

## NUCLEAR MAGNETIC RESONANCE SPECTRA OF PHENOXY-SILANES AND PHENOXYGERMANES

### EVIDENCE FOR $p_{\pi}-d_{\pi}$ BONDING IN Si-O AND Ge-O BONDS

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#### SUMMARY

PMR spectra of *para*-substituted phenoxysilanes and phenoxygermanes are interpreted to show that in these compounds the Si-O bond has more  $p_{\pi}-d_{\pi}$  character than the Ge-O bond, but that  $p_{\pi}-d_{\pi}$  bonding is not negligible in phenoxygermanes.

#### INTRODUCTION

There is much indirect evidence for the presence of a  $p_{\pi}-d_{\pi}$  contribution to the bond between silicon and oxygen<sup>1</sup>, and it is generally found that this  $\pi$ -bonding is greater for silicon than germanium. We have investigated the PMR spectra of a series of *para*-substituted phenoxysilanes and phenoxygermanes,  $\text{Bu}_3\text{MOC}_6\text{H}_4\text{X}$  (M = Si, Ge; X = substituent), and of the series of corresponding phenols in an attempt to find spectroscopic evidence for  $\pi$ -bonding in the Si-O and Ge-O bonds. Substituents with a wide range of M effects have been studied in order to detect any possible perturbation of the  $\pi$ -system of the benzene ring arising from the presence of competitive  $\pi$ -interaction in Si-O and Ge-O bonds.

#### EXPERIMENTAL

The phenoxysilanes were prepared by heating together tributylethoxysilane and the appropriate phenol<sup>2</sup>. Ethanol is evolved and the remaining phenoxysilane was purified by vacuum distillation. Phenoxygermanes were prepared by reaction of  $\text{Bu}_3\text{GeOH}$  or  $(\text{Bu}_3\text{Ge})_2\text{O}$  with the appropriate phenol, and purified by vacuum distillation. The purity of the compounds was checked by GLC analysis and from an examination of PMR and IR spectra. They were usually more than 99% pure, but occasionally contained a little of the parent phenol.

PMR spectra were measured in  $\text{CDCl}_3$  on a JEOL 100 MHz instrument at a concentration of 0.2 M with TMS as an internal standard.

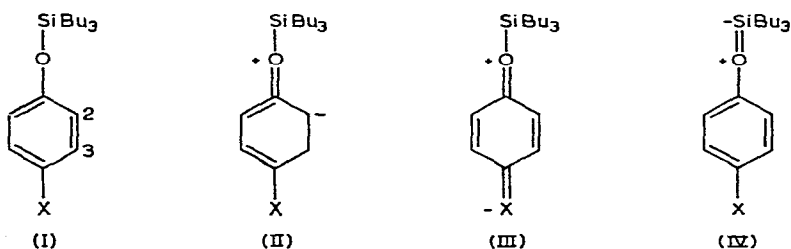
The spectra of the *para*-substituted compounds were analysed on a first-order basis; chemical shifts were taken as the mid-point of each group of peaks. This approximate procedure gave chemical shifts accurate to  $\pm 0.005$  ppm. The spectra of

unsubstituted compounds were analysed by a second-order procedure using the LCN3 computer program. The chemical shifts were assigned to H<sub>2</sub> or H<sub>3</sub> by analogy with well established trends in aromatic compounds<sup>3</sup>.

## RESULTS AND DISCUSSION

The Table gives the chemical shifts obtained, together with the chemical shift differences,  $\Delta_2$  and  $\Delta_3$ , for protons H<sub>2</sub> and H<sub>3</sub> between each phenoxysilane (or phenoxygermane) and the corresponding parent phenol. The numbering of ring positions is shown in structure (I). The  $\Delta$  values are significant to better than 0.01 ppm and hence the observed variations although small are real.

Trialkylsilyl groups have an inductive electron releasing effect (+I) relative to hydrogen, and hence the net inductive withdrawal effect of the Bu<sub>3</sub>SiO group (-I) will be smaller than that of the OH group. Mesomeric interactions of the oxygen lone pairs of electrons with the benzene ring [+M effect, structures (II) and (III)] will also be reduced for the Bu<sub>3</sub>SiO group relative to OH since there is a competitive mesomeric interaction with the 3d orbitals of the silicon atom [structure (IV)].



As H<sub>3</sub> is *meta* to the Bu<sub>3</sub>SiO group, no mesomeric effects will operate and the nearly constant negative values of  $\Delta_3$  (mean -0.028 ppm) reflect the reduced -I effect of Bu<sub>3</sub>SiO compared to OH, with the resulting increased shielding at H<sub>3</sub>.  $\Delta_2$  values are determined by the sum of inductive and mesomeric effects. If no mesomeric effects were present,  $\Delta_2$  would be much more negative than  $\Delta_3$  as -I effects from the Bu<sub>3</sub>SiO or OH groups are less attenuated at H<sub>2</sub>. When X (the *para* substituent in the benzene ring) does not have a -M effect (X=H, Me, F, MeO)  $\Delta_2$  is more positive than  $\Delta_3$  (mean -0.013 ppm), indicating that there must be a net positive contribution to  $\Delta_2$ . This is so if the +M effect of Bu<sub>3</sub>SiO is smaller than the +M effect of OH. When X is a substituent with a strong -M effect (X=NO<sub>2</sub>, CHO, CO<sub>2</sub>Et, CN)  $\Delta_2$  becomes more negative (mean -0.046 ppm). In these cases mesomeric contributions to  $\Delta_2$  are decreased as interactions of type (III) increase at the expense of those of type (II) and  $\Delta_2$  is then determined mainly by -I effects. These results indicate that  $p_\pi-d_\pi$  bonding in the Si-O bond as shown in (IV) occurs to an appreciable extent in these compounds.

