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Relationship Between the *J*(Sn–C–H) of the Dimethyltin Dichloride Adducts of some Pyridines and Anilines, and the Donor Strength of the Lewis Bases

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A study by titrimetric methods of the donor strength of pyridine and aniline and some of their *para*-substituted derivatives, and the $J(^{119}Sn\text{–}C\text{–}H)$ of their adducts with dimethyltin dichloride in nitrobenzene, has shown that the pK_b of a Lewis base and its *para*-substituted derivatives varies linearly with the $J(^{119}Sn\text{–}C\text{–}H)$ of the adducts of dimethyltin dichloride (Me_2SnCl_2), with the Lewis base dissolved in an inert solvent.

A graphical plot of the pK_b of a given series of Lewis bases versus the *J*(Sn–C–H) of their complexes with Me_2SnCl_2 in nitrobenzene (at the same temperature, and same complex concentration) gives a straight line with a negative gradient, making possible the deduction of the other parameter (e.g. pK_b) for a Lewis base in the series, where the one parameter (e.g. *J*(Sn–C–H) is known. The graph for each series of Lewis base has its own characteristic gradient, and the gradients appear proportional in magnitude to the donor strengths of each class of the bases, making it possible to deduce from such graphs which series of Lewis bases are the stronger donors.

Keywords: organotin complexes; base strengths; *J*(Sn–C–H) coupling constants; pK_b

INTRODUCTION

Several reports have considered the *J*(Sn–C–H) commonly observed in the PMR spectra of methyltin halides,[1–6] but they were mostly concerned with how the Sn–C–H coupling is produced,[1–3] and also with some of the factors which decide its magnitude.[3,6] Sn–C–H coupling is brought about by the magnetic interaction of the ^{117}Sn (7.54% abundance) and the ^{119}Sn (8.62% abundance) isotopes with the α-C$\underline{H}$ of an alkyl substituent on the tin.[7] Holmes and Kaesz[3] have proposed a linear relationship between *J*(Sn–C–H) and the percentage of *s*-character of tin in the Sn–C(H) bond; *J* was thought to increase directly with increasing percentage of *s*-character. Factors such as concentration, dielectric constant of the medium and temperature are known[6] to have influence on the magnitude of *J*(Sn–C–H).

However, it does not appear that much use has been found for Sn–C–H coupling constants other than their being informative in structural studies.

Titrimetric methods, sometimes potentiometric, have been the main routes in determining the base strengths of Lewis bases. Half-neutralization in the titration of a base with a strong acid is described by Eqn [1] or [2].

$$\text{pH} = \text{p}K^a = 14 - \text{p}K_b \qquad [1]$$

$$\text{p}K_b = 14 - \text{p}K_a \qquad [2]$$

The pK_b of a Lewis base, a measure of its donor strength, can therefore be obtained from its potentiometric titration curve. However, problems arise where the Lewis base is not strong or soluble enough to give a good titration curve, as then the end-point of the titration, and hence the pK_b, can be difficult to ascertain.

It has been observed that *J*(Sn–C–H) increases for a methyltin halide as it complexes with a Lewis base. Suggestions have been made to explain this increase.[5,6] However, little appears to have been reported on the conversion of this observation to meaningful analytical, or even qualitative, use in chemistry.

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This work was directed towards finding an alternative method to titration for correlation of the base strengths of similar Lewis bases, especially those which are poorly soluble in aqueous media. We report here a study of the variation of J(Sn–C–H) in nitrobenzene of dimethyltin dichloride adducts of pyridine and aniline, and some of their *para*-substituted derivatives, at constant temperature and concentration of adduct. The donor strengths of the pyridine and aniline Lewis bases were determined by potentiometric titration, and the pK_b values correlated with the J(Sn–C–H) values of the adducts.

