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# ULTRAVIOLET ABSORPTION SPECTRA OF SOME 2-SUBSTITUTED PYRIDINES. $\sigma$–$\pi$ CONJUGATION INVOLVING GROUP IV ELEMENTS

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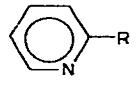
## SUMMARY

This study reports the electronic spectra, in cyclohexane and 95% ethanol solvents, of some members of several series of 2-substituted pyridines containing Group IV elements. The compounds all contain the Group IV elements separated by a saturated carbon atom from the pyridine chromophore. The positions and intensities of both the $^1L_b$ and $^1L_a$ pyridine bands are sensitive to the substituents. The results are interpreted in terms of carbon–metal ($\sigma$–$\pi$) hyperconjugation.

## INTRODUCTION

Recently there has been much interest in examining the variation of properties of an organic molecule attached to the series of Group IV elements. Since electronic absorption spectroscopy is often used to determine the effects of a Group IV element on the electronic properties of organic chromophores (*e.g.*, allyl, benzyl)[1], we have carried out a systematic study of the UV spectra of several series of 2-substituted pyridines (I).



(I)

($I_a$) $R=CH_3$
($I_b$) $R=CH_2CH_2Si(CH_3)_3$
($I_c$) $R=CH_2C(CH_3)_3$
($I_d$) $R=CH_2Si(CH_3)_3$
($I_e$) $R=CH[Si(CH_3)_3]_2$
($I_f$) $R=CH_2Ge(CH_3)_3$
($I_g$) $R=CH_2Sn(CH_3)_3$
($I_h$) $R=CH[Sn(CH_3)_3]_2$

Several considerations make the 2-substituted pyridine system attractive for study. The electronic spectra of substituted pyridines have been well characterized[2,3]. Because the distortion of the $D_{6h}$ symmetry of the benzenoid $\pi$-electron cloud is not great in pyridine, the $\pi\rightarrow\pi^*$ transitions correlate with the transitions observed for benzene. Thus, considerations applicable to the effects of substituents on the benzene chromophore will also apply to substituted pyridines.

An additional reason for selecting the 2-substituted pyridines was the possibility of an intramolecular donor–acceptor interaction between the nitrogen lone pair and the metal. Although intermolecular interactions between tetraalkyl substituted Group IV elements and pyridine or other lone pair donors have not been observed, an intramolecular interaction between the Group IV element and the pyridine nitrogen is quite probable. Such chelation effects often promote enhanced stability with respect to the unchelated system. If an intramolecular interaction occurs in this series the weak $n \rightarrow \pi^*$ transition of the pyridine chromophore would be expected to be perturbed in a manner similar to hydrogen bonding interaction[4,5]. Even though the $n \rightarrow \pi^*$ transition is difficult to observe, the shift of this transition in polar and non-polar solvents has been studied for some substituted pyridines[4,5].

## EXPERIMENTAL

### *Spectra*

UV absorption spectra were determined using a Cary 14 or Cary 15 spectrophotometer with 1.0 cm quartz cells and spectral grade cyclohexane or stock 95% ethanol. NMR spectra were determined using a Varian A-60 spectrometer with carbon tetrachloride solutions and are reported downfield from tetramethylsilane as external standard. Integrations of the NMR spectra are reported to the nearest integer ratio. IR spectra were determined using a Perkin–Elmer 237B spectrophotometer with neat liquid films. In all compounds the IR spectra showed the typical pyridine bands at ~1435, ~1475, ~1560, ~1580 $cm^{-1}$, and carbon–hydrogen bands between 2900 and 3100 $cm^{-1}$. Mass spectra were obtained for all compounds except the two tin compounds. Fragmentation patterns consistent with the proposed structures were observed.

### *Materials*

All compounds reported in this study were prepared by the reaction of 2-(lithiomethyl)pyridine[6] with a halogenated compound: $(CH_3)_3SiCH_2Cl$, $(CH_3)_3CX$ ($X = Cl$ and Br), $(CH_3)_3SiCl$, $(CH_3)_3GeBr$, or $(CH_3)_3SnBr$. Commercial 2-picoline (2-methylpyridine) was redistilled (b.p. 128–128.5° at 762 mm) and stored over potassium hydroxide.

