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X-Ray Photoelectron and Diffuse Reflectance Infrared Spectroscopic Studies of Hydrogen Bonding in Substituted Anilinium Chloride and Trichlorostannate (II) Derivatives

By

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It is reported how the N–H–Cl hydrogen bonding in anilinium chloride and trichlorostannate (II) derivatives is affected by methyl and methoxy substitutions in the phenyl ring of an aniline group. Such hydrogen bonding has been confirmed by close N–Cl contacts in an X-ray structure determination on 2-methylanilinium trichlorostannate (II). Crystals are orthorhombic: space group $P2_12_12_1$; $a = 0.7290(3)$ nm, $b = 1.9096(7)$ nm, $c = 0.8233(4)$ nm, $\alpha = \beta = \gamma = 90°$; $V = 1.1461(8)\ \text{nm}^3$, $Z = 4$. The degree of hydrogen bonding manifests itself in changes in the core electron binding energies of the N and Cl atoms as observed by X-ray photoelectron spectroscopy (XPS), and also by the characteristic shift in the N–H stretching frequency measured by diffuse reflectance infrared spectroscopy. Correlations are observed between changes in the anilinium ν(N–H) force constants and changes in the corresponding N(1s) and Cl(2p) binding energies. The varying degrees of hydrogen bonding depend on the positions and types of substituents on the aniline aromatic ring and correlate with their dissociation constants, pK_a; but, theoretical analysis of one of the methylaniline hydrochlorides shows that the position of the H atom in the hydrogen bond, N–H–Cl, is a significantly stronger influence on the fractional charge on nitrogen, suggesting that overall crystal structure may be the determining factor on N charge.

1. Introduction

In many predominantly ionic materials, hydrogen bonding is able to provide an additional stabilising effect for the crystal lattice, often with the weak interaction assisting in the provision of a specific directional character to a phase, especially at low temperature, leading to the ferroelectric effect (e.g., in ammonium sulfate at 223 K) [1].

The requirement for hydrogen bond formation is the simultaneous presence of an acidic hydrogen atom 'donor' moiety (A–H) and a basic 'acceptor' (B) giving rise to a charge distribution, often written as

$$A^- - H^+ - B^- .$$

Thus, atoms A and B must be strongly electronegative; and while the combinations A, B = oxygen or A = oxygen, B = nitrogen lead to quite strong hydrogen bonds, when A = nitrogen and B = chlorine, the effect is much weaker [2].

The hydrogen bond strength may be visualised as being dependent on the partial positive charge residing on the acidic hydrogen atom, which in turn is determined by the various

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Table 1
Substituted anilinium trichlorostannate (II) derivatives

sub-stituent**)	microanalysis (wt%)*)				MP (°C)
	C	H	N	Cl	
2-Me	25.17 (25.22)	3.09 (3.03)	4.10 (4.20)	31.94 (32.92)	168 to 170
3-Me	25.31 (25.22)	3.11 (3.03)	4.11 (4.20)	32.08 (32.92)	138 to 140
4-Me	25.34 (25.22)	3.18 (3.03)	4.15 (4.20)	32.91 (32.92)	107 to 108
2,3-Me	28.42 (27.67)	3.24 (3.48)	4.17 (4.03)	30.59 (30.63)	
2,4-Me	27.93 (27.67)	3.41 (3.41)	4.04 (4.03)	31.10 (30.63)	203 to 205
2,5-Me	27.46 (27.67)	3.41 (3.48)	3.88 (4.03)	31.55 (30.63)	159 to 161
2,6-Me	27.43 (27.67)	3.23 (3.48)	3.98 (4.03)	31.67 (30.63)	>210 dec.
3,5-Me	26.90 (27.67)	3.25 (3.48)	3.81 (4.03)	30.61 (30.63)	188 to 189
2-MeO	24.07 (24.07)	2.77 (2.89)	4.10 (4.01)	30.72 (30.46)	173 to 176
3-MeO	24.95 (24.07)	3.22 (2.89)	4.07 (4.01)	32.03 (30.46)	

*) Analyses performed by the Microanalytical Laboratory of the Department of Chemistry, University of Otago, Dunedin, New Zealand. Calculated values are in parentheses.
**) Me = CH_3 group; numbers represent the positions of substitution on the aniline aromatic ring.

electronic effects operating on the atoms adjacent to A. If A = nitrogen and the donor moiety is an organic base, the partial charge on hydrogen depends on whether the base is strong or weak, stronger bases neutralising a larger fraction of the charge than weaker ones. These relations have been put on a reasonably quantitative scale for interactions *in solution* by a large number of investigations leading to data compilations such as [3].

