# 138. *The* Si–C$_{\text{aromatic}}$ *Bond in Polyphenylsilyl Compounds : The Acid Strengths of the Series of Acids* $p$-$\text{Me}_{4-n}\text{Ph}_{n-1}\text{Si}{\cdot}\text{C}_6\text{H}_4{\cdot}\text{CO}_2\text{H}$.*

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The acid dissociation constants of the above series of acids have been measured (Table 1) and it is shown that the *Si*-phenyl group is just slightly more electron attracting than the *Si*-methyl group in this series. There is no marked discontinuity in the series of acid strengths, indicating that the sum of the opposing mesomeric ($+M$) and inductive effects ($-I$) of the *Si*-phenyl group changes very slightly and continuously as *Si*-methyl groups are replaced by *Si*-phenyl groups. The mesomeric effect might have been expected to show a discontinuity after more than two phenyl groups had been attached to the silicon atom.

We have shown that in the anion $p$-$\text{Me}_3\text{Si}{\cdot}\text{C}_6\text{H}_4{\cdot}\text{CO}_2^-$, $d_\pi$-$p_\pi$-bonding occurs between the silicon atom and the aromatic carbon atom.[1] The electrons in this $\pi$-type bond are provided from the $\pi$-molecular-orbital system of the aromatic nucleus, and the strength of the acid is a sensitive indication of the electron-attracting or -releasing properties of the silyl group.

The replacement of one of the methyl groups by a phenyl group introduces two opposing electronic effects which would influence the acid strength. The more electronegative phenyl group, by increasing the electron withdrawal in the $\sigma$-bond ($-I$), should enhance the acid strength. On the other hand, electron release from the phenyl group into a $d$-orbital of the silicon atom ($+M$) in $d_\pi$-$p_\pi$-bond formation should reduce the acid strength. It was of interest to see which of these effects predominates and whether the predominance of one over the other depends on the number of aromatic nuclei attached to the silicon atom. Kimball[2] has predicted that a tetrahedrally co-ordinated atom ($sp^3$) such as silicon can form a maximum of two strong and three weak $\pi$-bonds. We might expect therefore that the average mesomeric effect of the phenyl group would stay roughly constant until two aromatic nuclei were attached to the silicon atom, then fall rapidly as more phenyl groups were introduced. We have therefore prepared the series of phenylsilylbenzoic acids $p$-$\text{Me}_{4-n}\text{Ph}_{n-1}\text{Si}{\cdot}\text{C}_6\text{H}_4{\cdot}\text{CO}_2\text{H}$ (see footnote) and measured their acid strengths.

The acids were prepared by carboxylation of the Grignard reagent derived from the halides, $p$-$\text{Me}_{4-n}\text{Ph}_{n-1}\text{Si}{\cdot}\text{C}_6\text{H}_4\text{Br}$, which were obtained by the following series of reactions:

$$(1)\quad \text{Me}_2\text{PhSiCl} + p\text{-BrMg}{\cdot}\text{C}_6\text{H}_4\text{Br} \longrightarrow p\text{-Me}_2\text{PhSi}{\cdot}\text{C}_6\text{H}_4\text{Br}$$

$$(2)\quad \text{MeSiCl}_3 + p\text{-BrMg}{\cdot}\text{C}_6\text{H}_4\text{Br} \longrightarrow p\text{-Br}{\cdot}\text{C}_6\text{H}_4{\cdot}\text{SiMeCl}_2 \xrightarrow{\text{2PhMgBr}} p\text{-MePh}_2\text{Si}{\cdot}\text{C}_6\text{H}_4\text{Br}$$

$$(3)\quad \text{SiCl}_4 + p\text{-BrMg}{\cdot}\text{C}_6\text{H}_4\text{Br} \longrightarrow p\text{-Br}{\cdot}\text{C}_6\text{H}_4{\cdot}\text{SiCl}_3 \xrightarrow{\text{3PhMgBr}} p\text{-Ph}_3\text{Si}{\cdot}\text{C}_6\text{H}_4\text{Br}$$

The acid strengths were measured as previously described[1] and are recorded in Table 1.