All compounds were purified by preparative gas liquid partition chromatography (GLC) using a 5 ft. 20% SE-30 column. Combustion analyses were performed by Galbraith Laboratories, Knoxville, Tennessee; or Berkeley Microanalytical Laboratory, Berkeley, California.

*2-[2-(Trimethylsilyl)ethyl]pyridine.* (Chloromethyl)trimethylsilane (9 g, 50 mmole) was added dropwise to 2-(lithiomethyl)pyridine (52 mmole) in diethyl ether solvent (40 ml). The mixture was stirred 12 h and excess lithium reagent was then destroyed with wet ether. The liquid was distilled through a Teflon annular spinning band distillation column giving a fraction (b.p. 60–99° at 20 mm, ~50% yield) which was further purified by GLC. The product was identified on the basis of the IR, UV, NMR, and mass spectra. NMR spectrum: singlet, 0.10 ppm, 9H, $(CH_3)_3Si$–; multiplet, 0.67–0.99 ppm, 2H, Si–$CH_2$–; multiplet, 2.57–2.88 ppm 2H, C–$CH_2$–; multiplet, 7.00–8.78 ppm, 4H, $C_5H_4NR$.

*2-Neopentylpyridine.* tert-Butylchloride (55 g, 0.6 mole) and tert-butylbromide (14 g, 0.1 mole) were stirred with 2-(lithiomethyl)pyridine (0.4 mole) in diethyl ether solvent (300 ml) at room temperature for five days. The solution was then refluxed for two days until the lithium reagent was consumed as shown by the color change from dark red-brown to yellow. The solution was washed three times with 50 ml portions of water and the organic layer was dried over magnesium sulfate. Distillation through a 4″ Vigreux column furnished a fraction (b.p. 80–130° at 10 mm, ~2% yield) which was further purified by GLC. (Found: C, 80.70; H, 10.14; N, 9.14. $C_{10}H_{15}N$ calcd.; C, 80.42; H, 10.13; N, 9.39%.) NMR spectrum: singlet, 0.67 ppm, 9H, $(CH_3)_3C-$; singlet, 2.42 ppm, 2H, $-CH_2-$; multiplet, 6.62–8.33 ppm, 4H, $C_5H_4NR$.

*2-[(Trimethylsilyl)methyl]pyridine.* Trimethylchlorosilane (11 g, 0.1 mole) was added dropwise to 2-(lithiomethyl)pyridine (0.2 mole) in diethyl ether solvent (150 ml). The mixture was stirred 12 h and excess lithium reagent was then carefully destroyed with wet ether. Distillation through a 4″ Vigreux column furnished a fraction (b.p. 113–116° at 63 mm, ~40% yield) which was further purified by GLC. (Found: C, 65.41; H, 8.98; N, 8.22. $C_9H_{15}NSi$ calcd.; C, 65.39; H, 9.15; N, 8.44%.) NMR spectrum: singlet, 0.07 ppm, 9H, $(CH_3)_3Si-$; singlet, 2.20 ppm, 2H, $-CH_2-$; multiplet, 6.66–8.33 ppm, 4H, $C_5H_4NR$.

*2-[(Trimethylgermyl)methyl]pyridine.* Trimethylgermanium bromide was prepared by the method of Dennis and Patnode[7] from tetramethylgermanium which was prepared by the method of Dennis and Hance[8]. Trimethylgermanium bromide (4.4 g, 22 mmole) was added dropwise to 2-(lithiomethyl)pyridine (40 mmole) in diethyl ether solvent (30 ml) and stirred 6 h. The liquid was removed from the reaction flask and fractionated on a vacuum line furnishing the product (~25% yield), which was further purified by GLC. (Found: C, 51.62; H, 7.11; N, 6.60. $C_9H_{15}GeN$ calcd.: C, 51.52; H, 7.21; N, 6.68%.) NMR spectrum: singlet, 0.08 ppm, 9H, $(CH_3)_3Ge-$; singlet, 2.10 ppm, 2H, $-CH_2-$; multiplet, 6.33–8.00 ppm, 4H, $C_5H_4NR$.

