCl		259 sh	318 sh, 327 sh, 337 sh, 340 sh, 351 sh
(Ac <sub>2</sub> -DAP)2HCl		252 sh	453 b
(DAB)2HCl	114 b	313 sh	361 sh
(o-Ph)2HCl		214 sh	233 sh, 277 sh

b = broad; sh = sharp.

(1973) using AlK $\alpha$  photons of 1486.6 eV energy and at  $10^{-6}$ – $10^{-7}$  hPa (torr). All samples were dried in a desiccator over P<sub>2</sub>O<sub>5</sub> then pressed onto double-sided adhesive tape and mounted on a double-sided copper sample holder. The metal Cu2p<sub>3/2</sub> electron binding energy (932.5 eV) (Barr 1978) served as the calibrant level for all core level binding energies relative to the spectrometer Fermi Level. Tests for surface charging effects of these non-conducting samples were carried out by varying the intensity of the incident x-rays. No binding energy corrections were found necessary. Measured binding energies of spectral features were also measured to  $\pm 0.3$  eV (Liesegang *et al* 1984).

### 3. Results and discussion

Detailed infrared data for the diamine dihydrochlorides are presented in table 1 and assignments are relative to those for ethylenediamine dihydrochloride. The presence of a C–N<sup>+</sup>H<sub>3</sub> stretching vibration at 2044 cm<sup>-1</sup> as reported by Waldron (1953) is not confirmed by Powell (1960) or by the present study. For all salts, the C–H and N–H stretching bands are generally broad and are associated with submaxima. Powell (1960) has attributed these features to strong intermolecular hydrogen-bonding between the quaternary ammonium cations. The infrared spectra summarised in table 1 essentially characterise the diamine dihydrochlorides studied.

DTA data for these diamine dihydrochlorides are given in table 2. In general, for each salt, a melting endotherm and a series of decomposition endotherms are exhibited; (en)2HCl, (DAB)2HCl and ( $\phi_2$ en)2HCl additionally exhibit single dehydration endotherms. The thermal stability of these salts is reflected by the temperature corresponding to the first decomposition endotherm; and thus for the series, the lower and upper limits of thermal stability correspond to ( $\phi_2$ en)2HCl and (Ac<sub>2</sub>-DAP)2HCl respectively. Increase of the alkyl chain length between the quaternary nitrogen atoms or change of R-groups attached to these atoms produces no systematic variation in temperatures corresponding to the decomposition endotherms; and thus there is no obvious correlation of the thermal stability of these salts with chemical structure.

xps data for these diamine dihydrochlorides are given in table 3. Two general features of these xps data are apparent. Shoulders are associated with the main N 1s peaks for

Table 3.  $E_b^F$  (N 1s) and  $E_b^F$  (Cl 2p) data ( $\pm 0.3$  eV) for some diamine dihydrochlorides.

Diamine Dihydrochloride	$E_b^F$ (N 1s) (eV)	$E_b^F$ (Cl 2p) (eV)	$\Delta E_b^F$ (N 1s) (eV) <sup>a</sup>	$\Delta E_b^F$ (Cl 2p) (eV) <sup>b</sup>
(en)2HCl	397.3	193.0	-9.6	-14.8
	s 396.2	213.7	-10.7	+5.9
(Me <sub>2</sub> en)2HCl	397.4	192.6	-9.5	-15.2
	s 396.2	213.4	-10.7	+5.6
(Et <sub>2</sub> en)2HCl	397.1	193.0	-9.8	-14.8
		211.3		+3.5
( $\phi_2$ en)2HCl	398.3	191.7	-8.6	-16.1
		212.3		+4.5
(DAP)2HCl	397.6	193.2	-9.3	-14.6
		212.1		+4.3
(Ac <sub>2</sub> -DAP)2HCl	397.9	192.6	-9.0	-15.2
		212.1		+4.3
(DAB)2HCl	397.2	192.0	-9.7	-15.8
	s 395.9	215.1	-11.0	+7.3
( <i>o</i> -Ph)2HCl	396.2	193.1		-14.7
		212.8	-10.7	+5.0

<sup>a</sup>relative to  $E_b^F$  (N 1s) in KNO<sub>3</sub> = 406.9 eV (Jack and Hercules 1971); <sup>b</sup>relative to  $E_b^F$  (Cl 2p) in Cl<sub>2</sub> = 207.8 eV (Bakke *et al* 1980); s = shoulder.