EXPERIMENTAL

Dry dichloromethane was obtained by drying the AnalaR-grade compound over calcium chloride for 24 h, and was further dried by refluxing over P_2O_5 (16 g l^{-1}) for 3 h under nitrogen, and then distilled. Dry acetone was prepared by conventional methods. All melting temperatures (°C) are uncorrected. IR spectra (CsI disc) were obtained using a Perkin–Elmer 28 3B and a Fourier Transform 1710 IR spectrophotometer. ^1H NMR spectra were obtained using a T60 spectrometer at an operating temperature of 38 °C. Elemental Analyses (C, H and N) were done by the Analytical Laboratory, University of Sussex, UK; tin content was determined locally using the methods reported by Farnworth and Pekola.[9]

4-Picoline (4-Pic), 4-vinylpyridine (4-Vipy), pyridine (Py), 4-nitrobenzylpyridine (4-NiPy), 4-acetylpyridine (4-AcPy), 4-benzoylpyridine (4-BePy), 4-methoxyaniline (4-MexAn), 4-toluidine (4-MeAn), aniline (A_n), 4-chloroaniline (4-ClAn) and all other reagents used in this work were obtained from Aldrich. The dimethyltin dichloride (Me_2SnCl_2) was recrystallized from CH_2Cl_2/hexane before use.

Synthesis of the Me_2SnCl_2 adducts of 4-Pic, 4-ViPy, Py, 4-NiPy 4-BePy, 4-AcPy and the anilines

Stoichiometric amounts of dimethyltin dichloride (x mol) in dry CH_2Cl_2 (about 50 ml for 0.01 M Lewis acid) and the pyridine Lewis base ($2x$ mol), also in dry CH_2Cl_2 (about 20 ml for 0.01 M Lewis base), were mixed with stirring. The adducts appeared either as a precipitate immediately, or as crystals on standing overnight at room temperature. The products were isolated from the reaction mixture by filtration, washed a few times with the solvent, and dried *in vacuo*. The adducts of 4-acetylpyridine, 4-benzoylpyridine, and 4-*p*-nitrobenzyl)pyridine were purified further by recrystallization from dry acetone.

The same procedure was followed for the synthesis of the Me_2SnCl_2 adducts of 4-MexAn, 4-MeAn, An and 4-ClAn, but all products were purified by washing.

Titrimetic determination of the base strength of the Lewis bases

(A 0.1 M solution of each base in 20% aqueous ethanol was titrated with 0.1 M hydrochloric acid. The pH changes in the base solution in the course of titration were monitored with a pH-meter. A graph of pH against volume of HCl used was plotted and the pH at half-neutralization ($= pK_a$) noted. The pK_b of each base was calculated from $pK_b = 14 - pK_a$.

Determination of J(Sn–C–H) values of the adducts

A 0.5 ml portion of a 0.1 M solution of the adduct in nitrobenzene was measured into an NMR tube containing a drop of TMS. The ^1H NMR spectrum was then taken on a T60 NMR spectrometer at an operating temperature of 38 °C.

The solution of each adduct was obtained by dissolving the appropriate mass of the dry adduct in nitrobenzene in a volumetric flask. Alternatively, the adduct solution was obtained by mixing the appropriate amounts of the dimethyltin dichloride Lewis acid and the pyridine or aniline Lewis base, both in nitrobenzene, in a suitable volumetric flask. Care was taken to ensure accurate weighing and purity of the reactants.

Where the adduct crystallized out, the mixture was warmed to redissolve the crystals and the solution was left for a few minutes to cool to room temperature before the ^1H NMR spectrum was taken.

