EFFECTIVE SHIELDING VALUES OF THE PHENYL GROUP IN SOME GROUP IVB AND VB COMPOUNDS

M. T. RYAN AND W. L. LEHN
Analytical Branch, Materials Physics Division and the Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio (U.S.A.)

(Received March 30th, 1965)

INTRODUCTION

As methane is successively substituted, a paramagnetic shielding of the remaining protons is generally observed. Meyer and Gutowsky[1], Bothner-By and Naar-Colin[2] and Shoolery[3], as well as others, have studied the proton magnetic resonance spectra of substituted methanes.

Shoolery[3] has proposed an additivity rule for calculating the chemical shift of the protons in substituted methanes. This relationship is

$$\tau = 9.767 - \sum_i \sigma_{i\,eff}$$

where τ is the chemical shift of the protons in the substituted methane, 9.767 is the chemical shift of the protons in methane and σ_{eff} is the effective shielding constant of the i_{th} group. The chemical shifts are measured in ppm from $(CH_3)_4Si$ which has a τ value of 10.000.

We have measured the proton magnetic resonance spectra of some phenyl-substituted compounds of group IVb and Vb elements and calculated the value of the effective shielding constant of the phenyl group using a method similar to Shoolery's. The values of σ_{eff} for the phenyl group in these compounds appear to be dependent on the electronegativity of the element to which the phenyl group is bonded.

We have estimated the effective shielding constant of the methyl group in some group IVb compounds from chemical shift measurements in the literature and show that the additivity rule applies also to substituted silanes.

EXPERIMENTAL

The proton magnetic resonance spectra of the phenyl derivatives were measured using a Varian A-60 Nuclear Magnetic Resonance Spectrometer equipped with a room temperature probe. Dilute solutions in CCl_4 or $CDCl_3$ (2–10 %) were used and $Si(CH_3)_4$ was added as an internal standard. Several concentrations of each compound were measured and when the chemical shift appeared to vary with concentration, the value extrapolated to zero concentration was used. Since diphenylstannane is unstable in CCl_4 and $CDCl_3$, it was necessary to use benzene as a solvent for this compound.

MATERIALS

Diphenylsilane, triphenylsilane and diphenylamine were obtained from commercial sources and used without further purification. Aniline and diphenylphosphine were obtained commercially and purified by distillation. Triphenylgermane and diphenylgermane were prepared according to the procedure of Johnson and Harris[5]. Diphenylstannane was prepared using the method of Kuivilia, Sawyer and Armour[6]. Triphenylstannane, prepared according to Tamborski, Ford and Soloski[7], was kindly supplied by these authors. We also wish to thank Dr. D. SEYFERTH of Massachusetts Institute of Technology for supplying a sample of diphenylarsine.

HYDRIDE CHEMICAL SHIFTS

The chemical shifts of the hydride molecules and a number of other compounds taken from the literature are listed. The values for silane, ammonia and phosphine are the values for the "non-associated" gaseous state taken from Schneider, Bernstein and Pople[8]. These authors measured the chemical shift of simple hydride molecules in the liquid and gaseous states relative to methane gas and their values of the chemical shift for the gaseous state have been converted to τ values.

The value for arsine is taken from Gutowsky and Hoffman[9] who measured the screening constant of liquid arsine as well as several other liquids and gases. Using the relationship of Schneider, Bernstein and Pople[8] that "liquid association shift" = $\delta_{liq} - \delta_{gas} - \frac{2}{3} X_v \times 10^6$, where δ is the chemical shift and X_v is the volume susceptibility of the compound, and assuming that the "liquid association shift" of arsine is the same magnitude as that of phosphine, the chemical shift of gaseous arsine was calculated. The volume susceptibility of arsine was calculated from Pascal's constants and from the density relationship for liquid arsine given by Rees and Stewart[10].

The value for stannane is taken from the work of Flitcroft and Kaesz[11]. The value for germane is taken from the work of Potter, Pratt and Wilkinson[12].

DISCUSSION

Group IVb compounds

In calculating an effective shielding constant for a group in substituted methanes, the chemical shift of the remaining protons after each successive substitution is measured.

Assuming that electron withdrawal from the carbon atom causes the change in chemical shift, it becomes progressively harder to withdraw electrons as the number of electronegative groups is increased, so that the effective shielding constant for a group is obtained by taking an average of the shifts caused by successive substitutions of the group on methane. The value chosen for the effective shielding constant lies between the values for the first and second substitutions weighted a little more heavily in favor of the first. As pointed out by Jackman[4], the use of Shoolery's additivity rule has been found to reproduce the values of some twenty methylene protons with an average deviation of ± 0.05 ppm.