(en)2HCl, (DAB)2HCl and (Me<sub>2</sub>en)2HCl at  $E_b^F = 396.2, 395.9$  and  $396.2$  eV respectively. Nordberg *et al* (1968) have reported that under xps conditions, ammonium salts decompose to yield hydrogen chloride. Therefore it is assumed here that (en)2HCl, (DAB)2HCl and (Me<sub>2</sub>en)2HCl partially decompose to yield the corresponding free amine and HCl, the former being responsible for the N(1s) shoulders in the xps spectra of these salts. Further, all salts exhibit a broad set of secondary Cl 2p peaks, separated from the main Cl 2p peak by about 20 eV. These structures are assigned to a range of electron energy loss processes of a type described for example by Battye *et al* (1976).

The electron withdrawing effect of phenyl is apparent from the relatively high  $E_b^F$  (N 1s) of ( $\phi_2$ en)2HCl compared to the corresponding  $E_b^F$  (N 1s) for (Me<sub>2</sub>en)2HCl and (Et<sub>2</sub>en)2HCl.

The relatively low  $E_b^F$  (N 1s) for (*o*-Ph)2HCl compared to that of (en)2HCl is a reflection of  $\pi$ -electron delocalisation in (*o*-Ph)2HCl which tends to increase the electron density on the quaternary nitrogen atoms and decrease  $E_b^F$  (N 1s),

Some correlations of xps data with melting points of these salts will now be presented. In general, the salts with R-substituents attached to the quaternary nitrogen atoms have lower melting points than the corresponding unsubstituted diamine dihydrochlorides. Thus for (DAP)2HCl and (Ac<sub>2</sub>-DAP)2HCl, the melting points are 259 and 252°C respectively and the -I inductive effect of acetyl is reflected in the xps data for (Ac<sub>2</sub>-DAP)2HCl relative to that for (DAP)2HCl. A similar relationship between melting point and xps data emerges for the compounds: (en)2HCl, (Me<sub>2</sub>en)2HCl, (Et<sub>2</sub>en)2HCl and ( $\phi_2$ en)2HCl.

Siegbahn *et al* (1969), Baker and Betteridge (1972), Wagner (1975) and Furlani (1982) have defined the xps binding energy shift of a core level electron of an atom (*m*) bound

to atoms ( $l$ ) in terms of the corresponding partial charges  $q_m, q_l$ , the bond length  $r_{lm}$  and an extra-atomic relaxation energy term  $R^{ea}$ :

$$\Delta E_b^f(m) = K_m q_m + \sum_{l \neq m} \frac{K_l q_l}{r_{lm}} - R^{ea} \quad (1)$$

where  $E_b^f(m)$  is relative to a free atom  $m$  and  $K_m, K_l$  are constants. The term  $\sum_{l \neq m} (K_l q_l / r_{lm})$  is the molecular potential term which according to Siegbahn *et al* (1969) and Fadley *et al* (1968) is analogous to the Madelung Potential for a solid. In the case of diamine dihydrochlorides,  $q_m$  is the charge on the quaternary nitrogen atoms,  $q_l$  is the charge on the chloride ions and  $r_{lm}$  is the internuclear distance between these ions. Equation (1) indicates that binding energy shifts are critically dependent on the parameters  $q_m, q_l$  and  $r_{lm}$  and hence, to correlate xps data for diamine dihydrochlorides with corresponding melting points, it is necessary to consider the thermodynamic properties of these salts in terms of the same parameters.

For diamine dihydrochlorides, the sequential phase changes shown in figure 1 may be assumed to occur on heating.

$\Delta H_{\text{fus}}$ ,  $\Delta H_{\text{vap}}$  and  $\Delta H_{\text{dec}}$  are the fusion, vaporisation and decomposition enthalpies of the salt respectively. Huheey (1978) has defined the molar lattice energy  $U$  of an ionic solid as:

$$U = \Delta H_{\text{fus}} + \Delta H_{\text{vap}} + U_{ip} + U_c, \quad (2)$$

where  $U_{ip}$  and  $U_c$  are the respective energies associated with ion-pair and cluster-ion formation in the gas phase.  $U_{ip}$  and  $U_c$  are essentially dependent upon the polarising power of the component ions and since diamine hydrochlorides are associated with large cations and a relatively large anion, both  $U_{ip}$  and  $U_c$  are small. Further, diamine dihydrochlorides decompose in the liquid phase prior to boiling and hence