Table 1 Meeting points and elemental analyses for the Me_2SnCl_2 adducts of 4-(*p*-nitrobenzyl)pyridine, aniline and the *para*-substituted anilines

		Found (%)				Calcd %			
Compound	M.p. (°C)	C	N	N	Sn	C	H	N	Sn
$Me_2SnCl_2{\cdot}(4\text{-NiPy})_2$	150–152	48.10	4.00	8.62	18.68	48.14	4.01	8.64	18.0
$Me_2SnCl_2{\cdot}An_2$	121–123	41.56	4.67	7.10	27.88	41.38	4.93	6.90	27.2
$Me_2SnCl_2{\cdot}(4\text{-MexAn})_2$	150–151	41.40	4.95	5.92	24.58	41.20	5.15	6.01	25.4
$Me_2SnCl_2{\cdot}(4\text{-MeAn})_2$	146–148	43.97	5.32	6.25	26.58	44.20	5.53	6.45	27.2
$Me_2SnCl_2{\cdot}(4\text{-ClAn})_2$	109–111	35.70	4.01	6.07	24.37	35.38	3.79	5.90	25.0

RESULTS AND DISCUSSION

The synthesis and analysis of the pyridine and aniline adducts were necessary to be sure of their existence and nature. We have described the synthesis of most of the pyridine and substituted pyridine adducts of Me_2SnCl_2 in an earlier publication.[8] The *p*-nitrobenzylpyridine and aniline adducts were similarly synthesized.

The complexes were formed by simple addition of monodentate amine ligands to dimethyltin dichloride (Eqns [3] and [4]:

$$Me_2SnCl_2 + 2(4 - RPy) \rightarrow Me_2SnCl_2 \cdot (4 - RPy)_2 \quad [3]$$

$4 - RP_y = 4 - R$ – pyridyl; $R = Me, CH{=}CH_2, H, CH_2Ph, NO_2$, CO Ph and $COCH_3$

$$Me_2SnCl_2 + 2\,(4R'An) \rightarrow Me_2SnCl_2 \cdot (4 - R'An)_2 \quad [4]$$

$4 - R'An = 4 - R'$ – aniline; $R' = OMe, Me, H, Cl$

The results of the elemental analyses (Table 1) suggested the adducts to be 1 : 2 (Lewis acid/Lewis base). The ^1H NMR spectra were essentially those of the Lewis acids and bases, with little change in the chemical shift values on complexation. This has been extensively discussed in an earlier publication.[8]

The most noteworthy observation in the IR Spectra (Table 2) is the shift of the pyridyl aromatic *C*=*C* band from about 1580 cm^{-1} in the uncomplexed Lewis base to 1600 cm^{-1} in the adduct.[8] In the case of the aniline adducts, a shift of the N–H band inwards by about 150 cm^{-1} from 3475 cm^{-1} in the uncomplexed Lewis base was observed with the complexation of the Lewis base to the Me_2SnCl_2 Lewis acid. These shifts were used as evidence of binding of the pyridine and aniline Lewis bases to the $Me_2\ SnCl_2$.

The titrimetric determination of the base strength of the Lewis bases was not always straightforward. The very weak Lewis bases presented very poor end-points, and some of the pyridine Lewis bases dissolved poorly in the aqueous ethanol solvent. This further shows the need for a more effective method than titrimetry of determining the base strength of the bases.

Figures 1 and 2 show the potentiometric titration curves for the Lewis bases. The curves demonstrate that, in the pyridine series, 4-picoline is the strongest base whereas 4-benzoylpyridne is the weakest, i.e.

$$4 - Pic > 4 - ViPy > Py > 4 - NiPy > 4 - AcPy > 4 - BePy$$

In the aniline series, 4-methoxyaniline is the strongest, i.e

$$4 - MexAn > 4 - MeAn > An > 4 - ClAn$$

The order of donor strengths of the Lewis bases as shown by the titrimetric studies is as expected, and seems only to show the influence of the para-substituents by a combination of mesomeric and

Table 2 Infrared spectra of Me_2SnCl_2 adducts of 4-(*p*-nitrobenzyl)pyridine, aniline and the *para*-substituted anilines