*2-[(Trimethylstannyl)methyl]pyridine.* Trimethyltin bromide (3.9 g, 16 mmole), prepared by the method of Kraus and Sessions[9], was added to 2-(lithiomethyl)pyridine (17 mmole) in diethyl ether solvent (15 ml) and shaken 12 h. The liquid was removed from the reaction flask and fractionated on a vacuum line furnishing the product (~15% yield), which was further purified by GLC. (Found: C, 42.60; H, 6.14. $C_9H_{15}NSn$ calcd.: C, 42.24; H, 5.91%.) NMR spectrum: singlet, 0.05 ppm, 9H, $(CH_3)_3Sn-[J(^{119}Sn-CH_3) = 56\ Hz]$; singlet, 2.45 ppm, 2H, $-CH_2-[J(^{119}Sn-CH_2-) = 62\ Hz]$; multiplet, 6.33–8.35 ppm, 4H, $C_5H_4NR$.

*2-[Bis(trimethylstannyl)methyl]pyridine.* The product (~15% yield) was isolated from the above reaction mixture and further purified by GLC. (Found: C, 34.64; H, 5.56. $C_{12}H_{23}NSn_2$ calcd.: C, 34.42; H, 5.54%.) NMR spectrum: singlet, 0.1 ppm, 18H, $(CH_3)_3Sn_2-$ $[J(^{119}Sn-CH_3) = 53\ Hz]$; singlet, 2.18 ppm, 1H, $\rangle CH-$ $[J^{119}Sn-CH\langle) = 53\ Hz]$; multiplet, 6.50–8.30 ppm, 4H, $C_5H_4NR$.

## RESULTS AND DISCUSSION

### $\pi \rightarrow \pi^*$ *Transitions*

The energies and intensities of the transitions observed for the 2-substituted pyridines (I) are presented in Table 1, labelled with the systematic nomenclature of Platt[10], and assigned on the basis of the similarity to benzene and substituted benzenes[2]. The possibility that some of the observed bands might be due to excitation of an electron from the metal–carbon bonds was ruled rather unlikely on the basis of the spectra observed for $R_4M$ (M = Si, Ge or Sn), *e.g.*, the lowest energy absorption for $(n\text{-}Bu)_4Sn$ is at 49500 $cm^{-1}$ (ref. 1).

TABLE 1

ABSORPTION MAXIMA OF 2-SUBSTITUTED PYRIDINES

| Substituent | Solvent[a] | $^1L_b$ band | | | $^1L_a$ band | | |
|---|---|---|---|---|---|---|---|
| | | $\lambda_{max}$ (nm) | $\nu$ (cm$^{-1}$) | $\varepsilon$ | $\lambda_{max}$ (nm) | $\nu$ (cm$^{-1}$) | $\varepsilon$ |
| $CH_3$ | $C_6H_{12}$ | 261 | 38300 | 2600 | 203 | 49300 | 5850 |
| | $C_2H_5OH$ | 262 | 38200 | 3500 | 202 | 49500 | 5750 |
| $CH_2CH_2Si(CH_3)_3$ | $C_6H_{12}$ | 262 | 38200 | 3150 | 206 | 48500 | 7150 |
| | $C_2H_5OH$ | 263 | 38000 | 4350 | 205 | 48800 | 6550 |
| $CH_2C(CH_3)_3$ | $C_6H_{12}$ | 262 | 38200 | 2650 | 205 | 48800 | 6950 |
| | $C_2H_5OH$ | 262 | 38200 | 3800 | 206 | 48500 | 6150 |
| $CH_2Si(CH_3)_3$ | $C_6H_{12}$ | 269 | 37200 | 3400 | 215 | 46500 | 9350 |
| | $C_2H_5OH$ | 269 | 37200 | 4350 | 215 | 46500 | 8450 |
| $CH[Si(CH_3)_3]_2$ | n-$C_6H_{14}$ | 274 | 36500 | 3600 | 222 | 45000 | 11700[b] |
| $CH_2Ge(CH_3)_3$ | $C_6H_{12}$ | 272 | 36800 | 4150 | 219 | 45700 | 10900 |
| | $C_2H_5OH$ | 271 | 36900 | 4500 | 219 | 56700 | 9900 |
| $CH_2Sn(CH_3)_3$ | $C_6H_{12}$ | 276 | 36200 | 3650 | 228 | 43900 | 11600 |
| $CH[Sn(CH_3)_3]_2$[c] | $C_6H_{12}$ | 289 | 34600 | 4550 | 246 | 40700 | 15600 |