This paper investigates whether base character has any similar effect on *solid* materials with substituted anilinium cations being studied as their chloride and trichlorostannate (II) derivatives. Only a restricted range of $SnCl_3^-$ salts was available (Table 1), since not all aniline derivatives are able to form a salt having the anilinium $SnCl_3$ stoichiometry (including aniline itself, which forms a $SnCl_4^{2-}$ derivative). It was considered likely that any N–H–Cl hydrogen bonding in these compounds would be affected by the positions of methyl and methoxy substituents on the aromatic ring of the base.

2. Experimental Details

2.1 Syntheses

All reagents were obtained from the Aldrich Chemical Co., and used as supplied. The aniline derivatives employed are listed in Table 1. These were converted to their *hydrochloride salts* by reaction with concentrated hydrochloric acid in ice-cold ethanol [4]. The salts generally precipitated out under these conditions or crystallised on longer standing.

Tetraphenylborate salts were obtained by mixing aqueous solutions of the aniline hydrochloride and sodium tetraphenylborate (slight excess). In all cases, white precipitates were obtained which were filtered off, washed thoroughly with distilled water, and dried over concentrated sulfuric acid in a vacuum desiccator. Vigorous drying is required as these salts retain water quite well. They appear to be also somewhat light- or air-sensitive, slowly turning brown in air over several days.

Trichlorostannate salts normally were obtained by mixing solutions of the aniline hydrochloride and anhydrous $SnCl_2$ in warm (<50 °C) ethanol or concentrated hydrochloric acid and allowing the product to crystallise. The 4-methyl derivative is, however, very soluble and requires very concentrated solutions to be cooled in a refrigerator in order to induce crystallisation.

2.2 Spectroscopic measurements

X-ray photoelectron spectroscopy was performed with energy resolution of ≈ 1 eV on an instrument described previously [5] and using Al Kα (1486.6 eV) photons. Samples were in powder form on double-sided sticky tape on a double-sided copper metal sample holder ($10 \times 10 \times 2$ mm^3). Core level binding energies were measured for Sn(3d), N(1s), and Cl(2p) atoms in the samples, calibrated against Au(4f), Ag(3d), Cu(2p), and Ag(MNN) standard energy lines. The XPS charging shifts were corrected against the C(1s) C–H shift. The IR spectrometer used for this work was a Perkin Elmer model 1725X Fourier transform infrared spectrometer (FTIR) with the "Praying Mantis" diffuse reflectance attachment (DRA) produced by Harrick Scientific. Samples were prepared for infrared measurements by mixing approximately 10% sample, in finely ground spectroscopic grade KBr, and packed into a positioned DRA micro-cup (≈ 0.2 cm^3) so as to eliminate the possibility of "reststrahlung" interference from sample particle packing. Spectra were obtained in the wave number range of 4000 to 400 cm^{-1} at sample intervals of 4 cm^{-1} and a collection time corresponding to 40 full sweeps (approximately 1.5 min). The method minimises the possibility of ion exchange in infrared sampling. All the experiments were performed at room temperature.

2.3 Structure determination

Structure determinations for the complexes studied here are known for two of the hydrochlorides [6, 7], but for none of the chlorostannates. We have determined the crystal structure for 2-methylanilinium trichlorostannate (II) using a single crystal with dimensions $0.11 \times 0.58 \times 0.70$ mm^3, mounted on a thin glass fiber so that its longest dimension was nearly parallel to the axis of the Nicolet diffractometer. Data were collected at 20 ± 1 °C. Cell constants were derived from 15 reflections with $2\theta > 25°$ and the material was shown to crystallise in the orthorhombic space group $P2_12_1 - D_2^4$ (No. 19) (see Table 2). The data