Compound	$\nu(C{=}C)$ arom.	$\nu(Sn{-}Me)$	$\nu(NH_2)^a$
$Me_2SnCl_2{\cdot}(4\text{-NiPy})_2$	1605 s	790 m	
$Me_2SnCl_2{\cdot}An_2$	1600 s	795 m	3230 m (sy) 3135 m (as)
$Me_2SnCl_2{\cdot}(4\text{-MexAn})_2$	1600 s	795 m	3230 m (sy) 3140 s (as)
$Me_2SnCl_2{\cdot}(4\text{-MeAn})_2$	1600 s	795 m	3230 s (sy) 3125 s (as)
$Me_2SnCl_2{\cdot}(4\text{-ClAn})_2$	1600 s	795 m	3230 s (sy) 3140 s (as)

[a] sy, symmetric; as, asymmetric.

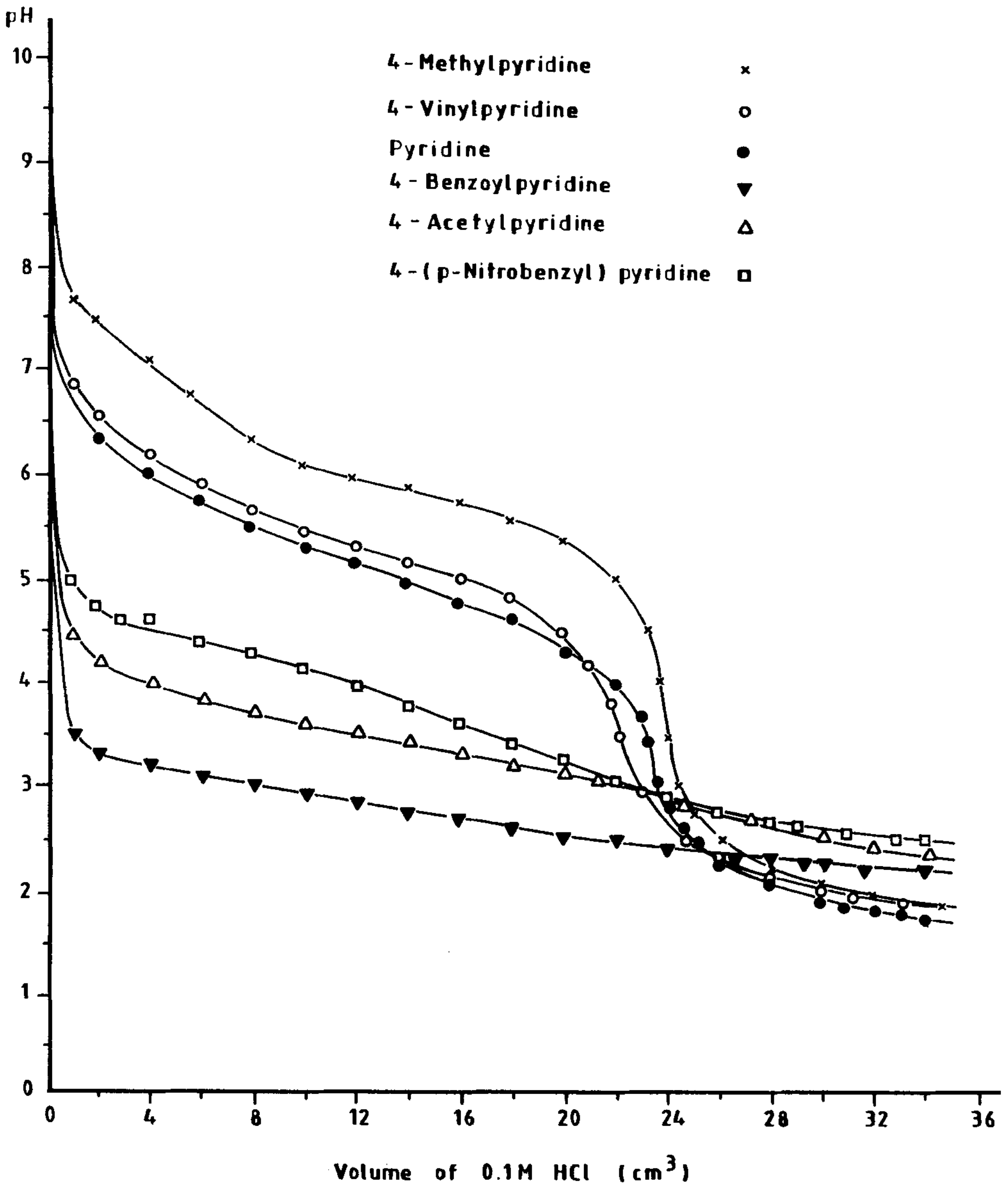

Figure 1 Potentiometric titration curves for the pyridine Lewis bases.

inductive effects, on the lone pair of electrons on the Lewis base N. The slightly electronegative vinyl group (C═C) in 4-vinylpyridine, compared with (for example) CH_3, makes 4-ViPy a weaker base than 4-picoline. 4-NiPy, 4-AcPy and 4-BePy, apparently in that order, are all weaker bases than pyridine. In 4-(*p*-nitrobenzyl)pyridine, the strongly electron-withdrawing effect of the NO_2 group is masked by the benzyl group to which it is attached, which renders it poorly effective at the Lewis base N. In the anilines, the methoxy and methyl substituents, in that order, would be expected to enhance the donor strength of aniline, while the chlorosubstituent should reduce it.

The solution chemistry of organotin halide–pyridine adducts have been little studied, but available evidence suggests that the ligation of the pyridine molecule to the tin centre in an organotin halide molecule tends to aid the ionization of the tin–halogen bond, especially in fairly polar media. Van den Berghe and Van der Kelen[10] have