[a] $C_6H_{12}$=cyclohexane, $C_2H_5OH$=95% ethanol, n-$C_6H_{14}$=n-hexane. [b] Ref. 11. [c] An additional peak was observed ($\nu$=51800 cm$^{-1}$, $\varepsilon$=37200).

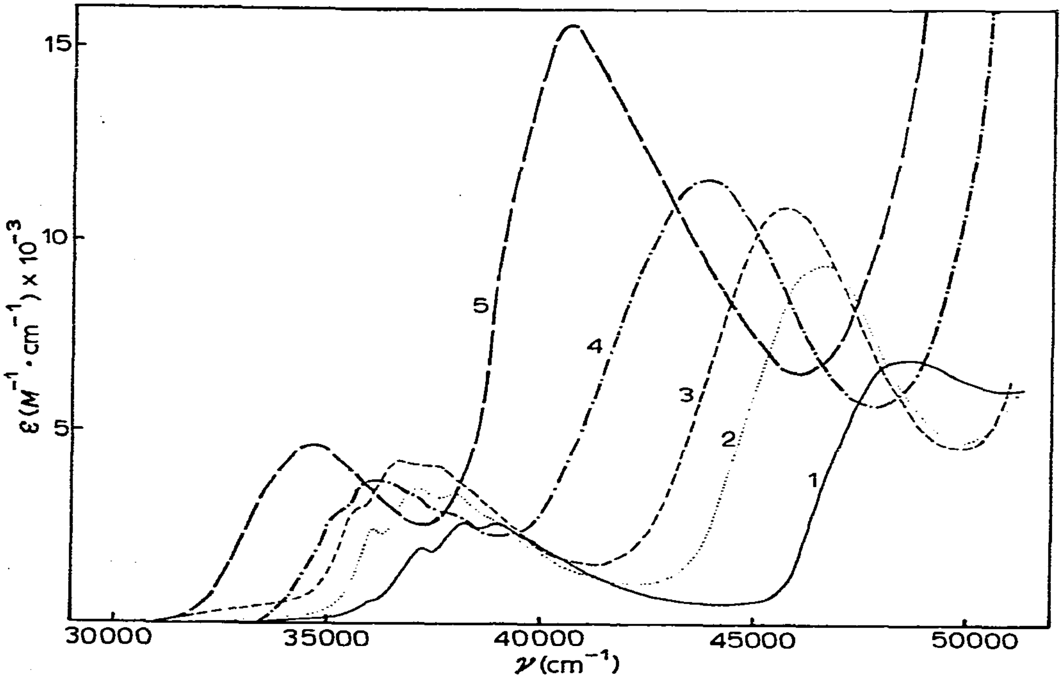


Fig. 1. UV spectra of (1), neopentylpyridine———; (2), 2-[(trimethylsilyl)methyl]pyridine··········; (3), 2-[(trimethylgermyl)methyl]pyridine– – – –; (4), 2-[(trimethylstannyl)methyl]pyridine–·–·–·–; (5), 2-[bis(trimethylstannyl)methyl]pyridine———; in cyclohexane.