Table 1. *The thermodynamic dissociation constants* ($K_a$) *of* $p$-$\text{Me}_{4-n}\text{Ph}_{n-1}\text{Si}{\cdot}\text{C}_6\text{H}_4{\cdot}\text{CO}_2\text{H}$ *in* 60·1% (*by weight*) *aqueous ethanol at* 25°.

| $n$ | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| $10^6K_a$ | 1·11 * | 1·28 | 1·51 | 1·81 |

* Taken from ref. 1 for comparison.

The acid strengths increase slightly with the number of phenyl groups, $n$, and so phenyl groups attached to silicon tend, on balance, to be only slightly more electron-attracting than methyl groups, *i.e.*, the influence of their inductive effects ($-I$) slightly outweighs that of their mesomeric effects ($+M$).

The observed increase in acid strength is continuous throughout the series from $n = 1$

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* $n$ = Total number of aromatic nuclei attached to the silicon atom.

[1] Chatt and Williams, *J.*, 1954, 4403.

[2] Kimball, *J. Chem. Phys.*, 1940, **8**, 188.

to $n = 4$. The discontinuity expected between $n = 2$ and $n = 3$ does not occur. There is the possibility of a discontinuity between $n = 1$ and $n = 2$. We cannot investigate this by using our series of acids, but the series of acids $Me_nPh_{3-n}Si\cdot CH_2\cdot CO_2H$ would be a suitable one in which to investigate that possibility. The strengths of two members have been recorded.[3] $Me_3Si\cdot CH_2\cdot CO_2H$ has $10^5K_a = 0{\cdot}60$ and $Me_2PhSi\cdot CH_2\cdot CO_2H$ has $10^5K_a = 0{\cdot}54$ in water at 25°. Here a slight decrease in acid strength has occurred on replacing the methyl group, suggesting that the first phenyl group to be introduced in place of a methyl group is, on balance, more electron-releasing than the methyl group. It is interesting to compare this small change in acid strength with the larger change, of opposite sign, produced in comparable carbon systems where only the inductive effects of the phenyl group can operate, *e.g.*, $Me\cdot CH_2\cdot CH_2\cdot CO_2H$ has [4] $10^5K_a = 1{\cdot}50$, but $Ph\cdot CH_2\cdot CH_2\cdot CO_2H$ has [5] $10^5K_a = 2{\cdot}19$.

It is evident that the replacement of an *Si*-methyl group by an *Si*-phenyl group has little effect on the electron-attracting or -releasing properties of the silyl group containing them. The negative inductive effect of the phenyl group is about balanced by its positive mesomeric effect. In the series of acids which we have studied there is never less than one benzene nucleus attached to the silicon atom. In these circumstances, on replacement of a methyl group by a phenyl group, the change in inductive effect ($-I$) just outweighs the change in mesomeric effect ($+M$).

This finding besides its interest for its own sake is of interest in co-ordination chemistry. When the tertiary organic derivatives of phosphorus, arsenic, and antimony are co-ordinated to a transition metal, the Group V element is in a similar state to silicon in the above series of silylbenzoic acids. For example, in the compound $[(PR_3)_2PtCl_2]$ the phosphorus is tetrahedrally co-ordinated and takes part in $\pi$-type bonding to the platinum atom. The platinum atom supplies the electrons from its *d*-orbitals as the aromatic system does from its $\pi$-molecular orbitals. If the phenyl groups in these complex compounds are also, on balance, electron-withdrawing as compared with alkyl groups, the tertiary aromatic phosphines, arsines, and stibines should be poorer donors than the aliphatic. Therefore, in the inner orbital complexes of metals, towards the ends of the transition series, with tertiary, organic phosphines, arsines, and stibines the $\sigma$-bond, which is a donor bond, should be weakened, and the $\pi$-type bond, which is an acceptor bond, should be strengthened when alkyl are replaced by aryl groups. The aromatic phosphines, etc., should therefore be more strongly double bonding to the metal than their aliphatic analogues. There is some experimental evidence in support of this. Increased double bonding by the atom, M (M = P, As, or Sb), should stabilise the *cis*-relative to the *trans*-isomer in complexes of the type $[(MR_3)_2PtCl_2]$.[6] It is interesting that only the *cis*-isomer of $[(PPh_3)_2PtCl_2]$ is known,[7] but that fact is not proof that the *trans*-isomer is unstable. More definite evidence of the influence of the phenyl group is provided by the equilibrium [8] between *cis*- and *trans*-$[(AsBu^n{}_2Ph)_2PtCl_2]$. It lies much further to the *cis*-side ($K = 9{\cdot}6$) than does the equilibrium between the isomeric forms of $[(AsBu^n{}_3)_2PtCl_2]$ ($K = 340$), as would be expected if the presence of the phenyl group increases the double-bond character of the As–Pt bond.