In Table 1 are tabulated the changes in chemical shift for each substitution, the average value, and Shoolery's value of the effective shielding constant (σ_{eff}) which is a weighted average.

TABLE 1

CHANGE IN CHEMICAL SHIFT OF METHANE PROTONS UPON SUBSTITUTION

	Cl	*Br*	*I*	*Ph*
$\tau(C\underline{H}_4) - \tau(C\underline{H}_3X)$	2.82[a]	2.45[a]	1.93[a]	2.10[a]
$\tau(C\underline{H}_3X) - \tau(C\underline{H}_2X_2)$	2.28[a]	2.26[a]	1.72[b]	1.59[a]
$\tau(C\underline{H}_2X_2) - \tau(C\underline{H}X_3)$	1.92[a]	1.88[a]	1.03[b]	1.48[c]
Average	2.34	2.20	1.56	1.72
Shoolery's σ_{eff}	2.53[d]	2.33[d]	1.82[d]	1.83[d]

[a] Values calculated from ref. 22. [b] Values for $C\underline{H}_2I_2$ and $C\underline{H}I_3$ from ref. 2. [c] τ value for $(C_6H_5)_3C\underline{H}$ from ref. 15. [d] Ref. 3.

TABLE 2

τ VALUES OF PROTONS IN GROUP IVb HYDRIDES AND PHENYL-SUBSTITUTED GROUP IVb COMPOUNDS

	Si	*Ge*	*Sn*			
$\tau(M\underline{H}_4)$	6.77[a]	6.83[b]	6.15[c]	6.11[b]	6.15[d]	
$\tau(M\underline{H}_3Ph)$	5.81[e]				5.07[d]	4.89[f]
$\tau(M\underline{H}_2Ph_2)$	5.14[g]	4.86[g]	3.78[h]		3.91[d]	3.98[f]
$\tau(M\underline{H}Ph_3)$	4.57[g]	4.27[g]	2.96[h]	3.17[g]	3.17[d]	3.16[f]

[a] Ref. 8. [b] Ref. 12. [c] Ref. 11. [d] Neat liquid, ref. 19. [e] Ref. 22. [f] In ether solution, ref. 19. [g] In $CDCl_3$. [h] In C_6H_6.

TABLE 3

CHANGES IN CHEMICAL SHIFT OF PROTONS IN GROUP IVb PHENYL-SUBSTITUTED COMPOUNDS

	C	*Si*	*Ge*	*Sn*		
$\tau(MH_4) - \tau(MH_3Ph)$	2.10	0.96			1.08[a]	1.17[a]
$\tau(MH_3Ph) - \tau(MH_2Ph_2)$	1.59	0.67			1.16[a]	1.00[a]
$\tau(MH_2Ph_2) - \tau(MHPh_3)$	1.54	0.57	0.59	0.82	0.87[a]	0.82[a]

[a] Ref. 19.

The τ values of the chemical shift for silane, stannane and the phenyl-substituted silanes, germanes and stannanes are shown in Table 2.

The changes in chemical shift for each successive substitution for the phenyl-substituted Group IVb compounds are shown in Table 3.

If Shoolery's method of calculating an effective shielding constant is applied to phenyl-substituted silanes, the effective shielding constant of the phenyl group in substituted silanes is approximately 0.80 compared to a value of 1.83 in substituted methanes. Although a complete series has not been measured for substituted germanes and stannanes the values obtained indicate the shielding constant of the phenyl group is close to the value in substituted silanes.

Webster[15] has studied the proton magnetic resonance spectra of *C*-H and *Si*-H protons in a series of methyl-, phenyl-substituted methanes and silanes and noted that in the carbon series, the change is much larger than in the silicon series. He attributed this to possible d_π-p_π bonding between silicon and the phenyl rings. However, his measurements on other trisubstituted silanes indicate that the effective shielding of other groups, as well as the phenyl group, is much lower in silanes than in methanes. For example, if the τ value he gives for $\text{Me}_3\text{Si}\underline{\text{H}}$, 6.149, is put into the equation $\tau = \tau(\text{Si}\underline{\text{H}}_4) - \Sigma\sigma_{eff}$, σ_{eff} for the methyl group is approximately 0.21 compared with Shoolery's value of 0.466 for the methyl group in substituted methanes[3].

Flitcroft and Kaesz[11] have measured proton shifts in some methyl stannanes. Their values for $(\text{CH}_3)_3\text{Sn}\underline{\text{H}}$, $\tau = 5.27$, and $\text{Sn}\underline{\text{H}}_4$, $\tau = 6.15$, put into the equation $\tau = \tau(\text{Sn}\underline{\text{H}}_4) - \Sigma\sigma_{eff}$ yields a value of about 0.29 for the effective shielding of the methyl group.