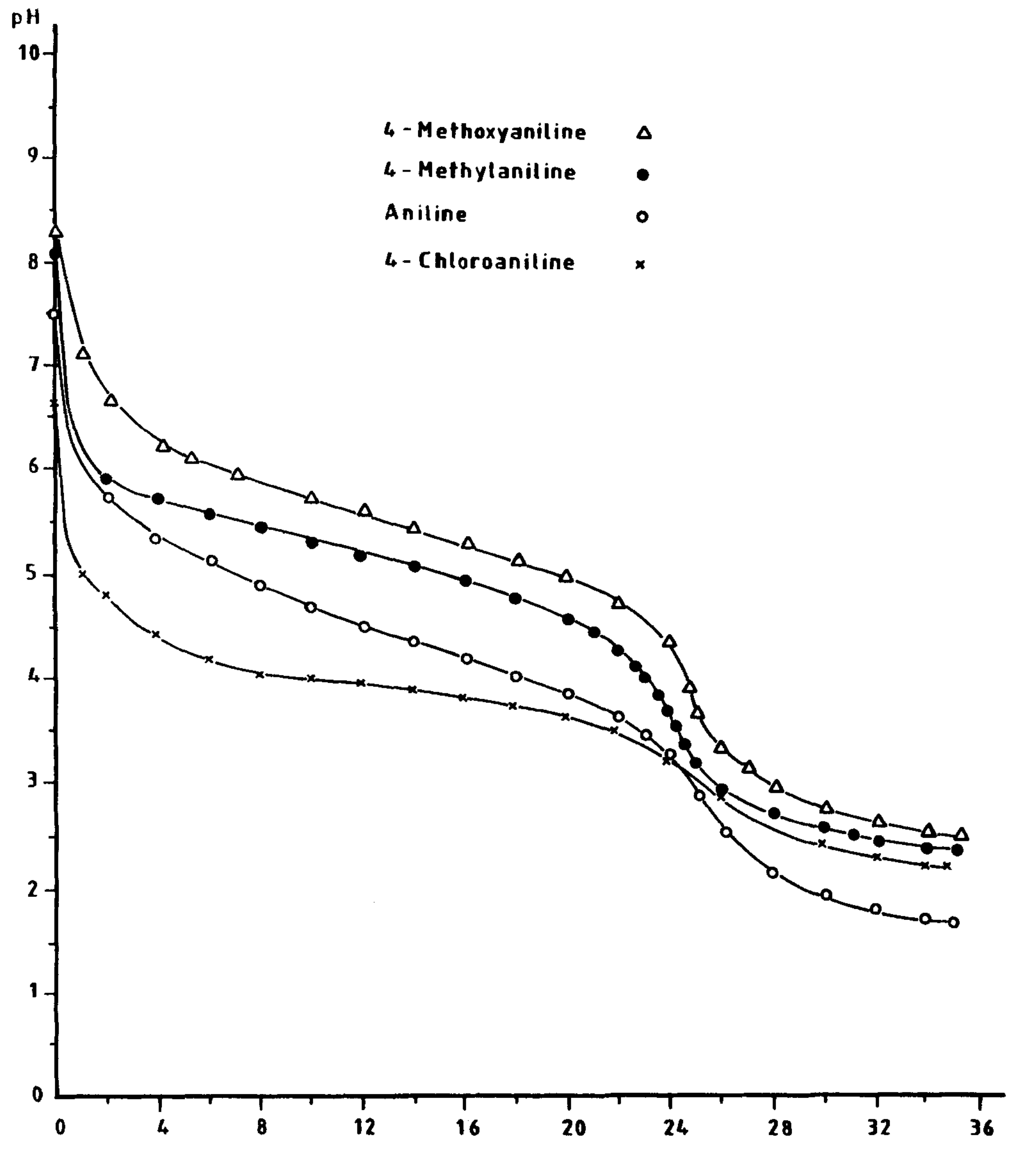

Figure 2 Potentiometric titration curves for the aniline Lewis bases.

proposed the existence in polar media of $Me_3SnCl{\cdot}Py$ as $[Me_3Sn{\cdot}Py]^+Cl^-$, supporting their proposal with Krus and Greer's observation[11] that the electrical conductivity of trimethyltin halide solutions in polar solvents increases on addition of pyridine. In this work, therefore, the ligation by the pyridine or aniline molecules of Me_2SnCl_2 would cause, in nitrobenzene, not complete ionization of in $Me_2SnCl_2{\cdot}2Y$ (where Y is pyridine or aniline) to $[Me_2Sn{\cdot}2Y]^{2+}$ $2Cl^-$, but at the least polarization and elongation of the Sn–Cl bond while the Lewis base molecules are drawn closer to the tin centre. An earlier publication[8] lends credence to this idea.

Only the *para*-substitued pyridines and anilines were chosen for this study, to ensure that the substituent gave no steric interference in the binding of the Lewis base to the dimethyltin dichloride Lewis acid.