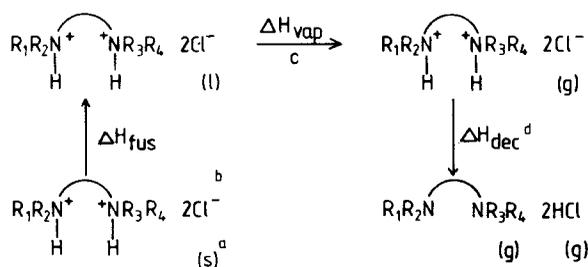
$$\Delta H_{\text{fus}} \gg |\Delta H_{\text{vap}} + U_{ip} + U_c| \quad (3)$$

or

$$U = c_1 \Delta H_{\text{fus}} \quad (4)$$

where  $c_1$  is a constant.  $\Delta H_{\text{fus}}$ , by Trouton's rule, is directly related to the melting point  $T_m$  and hence:

$$U = c_1 T_m \Delta S_{\text{fus}}. \quad (5)$$



**Figure 1.** Enthalpy Diagram for a diamine dihydrochloride: **a.** thermodynamic state: (s) solid, (l) liquid, (g) gas, **b.** general schematic structural formula for a diamine dihydrochlorides, **c.** assumes monomeric gaseous species, **d.** assumes complete decomposition.

$\Delta S_{\text{fus}}$ , the entropy of fusion, is dependent on the relative order associated with the solid and liquid phases and since the diamine dihydrochlorides studied have closely related chemical structures,  $\Delta S_{\text{fus}}$  is assumed to be constant for the series and hence:

$$U = c_2 T_m \quad (6)$$

with  $c_2$  constant.

$U$  is given by the Kapustinskii equation (Huheey 1978):

$$U = \frac{c_3 q_m q_l}{r_{lm}} \quad (7)$$

with  $c_3$  constant.

Combining (7) with (6) gives:

$$q_m = c_4 (r_{lm}/q_l) T_m \quad (8)$$

with  $c_4$  constant.

Combining (8) with (1) gives:

$$\Delta E_b^f(m) = c_5 (r_{lm}/q_l) T_m + \sum_{l \neq m} K_l q_l / r_{lm} - R^{ea} \quad (9)$$

with  $c_5$  constant.

(9) may be conveniently rewritten in the form:

$$\Delta E_b^f(m) = AT_m + B, \quad (10)$$

where

$$A = c_5 r_{lm} / q_l \quad (11)$$

and

$$B = \sum_{l \neq m} [K_l q_l / r_{lm}] - R^{ea} \quad (12)$$

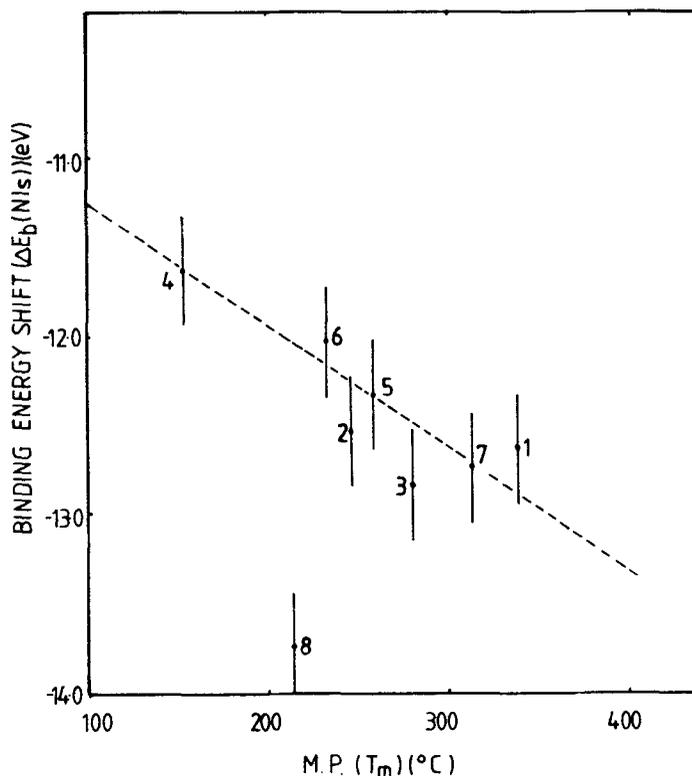
may be viewed as pseudo-constants.

It is apparent that if a linear relationship between  $\Delta E_b^f$  and  $T_m$  exists, then  $\Delta E_b^f$  is inherently more dependent on melting point than on all of the other variables in (9).

$\Delta E_b^f$  (N 1s) vs  $T_m$  and  $\Delta E_b^f$  (Cl 2p) vs  $T_m$  plots for the diamine dihydrochlorides studied are shown in figures 2 and 3 respectively. The respective negative and positive slopes are consistent with (9) since the slope sign is determined by the sign of  $q_l$ .