The measurements of Van der Kelen, Verdonck and Van de Vondel[20] on methylgermanes show that the τ values of protons bonded to germanium decrease with increasing number of methyl radicals bonded to germanium. Their results indicate the effective shielding value of the methyl group in germanes is about 0.31.

Further evidence for lower effective shielding values of groups in silanes than in methanes is seen in Fig. 1 which shows the effect of the progressive substitution of halogens and of the phenyl group on the chemical shift of the protons in substituted methanes and silanes. The data for the halosilanes are from the work of Ebsworth and Turner[21]. The relative positions of the curves for the halogens are in the expected order. The least electronegative halogen, iodine, causes the smallest change in chemical shift. The position of the curve for the phenyl group does not agree with the Taft σ^* values[13] of relative electron withdrawing power of various groups which place the phenyl group at a much lower value than any of the halogens. However, Dailey and Shoolery[14] have

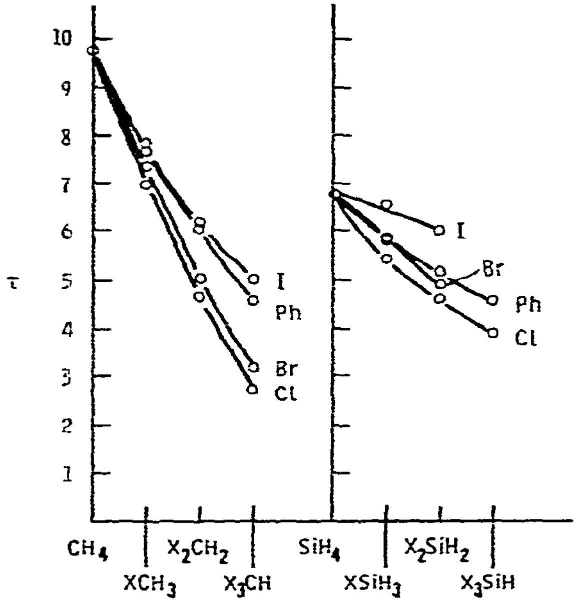

Fig. 1. τ values of protons in substituted methanes and silanes. (A similar curve for the halomethanes referenced to cyclohexane appears in ref. 17, p. 279.)

measured the electron withdrawal power of substituent groups using an empirical relationship which depends on the chemical shift difference of methyl and methylene protons in substituted ethanes. They place the electronegativity of the phenyl group between bromine and iodine which is the order shown in Fig. 1 for the substituted methanes and silanes. The slope of the lines for all substituents is less in silanes than in methanes.

Although d_π–p_π bonding has been invoked[15,21] to explain the relative decrease in chemical shift differences for substituted silanes as compared to methanes, this decrease in effective shielding of a group appears even in compounds where this type of bonding is not possible such as the methyl silanes, germanes and stannanes. The effective shielding for the phenyl group and for the methyl group in Group IVb compounds appears to be generally in the order of the relative electronegativities of the element to which the group is attached. According to Allred and Rochow[16], these are C $\gg$ Ge $>$ Sn $>$ Si.

Group Vb compounds

Our measurements of some phenyl substituted Group Vb compounds indicate an effect similar to that found for the Group IVb compounds. Table 4 lists the τ values of the protons in the compounds studied.

Since the complete series is not available, these may be compared by considering the change in chemical shift upon substitution of two phenyl groups. These values are shown in Table 5.

The effective shielding of the phenyl group would be approximately one-half the values shown in Table 5.

Additivity of substituent groups in Group Vb compounds would not be expected on the basis of limited data available in the literature on the chemical shifts of protons attached to nitrogen in primary and secondary amines. Pople, Bernstein and Schneider[17] have summarized the measurements on alkyl and aryl amines. They show the proton in secondary amines at a higher field than the protons in primary amines in contrast to the measurements reported here. However, the measurements in the literature have in many cases been made on pure liquids or concentrated solutions

TABLE 4

τ VALUES OF SOME GROUP Vb HYDRIDES AND PHENYL-SUBSTITUTED GROUP Vb COMPOUNDS

	N	*P*	*As*
$\tau(M\underline{H}_3)$	9.82[a]	8.29[a]	7.17[b]
$\tau(M\underline{H}_2Ph)$	6.43[c]		
$\tau(M\underline{H}Ph_2)$	4.37[c]	4.74[d]	5.02[c]

[a] Ref. 8. [b] Ref. 9. [c] In CCl_4. [d] In CCl_4. Center of doublet, P–H coupling constant 219 cps.