For the phenoxygermanes  $\Delta_3$  is again virtually constant (mean -0.064 ppm) and is more negative than  $\Delta_3$  for the phenoxysilanes. This shows that the -I effect of Bu<sub>3</sub>GeO is smaller than the -I effect of Bu<sub>3</sub>SiO. Bu<sub>3</sub>Ge thus has a greater +I effect than Bu<sub>3</sub>Si. This is in agreement with the order of +I effects which have been observed in aliphatic systems Me<sub>3</sub>MCH<sub>2</sub> (M=Si, Ge)<sup>4</sup>.  $\Delta_2$  should be much more

TABLE 1

THE CHEMICAL SHIFTS (ppm) OF PHENOLS, PHENOXY-SILANES, AND PHENOXYGERMANES, R-O-C<sub>6</sub>H<sub>4</sub>-X

X	R	H <sub>2</sub>	H <sub>3</sub>	Δ <sub>2</sub>	Δ <sub>3</sub>
<i>p</i> -OMe	Bu <sub>3</sub> Si	6.749	6.749	-0.022	-0.022
<i>p</i> -OMe	H	6.771	6.771		
<i>p</i> -F	Bu <sub>3</sub> Si	6.744	6.896	-0.008	-0.032
<i>p</i> -F	H	6.752	6.928		
<i>p</i> -Me	Bu <sub>3</sub> Si	6.708	6.998	-0.007	-0.031
<i>p</i> -Me	Bu <sub>3</sub> Ge	6.658	6.973	-0.070	-0.065
<i>p</i> -Me	H	6.715	7.029		
<i>p</i> -H	Bu <sub>3</sub> Si	6.823	7.206	-0.015	-0.030
<i>p</i> -H	Bu <sub>3</sub> Ge	6.770	7.170	-0.070	-0.065
<i>p</i> -H	H	6.838	7.236		
<i>p</i> -H	H <sub>3</sub> Si			0.094	0.09 <sup>a</sup>
<i>p</i> -H	H <sub>3</sub> Ge			0.009	0.00 <sup>a</sup>
<i>p</i> -NO <sub>2</sub>	Bu <sub>3</sub> Si	6.886	8.148	-0.037	-0.033
<i>p</i> -NO <sub>2</sub>	Bu <sub>3</sub> Ge	6.768	8.118	-0.155	-0.063
<i>p</i> -NO <sub>2</sub>	H	6.923	8.181		
<i>p</i> -CHO	Bu <sub>3</sub> Si	6.939	7.793	-0.034	-0.025
<i>p</i> -CHO	H	6.973	7.818		
<i>p</i> -CN	Bu <sub>3</sub> Si	6.875	7.537	-0.054	-0.016
<i>p</i> -CN	H	6.929	7.553		
<i>p</i> -CO <sub>2</sub> Et	Bu <sub>3</sub> Si	6.840	7.939	-0.058	-0.034
<i>p</i> -CO <sub>2</sub> Et	H	6.898	7.973		

<sup>a</sup> See ref. 5.

negative than Δ<sub>3</sub> if inductive effects only are present. Δ<sub>2</sub> is fractionally more negative than Δ<sub>3</sub> for compounds where X has no -M effect (X = H, CH<sub>3</sub>; mean -0.070 ppm) which shows that mesomeric effects are present and contribute to Δ<sub>2</sub>. They are present to a lesser extent than in the phenoxysilanes where Δ<sub>2</sub> was more positive than Δ<sub>3</sub>, but still make a positive contribution to Δ<sub>2</sub> showing that the +M effect of Bu<sub>3</sub>GeO is less than that for OH. When X has a large -M effect (X = NO<sub>2</sub>), Δ<sub>2</sub> becomes much more negative (-0.115 ppm) and is mainly determined by inductive effects. This confirms that mesomeric effects are still present, and that *p*<sub>π</sub>-*d*<sub>π</sub> bonding in the Ge-O bond is not negligible. If there were no *p*<sub>π</sub>-*d*<sub>π</sub> bonding the +M effects of Bu<sub>3</sub>GeO and OH should be the same, and there would be no change in Δ<sub>2</sub> with the nature of the substituent X. Although there will be some "through space" effects present these will be constant throughout each series and will hence make a constant contribution to Δ<sub>2</sub>. The "through space" effects for the phenoxysilanes and phenoxygermanes are not likely to be very different [since the butyl groups are two atoms away from the benzene ring, and the covalent radii of Si and Ge are very similar (Si 117, Ge 122 pm)] and their presence does not affect the above conclusions. Some support for these conclu-

sions is found in the values of  $\Delta_2$  and  $\Delta_3$  for the corresponding phenoxysilane and phenoxygermane with no alkyl groups (see Table). These are calculated from literature data<sup>5</sup> for spectra determined under different conditions but in both cases there is a positive trend from  $\Delta_2$  to  $\Delta_3$  confirming the presence of a mesomeric interaction between the Si or Ge and the O atom.

To summarise, the chemical shifts in phenoxysilanes and phenoxygermanes confirm that the Si-O bond has more  $p_\pi-d_\pi$  character than the Ge-O bond, and indicate that  $p_\pi-d_\pi$  bonding is not negligible in phenoxygermanes.

#### ACKNOWLEDGEMENT

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