Table 2

Summary of crystallographic data and processing parameters for 2-methylanilinium trichlorostannate (II)

space group	$P2_12_1$
a (nm)	0.7290(3)
b (nm)	1.9096(7)
c (nm)	0.8233(4)
α, β, γ	90.00°
V (nm^3)	1.1461(8)
molecular formula	$C_7H_{10}NCl_3Sn$
molecular weight	333.2
density (g/cm^3) (calc; $Z = 4$)	1.931
abs. coeff. (mm^{-1})	2.88
λ (nm) (Mo Kα)	0.071073
total No. of data collected	1523
final $R_1 = \sum \lVert F_0\rvert - \lvert F_c\rVert / \sum \lvert F_0\rvert$	0.042
final $R_2 = \{\sum w(\lvert F_0\rvert - \lvert F_c\rvert)^2 / \sum w \lvert F_0\rvert^2\}^{1/2}$	0.066

set was corrected for Lorentz and polarisation effects and numerical absorption corrections applied. The structure was solved from the Patterson map by using tin as the heavy atom. Refinements of positional and thermal parameters, followed by calculation of difference Fourier maps located the nonhydrogen atoms.

The amine and methyl groups (N, C_7, and their hydrogens) were refined as rigid rotors with sp^3-hybridised geometry and N–H and C–H bond length of 0.085 and 0.096 nm, respectively. The initial orientation of each group was determined from difference Fourier position for the hydrogen atoms. The final orientation of each group was determined by three rotational parameters. The refined positions for the rigid rotor groups gave C–N–H and C–C–H angles which ranged from 90° to 126°. The remaining hydrogen atoms were included in the structure factor calculations as idealised atoms (assuming sp^2-hybridisation of the carbon atoms and a C–H bond length of 0.096 nm) "riding" on their respective carbon atoms. The isotropic thermal parameter of each hydrogen atom was fixed at 1.2 times the equivalent isotropic thermal parameter of the nitrogen or carbon atom to which it is covalently bonded.

The top six peaks (840 to 520 e^-/nm^3) in the final difference Fourier map were within 0.13 nm of a Sn or Cl atom; there were no other peaks present above the background level (470 e^-/nm^3).

3. Results and Discussion

"Crystal engineering" seeks to define the rules governing the intermolecular forces which are responsible for the stability of a crystalline lattice and to gain an appreciation of the factors which control basically organic structures. Generally, it is the weak intermolecular interactions which are of considerable value in this endeavour [8, 9].

Aniline derivatives were chosen for this work because substitution around the aromatic ring produces compounds of varying basicity. In many cases, not only are hydrochloride salts well known, but anilinium ions are clearly able to stabilise chlorometallate salts. The trichlorostannate (II) anions were chosen originally because it was considered possible that the lone pair electrons on the tin atom could give rise to a defined direction of the crystal lattice. In the outcome, this proved not to be the case. In all, a series of ten substituted anilinium cations was obtained, which yielded both hydrochloride ($RNH_3^+Cl^-$) and trichlorostannate derivatives, the latter having a common stoichiometry: $RNH_3^+SnCl_3^-$. (Curiously, aniline itself yielded only a compound with the formula $(RNH_3)_2SnCl_4$, while other substituted derivatives failed to produce either stable hydrochloride or chlorostannate salts.)

The 2-methylaniline derivative easily produces large crystals of its $SnCl_3$ salt. Atomic coordinates are given in Table 3, while derived bond distances and angles are given in Table 4. Discrete anilinium and $SnCl_3^-$ ions are observed (Fig. 1). This is similar to the case of the cesium salt [10], although the Sn–Cl distances are slightly longer in the anilinium derivative (Table 4) than in either the cesium derivative or in the potassium double salt [11]. Both these structures were, however, determined from film data and had rather high *R* (reliability index) values.

Hydrogen-bonding interactions between the aminium group and the Cl_3 atom of the $SnCl_3$ group are evident in the structure (see Fig. 1), with the $N-Cl_3$ distance being 0.3307 nm (cf. the sum of N and Cl van der Waals radii of $\approx$0.345 nm), but the N–H–Cl angle is sharper (118°, Table 5) indicating that the whole NH_3^+ group may be involved in an asymmetrically bifurcated hydrogen bonding system.