## EXPERIMENTAL

Microanalyses are by Messrs. W. Brown and A. G. Olney of these laboratories.

*Preparation of Acids.*—p-*Bromophenyldimethylphenylsilane.* Chlorodimethylphenylsilane (76 g., 1 mol.) in ether (100 c.c.) was added to the Grignard reagent prepared from *p*-dibromobenzene (208 g., 2 mol.) in ether (700 c.c.) and magnesium (21·2 g., 2 mol.) in ether (50 c.c.). The mixture was boiled under reflux for 18 hr. and then hydrolysed. The ethereal layer was washed

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[3] Sommer, Gold, Goldberg, and Marans, *J. Amer. Chem. Soc.*, 1949, **71**, 1509.
[4] Dippy, *J.*, 1938, 1222.
[5] Dippy and Lewis, *J.*, 1937, 1008.
[6] Chatt and Williams, *J.*, 1951, 3061; Craig *et al.*, *J.*, 1954, 332; Jaffé, *J. Phys. Chem.*, 1954, **58**, 185.
[7] Jensen, *Z. anorg. Chem.*, 1936, **229**, 242.
[8] Chatt and Wilkins, *J.*, 1956, 525.

with water and dried ($Na_2SO_4$), then fractionated, and the fraction (60 c.c.) of b. p. 153—205°/12 mm. collected. It was purified further by fractionation up a column packed with Dixon rings, and the fraction of b. p. 187—188°/16 mm. collected. This silane (15·5 g.) was sufficiently pure for the next stage in the synthesis (Found: C, 58·7; H, 5·5. Calc. for $C_{14}H_{15}BrSi$: C, 57·7; H, 5·2%).

p-(*Dimethylphenylsilyl*)*benzoic acid.* The above silane (15·5 g., 1 mol.) in ether (175 c.c.) was added with stirring to magnesium (38·5 g., 30 mol.) covered with ether (100 c.c.). During the addition (2 hr.) the magnesium suspension was very vigorously stirred and kept at the boil by external heating. This was continued for a further 2½ hr., then the Grignard reagent, so prepared, was poured on solid carbon dioxide and set aside overnight. The product was hydrolysed with dilute hydrochloric acid, and the ether layer extracted with sodium carbonate solution. Dissolved ether was removed from this solution by warming it, and then, after it had cooled, it was acidified to precipitate the crude acid (10 g.). Recrystallised once from aqueous ethanol, four times from light petroleum, and twice from ethanol, the *acid* was obtained in white crystals (2 g.), m. p. 110—111° (Found: C, 70·2; H, 6·35%; equiv., 258. $C_{15}H_{16}O_2Si$ requires C, 70·3; H, 6·3%; equiv., 256·3).

p-*Bromophenylmethyldichlorosilane.* The Grignard reagent from *p*-dibromobenzene (236 g., 1 mol.) in ether (1000 c.c.) was added slowly (2 hr.) with stirring to methyltrichlorosilane (150 g., 1 mol.). Throughout the addition the mixture was kept at such a temperature that the ether boiled under reflux and the boiling was continued for a further 4½ hr. after the addition. The resultant ethereal reaction mixture was not hydrolysed but was filtered under dry conditions, and the residue extracted with ether. The ethereal extract and filtrate were combined and fractionated. The fraction, b. p. 115—130°/11 mm., was collected (70 g.) and used without further purification or characterisation in the following preparation.

p-*Bromophenylmethyldiphenylsilane.* The above product (70 g., *ca.* 1 mol.) in benzene (100 c.c.) was added to the Grignard reagent obtained from bromobenzene (155 g., 4 mol.) and magnesium (24 g., 4 mol.) in ether (400 c.c.), and the mixture boiled under reflux for 7 hr. After 14 hr. at room temperature, the product was hydrolysed with ammonium chloride solution, and the ether layer removed. This was washed, dried, and distilled. The fraction, b. p. 180—220°/0·5 mm., solidified and after four recrystallisations from ethanol gave the pure *silane*, m. p. 102—103° (8·1 g.) (Found: C, 64·6; H, 4·7. $C_{19}H_{17}BrSi$ requires C, 64·6; H, 4·85%).