It is appropriate to comment on those diamine dihydrochlorides, the xps/ $T_m$  data for which correspond to deviation from the 'best-fit' lines of figures 2 and 3. If it is assumed that these deviations result primarily from 'abnormal'  $A$  and  $B$  values, then an explanation is possible based on operative inductive effects, although other factors such as abnormal fusion entropies may contribute. Inductive effects fundamentally define the magnitude of  $q_l$  and hence  $A$  and  $B$  and thus the discussion of deviations is confined to an assessment of these variables, duly recognising that the variations in  $R^{ea}$  are assumed to be small within the series of diamine dihydrochlorides studied and that the proposed theoretical model is approximate.

(*o*-Ph)<sub>2</sub>HCl is clearly the most abnormal and exhibits deviation in both cases. Charge delocalisation in the cation tends to decrease the positive charge on the quaternary nitrogen atoms and increase the negative charges  $q_l$ , thereby increasing the charge on chlorine (figure 2) or decreasing this charge in the context of figure 3. Steric hindrance between the two adjacent quaternary nitrogen groups tends to increase  $r_{lm}$ . If it is assumed that the variation in  $q_l$  is the predominating influence, then the overall effect



**Figure 2.** The variation of N 1s binding energy shift with  $T_m$  for diamine dihydrochlorides. 1. (en)2HCl 2. (Me<sub>2</sub>en)2HCl 3. (Et<sub>2</sub>en)2HCl 4. ( $\phi_2$ en)2HCl 5. (DAP)2HCl 6. (Ac<sub>2</sub>DAP)2HCl 7. (DAP)2HCl 8. (o-Ph)2HCl.

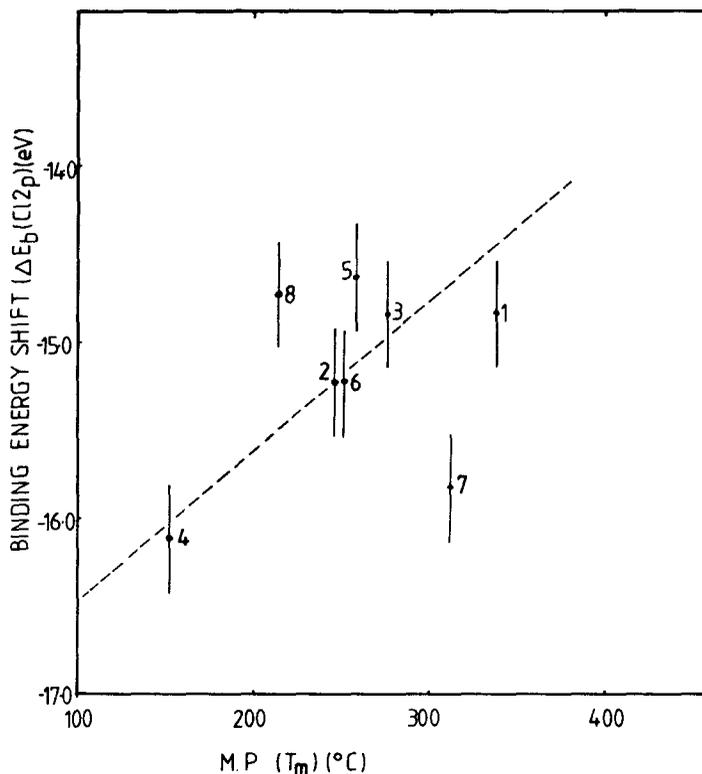
for (o-Ph)2HCl is a decreased  $A$  and  $B$  (figure 2) or conversely, an increased  $A$  and  $B$  (figure 3).

(Et<sub>2</sub>en)2HCl exhibits a lower  $A$  than (en)2HCl (figure 1). The +I inductive effect of ethyl tends to reduce the charge on the quaternary nitrogen atoms and thereby increases  $q_i$  and decreases  $r_{im}$ , resulting in a decrease in both  $A$  and  $B$ . However, within the limits of experimental error, (en)2HCl and (Me<sub>2</sub>en)2HCl are on the 'best fit' line (figure 2) which suggests that the inductive effect of R-group substituents is not the only influence on  $q_i$ .

The deviation of (en)2HCl, (DAP)2HCl and (DAB)2HCl (figure 3) may be a reflection of hydration of (en)2HCl and (DAB)2HCl relative to anhydrous (DAP)2HCl. Hydration tends to effect the environment of Cl<sup>-</sup> to a greater extent than that of quaternary nitrogen, and hence is more apparent in the  $E_b^F(Cl 2p)$  data than in the corresponding  $E_b^F(N 1s)$  data.

Apart from (o-Ph)2HCl, the deviations shown in figures 2 and 3 relate to different diamine dihydrochlorides which essentially reflect the differential influence of inductive and steric effects and hydration on the N and Cl environments in these compounds.