To study of the variation of *J*(Sn–C–H) with Lewis base donor strength, nitrobenzene, which is capable of dissolving reactants and adduct with-

Table 3 pK_b for the amines and respective J^{119} values for their complexes with dimethyltin dichloride

Lewis base	pK_b	Complex	J^{119}Sn–C–H for complex (Hz)		Melting point (°C)
Picoline	(8.00)	$Me_2SnCl_2 \cdot (4\text{-}MePy)_2$	94	20	162–164
4-Vinylpyridine	(8.10)	$Me_2SnCl_2 \cdot (4\text{-}ViPy)_2$	93	19	160–162 (dec)
Pyridine	9.16	$Me_2SnCl_2 \cdot Py)_2$	88	14	161–162
4-(*p*-nitrobenzyl) pyridine	9.80	$Me_2SnCl_2 \cdot (4\text{-}NiPy)_2$	86	12	150–152
4-Benzoylpyridine	11.15	$Me_2SnCl_2 \cdot (4\text{-}BePy)_2$	80	6	157–159
4-Acetylpyridine	10.50	$Me_2SnCl_2 \cdot (4\text{-}AcPy)_2$	70	5	117–119
		Me_2SnCl_2	74		
4-Methoxyaniline	8.40	$Me_2SnCl_2 \cdot (4\text{-}MexAn)_2$	78	4	150–151
4-Methylaniline	8.80	$MeSnCl_2 \cdot (4\text{-}MeAn)_2$	77	3	146–148
Aniline	9.51	$Me_2SnCl_2 \cdot An_2$	76	2	121–123
4-Chloroaniline	10.05	$Me_2SnCl_2 \cdot (4\text{-}ClAn)_2$	75	1	109–111