The positions and intensities of both the $^1L_b$ and $^1L_a$ bands are sensitive to the substituents, (Fig. 1) and, as is generally observed[2], both bands are affected similarly by a given substituent. Some pertinent observations are: (*a*) the bands undergo progressive red shifts and intensity increases in the order $CH_2C(CH_3)_3 < CH_2Si(CH_3)_3 < CH_2Ge(CH_3)_3 < CH_2Sn(CH_3)_3$, (*b*) the effect of the $CH_2Si(CH_3)_3$ group is similar to a $OCH_3$ group while the $CH[Sn(CH_3)_3]_2$ groups effect is similar to an $NH_2$ group[2], (*c*) the effect of the $CH[Si(CH_3)_3]_2$ group is approximately twice that of the $CH_2Si(CH_3)_3$ group[11] and the same holds for the $CH[Sn(CH_3)_3]_2$ group compared to the $CH_2Sn(CH_3)_3$ group and, (*d*) the influence of $CH_3$ or $CH_2CH_2Si(CH_3)_3$ is essentially the same as $CH_2C(CH_3)_3$.

The results obtained for the $(CH_3)_3M$ ($M = C, Si, Ge, Sn$) substituted 2-picolines are similar to those reported for the benzyl substituted organometallics[12]. In the pyridine series, however, the spectra were examined in solvents of different polarity to ensure that solvation effects were not contributing to the observed shifts.

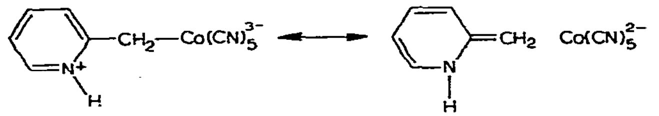
As in the benzyl series, the magnitude of the spectral changes suggests a strong perturbation of the $\pi$-symmetry wavefunctions. Several explanations have been offered (*d*-orbital effects, inductive effects, $\sigma$–$\pi$ hyperconjugation)[1] to account for this variation in spectral properties of the benzenoid chromophore as the metal atom in the $(CH_3)_3MCH_2$ substituent is varied.

The currently accepted explanation of the interaction is based on a study of charge transfer spectra of a series of monosubstituted benzenes with TCNE or DCMA[13]. Although the series studied did not include a systematic variation of similarly substituted Group IV elements attached to a benzyl carbon or any disubstituted derivatives, the observed vertical stabilization of the cation formed in the charge transfer process was shown to result from a $\sigma$–$\pi$ hyperconjugative interaction rather than from inductive or *d*-orbital effects.

The results of the spectral analysis of the $(CH_3)_3M$ ($M = C, Si, Ge, Sn$) substituted 2-picolines are consistent with $\sigma$–$\pi$ hyperconjugation.

The effect of two $Si(CH_3)_3$ or two $Sn(CH_3)_3$ groups would be larger than one $Si(CH_3)_3$ or one $Sn(CH_3)_3$ group since two of the three group orbitals of $CH[M(CH_3)_3]_2$ ($M = Si$ or $Sn$) have $\pi$-symmetry and can partially overlap with the ring $\pi$-system[14,15]. The separation of charge on excitation can be accommodated with some positive charge residing on the polarizable $M(CH_3)_3$ group ($Sn > Ge > Si > C$)[1] and some negative charge on the nitrogen containing ring. The red shifts which occur with increasing atomic number of M may be related to the decreasing ionization potentials of the $R_4M$ compounds[16] which, in turn, are related to the decreasing energies of the M–C $\sigma$ bonds.

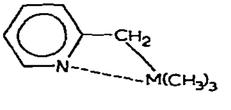
Similar $\sigma$–$\pi$ conjugation in picolines has been reported[17] in (2-pyridylmethyl)-pentacyanocobaltate(III). The UV spectrum of the 2-isomer was found to undergo a large change on protonation whereas the protonated form and the conjugate base of the 3-isomer gave spectra almost identical with the spectrum of the conjugate base of the 2-isomer.