It is relevant to discuss the xps data presented in table 4. The compounds listed are



**Figure 3.** The variation of Cl2p binding energy shift with  $T_m$  for diamine dihydrochlorides. 1. (en)2HCl 2. (Me<sub>2</sub>en)2HCl 3. (Et<sub>2</sub>en)2HCl 4. ( $\phi_2$ en)2HCl 5. (DAP)2HCl 6. (Ac<sub>2</sub>DAP)2HCl 7. (DAB)2HCl 8. (*o*-Ph)2HCl.

either amines, amine salts or tetraalkyl ammonium salts and hence are structurally related to diamine dihydrochlorides. The xps data for these compounds are readily interpreted in terms of inductive effects. With respect to the primary amines  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ , increase of the alkyl chain length decreases the  $E_b^f(\text{N } 1s)$  in accordance with an increased alkyl group inductive effect. With reference to  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  and  $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}$ , replacement of one H atom on the former amine with a propyl group also decreases  $E_b^f(\text{N } 1s)$  as a consequence of an increased inductive effect of propyl versus hydrogen. With respect to the tetraalkyl ammonium halides,  $(\text{CH}_3)_4\text{NF}$ ,  $(\text{CH}_3)_4\text{NCl}$  and  $(\text{CH}_3)_4\text{NBr}$ , as the electron withdrawing effect of the halide decreases,  $E_b^f(\text{N } 1s)$  decreases. With reference to  $(\text{CH}_3)_4\text{NI}$ , the extraneous  $E_b^f(\text{N } 1s)$  peak at 402.30 eV is explained by Nordberg *et al* (1968) as due to decomposition of the salt to trimethylamine.

Formation of piperidine hydrochloride from piperidine increases  $E_b^f(\text{N } 1s)$  as a direct consequence of an increased positive charge on the ring nitrogen and the electron withdrawing inductive effect of chloride ion. With respect to  $(\text{CH}_3)_4\text{N}^+\text{Cl}^-$  and  $(\text{CH}_3)_4\text{N}^+\text{O}^-$ , the exchange of  $\text{Cl}^-$  by  $\text{O}^-$  has the effect of increasing  $E_b^f(\text{N } 1s)$  as a consequence of the increased  $-I$  effect of  $\text{O}^-$  compared to  $\text{Cl}^-$ .

Table 4. A summary of literature XPS data for selected nitrogen compounds.

Compound	$E_f^F$ (N 1s) ( $\pm 0.3$ eV)
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2^{\text{a}}$	398.1
 $\text{NH}^{\text{a}}$	397.8
 $\text{N}^+\text{H}_2\text{Cl}^{-\text{a}}$	400.4
$(\text{CH}_3\text{CH}_2)_3\text{N}^+\text{HCl}^{-\text{a}}$	400.4
$(\text{CH}_3)_4\text{N}^+\text{Cl}^{-\text{a}}$	401.5
$(\text{CH}_3)_4\text{N}^+\text{O}^{-\text{a}}$	402.2
$(\text{CH}_3\text{CH}_2)_4\text{N}^+\text{I}^{-\text{a}}$	397.1
	402.3
$(\text{CH}_3)_4\text{N}^+\text{F}^{-\text{b}}$	401.2
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2^{\text{c}}$	405.0
$(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}^{\text{c}}$	404.5
$(\text{CH}_3\text{CH}_2)_4\text{N}^+\text{ClO}_4^{-\text{d}}$	401.1
$(\text{CH}_3\text{CH}_2)_4\text{N}^+\text{ClO}_4^{-\text{d}}$	400.5
$(\text{CH}_3\text{CH}_2)_3\text{N}^+\text{HBr}^{-\text{d}}$	399.7
$(\text{CH}_3)_4\text{N}^+\text{Br}^{-\text{d}}$	400.7

<sup>a</sup>Nordberg *et al* (1968); <sup>b</sup>Baker and Betteridge (1972);  
<sup>c</sup>Bakke *et al* (1980); <sup>d</sup>Jack and Hercules (1971).

#### 4. Conclusion

N 1s and Cl 2p binding energies for a series of diamine dihydrochlorides have been interpreted in terms of the electronic environments of nitrogen and chlorine in these salts. The XPS data have also been correlated with the melting points of these salts and deviations from the empirical linear relationship have been explained in terms of structural features such as variable ionic character in the N-Cl bond of the salt, hydration effects and non-systematic inductive effects. XPS data for some related compounds as reported in the literature are also discussed in relation to similar data for diamine dihydrochlorides.

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