[a] Values in parentheses are.

out side reactions, was chosen as solvent. Common concentrations for the adducts, volume of the solution and the same temperature (38 °C) were chosen for the study. The $J(^{119}Sn\text{–}C\text{–}H)$ values are given in Table 3, which shows clearly that the coupling constants follow the order:

$$(4 - \mathrm{Pic})_2 \cdot \mathrm{LA} > (4 - \mathrm{ViPy})_2 \cdot \mathrm{LA} > \mathrm{Py}_2 \cdot \mathrm{LA} > (4 - \mathrm{NiPy}) \cdot_2 \mathrm{LA} > (4 - \mathrm{Be} \cdot \mathrm{Py}) \cdot_2 \mathrm{LA} > (4 - \mathrm{AcPy}) \cdot_2 \mathrm{LA}$$

and

$$(4 - \mathrm{MexAn}) \cdot_2 \mathrm{LA} > (4 - \mathrm{MeAn}) \cdot_2 \mathrm{LA} > \mathrm{An} \cdot_2 \mathrm{LA} > (4 - \mathrm{ClAn}) \cdot_2 \mathrm{LA}$$

where LA is Me_2SnCl_2.

A comparison of pK_b values for the Lewis bases, as obtained above, with the corresponding J(Sn–C–H) of their complexes with Me_2SnCl_2 in nitrobenzene shows a clear relationship.

It is interesting to note that J(Sn–C–H) for the 4-benzoylpyridine adduct is higher than that for the 4-acetylpyridine adduct, while the reverse is the case for the pK_b values. The larger pK_b of 4-benzoylpyridine suggests that the base is a weaker donor than 4-acetylpyridine, but the J(Sn–C–H) values suggest the opposite to be true. If mesomeric effects are considered in the structures of 4-benzoylpyridine and 4-acetylpyridine, it can be seen that 4-benzoylpyridine should be a stronger donor than 4-acetylpyridine. This method of correlating donor strengths of Lewis bases is therefore advantageous over titrimetric methods.

Table 3 shows that with an increase in pK_b of the Lewis base, J(Sn–C–H) for its complex with Me_2SnCl_2 decreases. A plot of the pK_b of each series of Lewis bases against the change in $J(^{119}Sn\text{–}C\text{–}H)$, compared with the Sn–C–H coupling constant for Me_2SnCl_2, shows that the relationship is linear (Fig. 3). Straight-line graphs are obtained, which can be described by Eqn [5]:

$$\mathrm{p}K_b = m\delta J + c \qquad [5]$$

where m is the slope and c is the pK_b intercept.

However, the values of m and c appear to be characteristic for each series of Lewis bases. This implies that Eqn [5] is separately valid for each series of Lewis bases. The intercept c appears to reflect the donor strength of the two classes of Lewis bases. For example, c for the anilines is lower than that for the pyridines, suggesting that the anilines are stronger bases than the pyridines. The gradient m appears to reflect the donor strengths of the Lewis bases. Thus, the stronger anilines have larger gradients than the weaker pyridines. It follows then that donor strengths of two or more classes of Lewis bases can be compared through the gradient value of each series. To date we do not know the concentration limits within which the equation holds.

This appears to be a more precise method for correlating the donor strength of a Lewis base and its substituted derivatives, for predicting the pK_b of any Lewis base, and for correlating the donor strengths of different series of Lewis bases.