Table 3

Atomic coordinates for other than hydrogen atoms in crystalline $[C_6H_4(CH_3)(NH_3)][SnCl_3]$*)

atom type**)	fractional coordinates 10^4x	10^4y	10^4z	equivalent isotropic thermal parameter B $^+$) ($10\,nm^2$)
Sn	2542(1)	130(1)	64(1)	0.32(1)
Cl_1	2564(5)	−992(1)	−1732(2)	0.49(1)
Cl_2	5073(4)	−466(2)	1747(3)	0.37(1)
Cl_3	− 48(4)	−477(2)	1580(3)	0.45(1)
N	−2336(1)	833(4)	3252(8)	0.33(2)
C_1	−2495(18)	1472(4)	2235(9)	0.37(2)
C_2	−2431(19)	2117(5)	2979(12)	0.46(2)
C_3	−2702(22)	2702(6)	1948(15)	0.72(4)
C_4	−2333(30)	2634(12)	288(19)	0.98(7)
C_5	−2112(18)	1986(9)	− 408(17)	0.70(5)
C_6	−2571(24)	1370(7)	577(12)	0.59(4)
C_7	−2158(14)	2197(7)	4788(12)	0.49(3)

*) The numbers in parentheses are the estimated standard deviations in the last significant digit.

**) Atoms are labeled in agreement with Fig. 1.

$^+$) This is one-third of the trace of the orthogonalised B_{ij} tensor.

One of the well-known manifestations of hydrogen bonding is that the A–H stretching mode of the donor broadens and moves to lower wave number in the infrared spectrum [2]. For the anilinium chloride and chlorostannate salts, the spectra indeed exhibit broad bands in the ν(N–H) region. In order to ascertain the shifts involved, the behavior of the N–H modes in a nonhydrogen bonded environment needed to be determined. For this, the tetraphenylborate (TPB) salts were synthesised. The spectra displayed the two relatively

Table 4

Bond lengths and angles for other than hydrogen atoms in crystalline $[C_6H_4(CH_3)(NH_3)][SnCl_3]$*)

type**)	length/angle	type**)	length/angle
$Sn-Cl_1$	0.2603(2) nm	$N-C_1$	0.148(1) nm
$Sn-Cl_2$	0.2573(3) nm		
$Sn-Cl_3$	0.2542(3) nm	C_2-C_7	0.151(1) nm
C_1-C_3	0.138(1) nm	C_3-C_4	0.140(2) nm
C_1-C_6	0.138(1) nm	C_4-C_5	0.137(3) nm
C_2-C_3	0.142(2) nm	C_5-C_6	0.147(2) nm
$Cl_1-Sn-Cl_2$	86.4(1)°	$C_1-C_2-C_7$	122.3(9)°
$Cl_1-Sn-Cl_3$	84.8(1)°	$C_3-C_2-C_7$	122.0(10)°
$Cl_2-Sn-Cl_3$	93.8(1)°	$C_2-C_3-C_4$	119.0(13)°
$N-C_1-C_2$	118.8(7)°	$C_3-C_4-C_5$	121.0(17)°
$N-C_1-C_6$	116.5(8)°	$C_4-C_5-C_6$	117.7(13)°
$C_2-C_1-C_6$	124.6(9)°	$C_1-C_6-C_5$	115.2(11)°
$C_1-C_2-C_3$	115.7(9)°		

*) The numbers in parentheses are the estimated standard deviations in the last significant digit.

**) Atoms are labeled in agreement with Fig. 1.

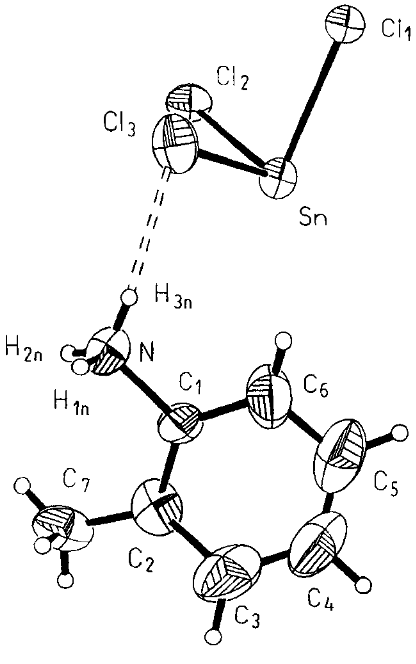

Fig. 1. Perspective drawing of the asymmetric unit for crystalline $[C_6H_4(CH_3)(NH_3)][SnCl_3]$ with nonhydrogen atoms represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density. Hydrogen atoms are represented by arbitrarily small spheres which are in no way representative of their true thermal motion. The single hydrogen-bonding interaction between ions of the asymmetric unit is represented by a dashed open bond

sharp (symmetric and asymmetric) modes expected for the C_{3v} local symmetry of the NH_3^+ group in the 3200 cm^{-1} region (Fig. 2). The force constants (K) for the ν(N–H) modes were calculated from these values via the method outlined by Linnett [12].