TABLE 5

CHANGE IN CHEMICAL SHIFT OF PROTONS IN GROUP Vb PHENYL-SUBSTITUTED COMPOUNDS

	N	*P*	*As*
$\tau(M\underline{H}_3) - \tau(M\underline{H}Ph_2)$	5.45	3.55	2.15

so that the effect of hydrogen bonding on the chemical shift values needs clarification. Our measurements which were extrapolated to zero concentration indicate a successive decrease in the shielding of the protons attached to nitrogen as the number of phenyl substituents is increased.

Although further work on substituted amines and phosphines is needed to confirm this, on the basis of our present measurements, it appears that the shielding of the phenyl group in Vb compounds, as shown in Table 5, is also in the order of the electronegativities of the elements to which the phenyl group is attached. According to Allred and Hensley[18], the order of electronegativities is $N \gg P > As$.

SUMMARY

The effective shielding of the phenyl group is lower in silanes, germanes and stannanes than in methanes. It is also lower in phosphines and arsines than in amines. On the basis of limited data available in the literature, it appears that other groups also exhibit a lower effective shielding in silanes, germanes and stannanes than in methanes. The dependence on electronegativity which the effective shielding values show indicate that the shielding values may be a measure of the ability of the element to transmit the inductive effect of an electronegative substituent.

The effective shielding constants of substituent groups in silanes, as in methanes, can be used to determine the τ values of the remaining protons. For example, using the values of σ_{eff} of 0.80 for the phenyl group and 0.21 for the methyl group and the relation that $\tau = \tau(\mathrm{Si\underline{H}_4}) - \Sigma_i \sigma_{i_{eff}}$ the calculated values for the proton attached to silicon in Me_2PhSiH and $MePh_2SiH$ are 5.55 and 4.96, respectively. The observed values, as reported by Webster[15], for these compounds are 5.57 and 5.08.

REFERENCES

1 L. H. MEYER AND H. S. GUTOWSKY, *J. Phys. Chem.*, 57 (1953) 481.
2 A. A. BOTHNER-BY AND C. NAAR-COLIN, *J. Am. Chem. Soc.*, 80 (1958) 1728.
3 J. N. SHOOLERY, *Technical Information Bulletin Varian Associates*, Palo Alto, California, 2, No. 3, 1959.
4 L. M. JACKMAN, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, New York, 1959, p. 59.
5 O. H. JOHNSON AND D. M. HARRIS, *J. Am. Chem. Soc.*, 72 (1950) 5564.
6 H. G. KUIVILA, A. K. SAWYER AND A. G. ARMOUR, *J. Org. Chem.*, 26 (1961) 1426.
7 C. TAMBORSKI, F. E. FORD AND E. J. SOLOSKI, *J. Org. Chem.*, 28 (1962) 181.
8 W. G. SCHNEIDER, H. J. BERNSTEIN AND J. A. POPLE, *J. Chem. Phys.*, 28 (1958) 601.
9 H. S. GUTOWSKY AND C. J. HOFFMAN, *J. Chem. Phys.*, 19 (1951) 1259.
10 A. L. G. REES AND K. STEWART, *Trans. Faraday Soc.*, 45 (1949) 1028.
11 N. FLITCROFT AND H. D. KAESZ, *J. Am. Chem. Soc.*, 85 (1963) 1377.
12 P. E. POTTER, L. PRATT AND G. WILKINSON, *J. Chem. Soc.*, (1964) 524.
13 R. W. TAFT, JR., *J. Chem. Phys.*, 26 (1957) 93.
14 B. P. DAILEY AND J. N. SHOOLERY, *J. Am. Chem. Soc.*, 77 (1955) 3977.
15 D. E. WEBSTER, *J. Chem. Soc.*, (1960) 5132.
16 A. L. ALLRED AND E. G. ROCHOW, *J. Inorg. Nucl. Chem.*, 5 (1958) 269.
17 J. A. POPLE, W. G. SCHNEIDER AND H. J. BERNSTEIN, *High Resolution Nuclear Magnetic Resonance*, McGraw-Hill, New York, 1959, p. 272.
18 A. L. ALLRED AND A. L. HENSLEY, *J. Inorg. Nucl. Chem.*, 17 (1961) 43.
19 E. AMBERGER, H. P. FRITZ, C. KREITER AND M. KULA, *Chem. Ber.*, 96 (1963) 3270.
20 G. P. VAN DER KELEN, L. VERDONCK AND D. VAN DE VONDEL, *Bull. Soc. Chim. Belges*, 73 (1964) 733.
21 E. A. V. EBSWORTH AND J. J. TURNER, *J. Phys. Chem.*, 67 (1963) 805.
22 G. V. D. THIERS, *Proton Nuclear Resonance Shielding Values*, Minnesota Mining and Mfg. Co., St. Paul 6, Minn., (U.S.A).