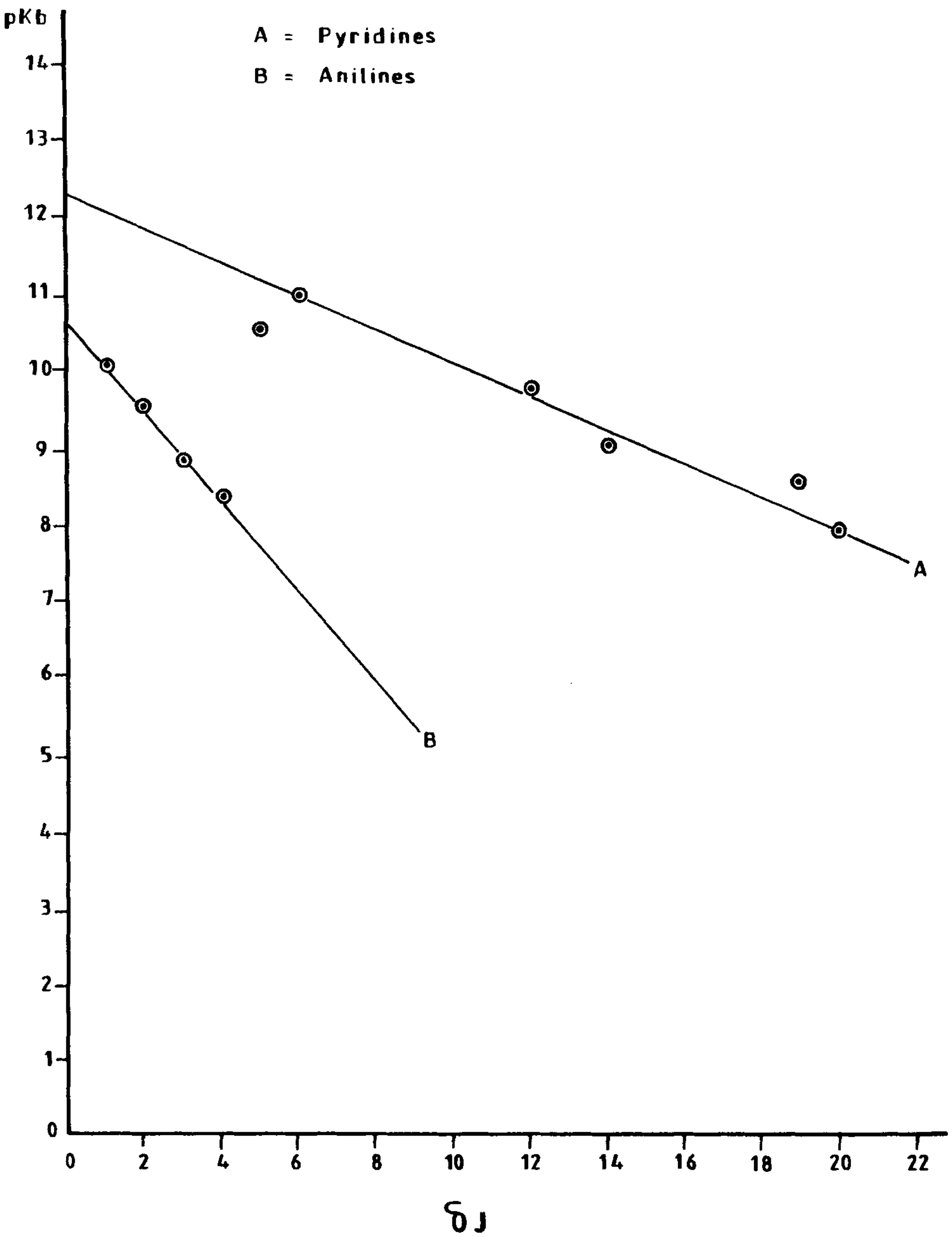

Figure 3 pK_b versus increase in J(Sn–C–H), δJ, of dimethyltin dichloride.

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