The N–H$^+$ bond strength is expected to be affected by the availability of the base lone pair which, in turn, is related to the influence of any substituent groups on the aromatic ring via separate inductive and resonance effects. The basicities in turn are reflected in their pK_a values, defined by the reaction

$$R{-}NH_{3(aq)}^+ + H_2O \rightleftharpoons R{-}NH_{2(aq)} + H_3O_{(aq)}^+ .$$

Thus, a correlation between decrease in the aniline pK_a and increase in the force constant for the ν(N–H) mode in the TPB salts is to be expected. That this is largely the case follows from Table 6 in which the data in columns 2 and 4 correlate with $R = -0.75$.

The contrast between the N–H stretching regions of the infrared spectra of the TPB and the chloride and chlorostannate salts is shown in Fig. 2. The clearly-defined N–H doublet in the TPB salts is replaced by very broad features which also dominate and obscure the C–H stretching region. The centers of these broad peaks are not easy to establish, but it

Table 5

Close contacts involving other than hydrogen atoms in crystalline $[C_6H_4(CH_3)(NH_3)][SnCl_3]$

donor unit (D)*)	acceptor atom (A)	distance D–A (nm)	distance H–A (nm)	angle D–H–A	angle H–D–A	angle H–A–Sn	asymmetric unit of A**)
N–H_{1n}	Cl_3	0.3407	0.278	132°	37°	88°	$-1/2-x, -y, 1/2+z$
N–H_{2n}	Cl_2	0.3390	0.260	156°	18°	89°	$1/2-x, -y, 1/2+z$
N–H_{3n}	Cl_3	0.3307	0.251	158°	17°	107°	x, y, z
N–H_{3n}	Cl_2	0.3356	0.287	118°	49°	113°	$-1+x, y, z$

*) The hydrogen atom involved in the interaction is also indicated.

**) All donor atoms belong to the asymmetric unit for which fractional atomic coordinates are given in Table 3.

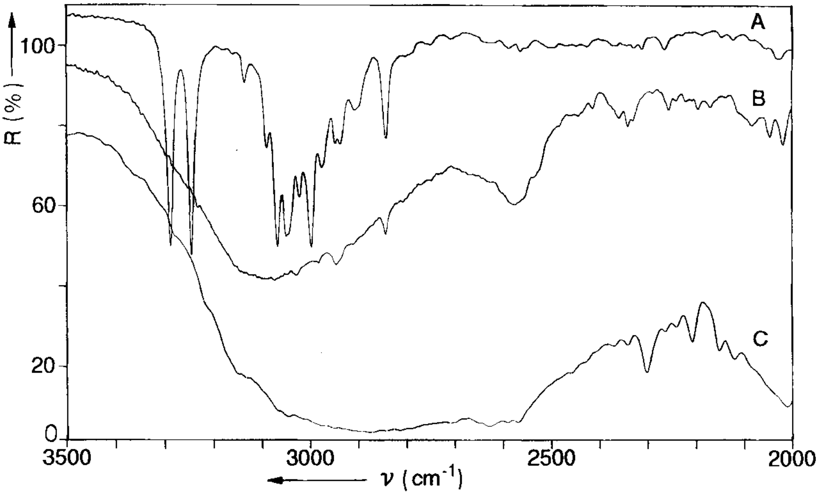

Fig. 2. Infrared spectra of 2-methoxyanilinium derivatives in the 3500 to 2000 cm^{-1} region; A tetraphenylborate, B trichlorostannate, C chloride

was again evident that the different compounds have their mean N–H stretching frequencies in different positions. The ability to expand this particular wave number region using the computer enhancement of the FTIR spectrometer permits these mean peak positions to be estimated with a confidence of $\approx 10\,\text{cm}^{-1}$ in the case of the $SnCl_3^-$ compounds. On the other hand, the extremely broad absorptions for the chloride salts lead to rather less confident estimation of their mean frequencies. Reasonable estimates are, nevertheless, possible in all cases. From these values, the changes in the N–H force constants between the TPB and the $SnCl_3$ or chloride salts may be calculated. That these force constant differences also correlate with the aniline pK_a values is shown in Fig. 3 (see also Table 6).