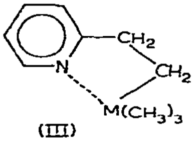
This interaction is supposedly much less important in the free bases than in the protonated derivatives. Therefore it is somewhat surprising that the spectra of the substituted picolines in ethanol (a hydrogen bonding solvent) are almost identical with the spectra in cyclohexane. If protonation of nitrogen favors $\sigma$–$\pi$ conjugation a large solvent effect might have been expected.

*Intramolecular interactions*

We have previously considered the possibility that the intensification of the $n \rightarrow \pi^*$ transition in $(CH_3)_3SiCH_2COCH_3$ could be rationalized by an intramolecular interaction between the non-bonding electrons of the oxygen and the *d*-orbitals of silicon[18,19]. Likewise, an intramolecular interaction between bromide and tin was reported to occur in (4-bromo-*cis*, *cis*-1,2,3,4-tetraphenyl-1,3-butadienyl)dimethyltin bromide on the basis of an NMR analysis in $CCl_4$ and a crystal structure determination[20]. A similar interaction is also possible in the series of 2-substituted pyridines,



(II)



(III)

(II) and (III); it was of interest to examine the $n \rightarrow \pi^*$ transition and other physical properties to determine whether such an interaction occurs.

Unfortunately the $n \rightarrow \pi^*$ band is so weak and so close to the $^1L_b$ band and the unreliability of the differencing method is so great[4,5], that we did not attempt to assign energies and intensities to possible low energy bands under the $^1L_b$ absorption tails. In addition, rapid hydrolysis of the tin–methylene carbon bond in ethanol prevented determination of the spectrum of either tin compound in this solvent. The silicon-methylene carbon bond and the germanium–methylene carbon bond were also hydrolyzed in ethanol but at a rate slow enough to allow easy determination of the spectra. However, intensification of the $^1L_b$ band in ethanol complicates the analysis of all the observed spectra by obscuring shifts in position of the weak $n \rightarrow \pi^*$ band.

The low energy absorptions of 2-methylpyridine and 2-neopentylpyridine are consistent with the behavior of the $n \rightarrow \pi^*$ transition in non-polar and polar solvents, *i.e.*, a tail or shoulder on the $^1L_b$ band in cyclohexane "disappears," or moves to higher energy, under the intensified $^1L_b$ band in the hydrogen bonding solvent ethanol. 2-[(Trimethylsilyl)methyl]pyridine shows identical low energy absorption in both solvents. This could be due either to a direct nitrogen–silicon interaction or, more likely, to a shift of the $^1L_b$ band to lower energy on silicon substitution which obscures the $n \rightarrow \pi^*$ band. 2-[2-(Trimethylsilyl)ethyl]pyridine shows more of an absorption tail in ethanol than in cyclohexane which is probably due to the greater intensity of the $^1L_b$ band. However, 2-[(trimethylgermyl)methyl]pyridine shows an unexpected $^1L_b$ band tail in cyclohexane but not in ethanol. A simple explanation of this absorption tail would be that the $n \rightarrow \pi^*$ band has been red shifted by an amount equal to the $^1L_b$ band shift. However there is no reason to assume that the shifts would be equal in the germanium derivative since corresponding shifts of both bands are not observed in the silicon analogue.

The IR spectra of these compounds are consistent with the absence of intramolecular donor–acceptor interaction. Various workers have correlated shifts to higher frequency of the pyridine ring breathing modes with donor–acceptor interactions at the nitrogen[21–25]. We observed insignificant shifts in these bands on the order of $\pm 5$ cm$^{-1}$ relative to 2-picoline.

A comparison of the energies of the $^1L_b$ and $^1L_a$ bands of any of the compounds in both ethanol and cyclohexane shows that the energies are unaffected by hydrogen bonding interaction at nitrogen. While our data do not eliminate the possibility of some nitrogen–metal interaction, we can rule out the possibility of such a mechanism causing the spectral changes in the $^1L_b$ and $^1L_a$ bands.

## ACKNOWLEDGEMENT

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