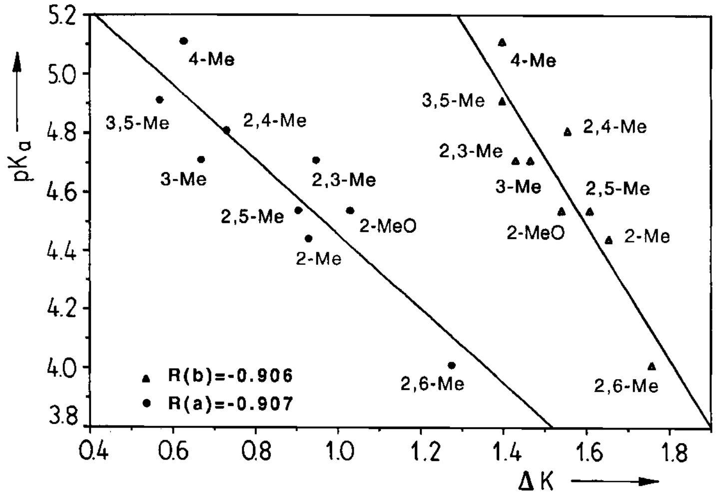

Fig. 3. Plots of dissociation constant (pK_a) vs. change in force constant (ΔK) between TPB and $SnCl_3^-$ derivatives (a) and Cl^- derivatives (b)

Table 6
N–H stretching mode frequencies (cm^{-1}) and force constants $K(10^2\ N/m)$

substituent	pK_a	TPB salt ν(N–H)*)	TPB salt K	$SnCl_3^-$ salt ν(N–H)	$SnCl_3^-$ salt K	Cl^- salt ν(N–H)	Cl^- salt K	ΔK [TPB – $SnCl_3^-$]	ΔK [TPB – Cl^-]
2-Me	4.44	3288.3	6.248	3034.0	5.319	2820.0	4.595	0.929	1.653
3-Me	4.71	3256.9	6.129	3074.0	5.460	2841.0	4.664	0.669	1.465
4-Me	5.11	3245.0	6.084	3073.0	5.459	2848.0	4.687	0.625	1.397
2,3-Me	4.71	3277.2	6.206	3017.0	5.259	2875.0	4.776	0.947	1.430
2,4-Me	4.81	3280.7	6.219	3082.0	5.491	2841.0	4.665	0.728	1.554
2,5-Me	4.54	3276.5	6.203	3029.0	5.301	2820.0	4.595	0.902	1.608
2,6-Me	4.01	3286.7	6.242	2932.0	4.967	2786.0	4.485	1.275	1.757
3,5-Me	4.91	3244.3	6.082	3089.0	5.513	2848.0	4.686	0.569	1.396
2-MeO	4.54	3267.0	6.167	2982.0	5.138	2830.0	4.628	1.029	1.539
3-MeO		3245.5	6.086	3026.0	5.291	2841.0	4.664	0.795	1.422

* Average value of symmetric and asymmetric modes.

Table 7

Core level XPS binding energies E_b (eV) in tetraphenylborate, trichlorostannate, and chloride derivatives

sub-stituent	$E_b\{N(1s)\}$ [TPB]	$E_b\{N(1s)\}$ [$SnCl_3^-$]	$E_b\{N(1s)\}$ [Cl^-]	$E_b\{Cl(2p)\}$ [$SnCl_3^-$]	$\Delta E_b\{N(1s)\}$ [TPB–$SnCl_3^-$]	$\Delta E_b\{N(1s)\}$ [TPB–Cl^-]
2-Me	400.86	402.56	401.48	198.09	−1.70	−0.62
3-Me	399.30	403.26	401.67	198.21	−3.96	−2.37
4-Me	398.01	403.65	402.78	198.96	−5.64	−4.77
2,3-Me	400.60	402.68	400.80	197.98	−2.08	−0.20
2,4-Me	400.02	402.69	400.67	198.08	−2.67	−0.65
2,5-Me	400.56	401.99	401.53	197.46	−1.43	−0.97
2,6-Me	403.69	402.21	400.98	197.81	+1.48	+2.71
3,5-Me	397.75	402.62	401.59	198.40	−4.87	−3.84
2-MeO	401.27	402.22	400.71	197.60	−0.95	+0.56
3-MeO	399.67	402.83	400.91	198.27	−3.16	−1.24

It may be seen that since substituents affect the reactivity of the anilinium cation, it may be expected that the hydrogen bonded moiety will mirror such an effect through the 'strength' of the hydrogen bond. This 'strength' may then be seen as change in the force constant of the N–H bond: the stronger the N–H bond, the greater the shift to lower absorption frequencies in the compounds. Thus it is reasonable to expect a correlation between the difference in force constant with pK_a, as presented.

In addition, electron availability should be reflected in the core level binding energies and in particular, for the different bases, some variation of the N(1s) binding energy with different substitution is expected. Data are listed in Table 7. Again, correlation of E_b with pK_a is strong ($R = -0.94$) and is stronger than that obtained for the infrared data.

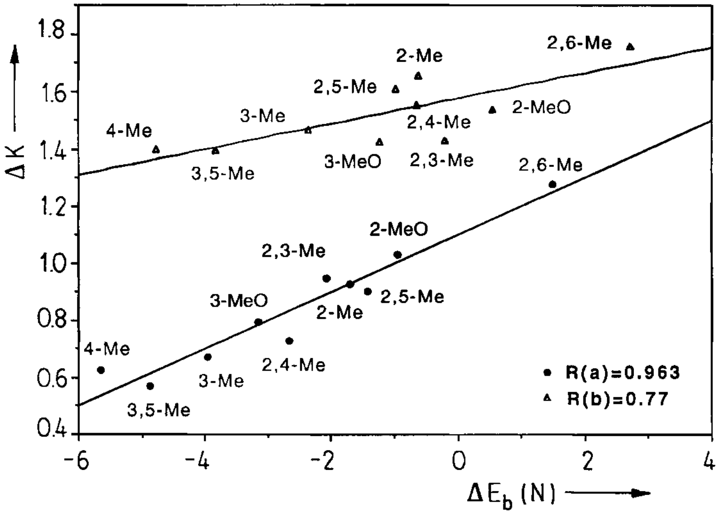

Fig. 4. Plots of change in force constant (ΔK) vs. change in N(1s) binding energy (ΔE_b) between TPB and $SnCl_3^-$ derivatives (a) and Cl^- derivatives (b)

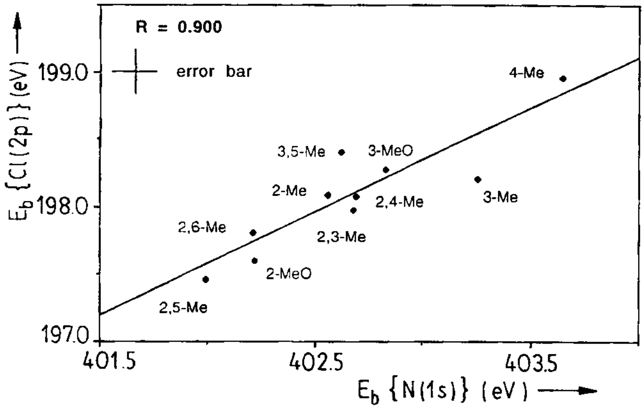

Fig. 5. Plot of binding energy for Cl(2p) vs. binding energy for N(1s) in $SnCl_3^-$ derivatives

Since the H bond occurs between an electronegative atom A (e.g., nitrogen which attracts hydrogen and leaves the hydrogen atom slightly positive, $H^{\delta+}$), and an acceptor ionic group B which has high electron density capable of interacting strongly with the acidic hydrogen (e.g., chlorine), the core level electron binding energies of nitrogen should reveal effects of charge transfer through the H bond as well as the change in N–H bond stretching frequency. Fig. 4 displays correlations between the shift in force constant and the shift in binding energy due to the H-bond effect for the anilinium $SnCl_3$ and anilinium Cl salts, respectively.

Because hydrogen makes a bridge joining A and B, the different positions and types of substituent influence the charge distribution not only on A (e.g., nitrogen) but also on B (e.g., chlorine). Fig. 5 shows the binding energy shifts of nitrogen and chlorine with different ring substituents.

4. Theoretical Considerations

In order to analyse theoretically the activity of hydrogen bonding in the compounds which we discuss here, we have investigated a hydrochloride derivative, in which a relatively strong H bond is obtained. Use was made of the AM1 formulation and the MOPAC (Version 6.00) programme [13]. This is a large semi-empirical, quantum mechanical molecular orbital programme. MOPAC has been employed to calculate the atomic charges in some of the complexes. The molecular geometry is input in Gaussian *Z*-matrix format, with cartesian coordinates created automatically in the process.

The particular derivative structure used for calculation was based on 4-methylanilinium chloride, for which reasonably complete structural information is available [6]. To model the charge on the N, two processes were considered:

a) dependence of N charge with variation in substituent position, fixing H–Cl at 0.225 nm [6] and allowing the structure to optimise via MOPAC; and

b) dependence of N charge with variation in N–H distance keeping N–Cl distance fixed and using a 4-methylanilinium ring.

In order to model the H-bonded network, a molecular unit was constructed (similar to that in Fig. 1) in which three Cl atoms were placed a their experimentally determined

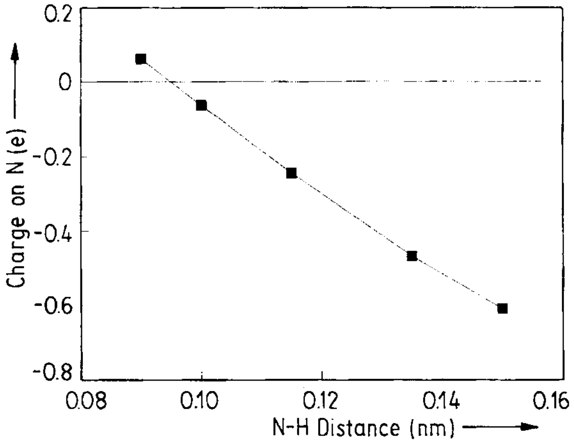

Fig. 6. Variation of charge on nitrogen with N–H interactomic distance using a model based on 4-methylanilinium chloride, charge calculated using the MOPAC program (see text)

positions (for 4-methylanilinium chloride) and bonded to the NH_3 unit. The total charge of this ionic aggregate was thereby restricted to $-2e$.

The MOPAC program results indicate that:

a) the N–H optimised bond length remains approximately constant at 0.104 nm and the charge on nitrogen changes only vary slightly, being $-(0.09 \pm 0.01)\,e$ as a result of varying the position of ring substituents; but

b) marked changes to the charge on nitrogen occur through variation of the position of the hydrogen atoms in N–H–Cl (Fig. 6).

The degree of hydrogen bonding is thus strongly dependent on the location of the hydrogen atom. Compared with the experimental results, these results from the MOPAC program imply that the position and type of substituent in the crystal do not greatly affect the degree of hydrogen bonding by influencing the electronic charge of nitrogen. The result a) above would indicate that N(1s) binding energy shifts (XPS) would be approximately constant (401 eV [14]) for the hydrochloride derivatives, whereas we observe them to vary from 400.7 to 402.8 eV (Table 7). It seems clear that structural changes to the N–H bond length caused by variation of crystal structure amongst the various derivatives is mainly responsible for these shifts (as illustrated by result b) above).

5. Conclusion

We have examined a related series of salts with infrared spectroscopy and XPS. H bonding is evident in all of them and reasonably strong correlations have been shown to exist between: (ΔK, ΔE_b), (ΔK, pK_a), and (E_b(Cl(2p)), E_b(N(1s))). Scatter in these correlations are attributed to structural differences.

Given the close packing of ions in the solid state in comparison with their dispersed nature when reacting in solution, it is nevertheless significant that the solution parameter pK_a correlates so well with hydrogen bond strength parameters. This suggests that some simple concepts of solution chemistry may be usefully transferred to crystal engineering. Thus, a specific interaction such as a hydrogen bond might be incorporated so as to achieve a particular property (e.g., a magnetic or electric phase change).

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