p-(*Methyldiphenylsilyl*)*benzoic acid* was prepared from the above silane (8·1 g.) in the same way as its dimethylphenyl analogue (above). The crude *acid* (6 g.) was recrystallised twice from ethanol to give 2·8 g. of pure material, m. p. 200—201·5° (Found: C, 75·45; H, 5·9%; equiv., 320. $C_{20}H_{18}O_2Si$ requires C, 75·4; H, 5·7%; equiv., 318).

p-*Bromophenyltriphenylsilane.* *p*-Bromophenyltrichlorosilane [9] (74·3 g., 1 mol.) was added in toluene (200 c.c.) to the Grignard reagent prepared from bromobenzene (180 g., 4·5 mol.) and magnesium (27·5 g., 4·5 mol.) in ether (600 c.c.). The ether was then distilled away, a further 350 c.c. of toluene were added, and the mixture was boiled under reflux for 16 hr. The product was hydrolysed by dilute hydrochloric acid, and the organic layer removed, dried, and distilled until about 150 c.c. of liquid residue remained. The addition of ethanol (500 c.c.) caused separation of the crude silane (50 g.), m. p. 160—174°. Seven recrystallisations from benzene–ethanol did not yield a pure product (Found: C, 71·3; H, 4·6. Calc. for $C_{24}H_{19}BrSi$: C, 69·4; H, 4·6%). This material was converted into the acid.

p-(*Triphenylsilyl*)*benzoic acid.* The Grignard reagent derived from the preceding silane was prepared by the "entrainment method." The silane (5·6 g.) and ethyl bromide (5·7 g.) in ether (50 c.c.) were slowly added with stirring to magnesium (2·5 g.) in ether (10 c.c.), and the mixture boiled under reflux for 1 hr. after the addition. The mixture was then poured on solid carbon dioxide, kept overnight, and hydrolysed with dilute hydrochloric acid, and the organic product extracted with benzene. The benzene solution was evaporated to a small volume and shaken with sodium carbonate solution. The precipitate of the sodium salt which was formed was filtered off and suspended in water. This suspension was made acid with hydrochloric acid and filtered, and the solid residue recrystallised from benzene–light petroleum. One further recrystallisation gave the pure white *acid*, m. p. 217—218·5° (1 g.) (Found: C, 78·3; H, 5·5%; equiv., 381. $C_{25}H_{20}O_2Si$ requires C, 78·3; H, 5·3%; equiv., 380·5).

*Dissociation Constants.*—These were determined by the method and under the conditions used for the trimethylsilylbenzoic acid.[1] The results are listed in Table 2 corresponding to Table 3 of the previous publication.[1]

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[9] Grüttner and Krause, *Ber.*, 1917, **50**, 1559.

TABLE 2. *Experimental quantities determined to measure the thermodynamic acid dissociation constants, K, in* 60·1% *ethanol* (*by wt.*) *at* 25°.

| $10^3I$ | $10^2C_A$ | $10^4P$ | $10^6K'$ | $10^6K$ | $10^3I$ | $10^2C_A$ | $10^4P$ | $10^6K'$ | $10^6K$ |
|---|---|---|---|---|---|---|---|---|---|
| *p*-$Me_2PhSi{\cdot}C_6H_4{\cdot}CO_2H$. | | | | | | | | | |
| 3·080 | 0·4584 | 4·048 | 1·754 | 1·278 | 3·011 | 0·5304 | 4·357 | 1·751 | 1·280 |
| 3·344 | 0·4543 | 4·021 | 1·746 | 1·255 | 2·536 | 0·6368 | 4·673 | 1·670 | 1·253 |
| 2·767 | 0·5352 | 4·376 | 1·751 | 1·297 | 2·938 | 0·6256 | 4·803 | 1·782 | 1·308 |
| $K = 1{\cdot}279 \times 10^{-6}$; standard deviation ±0·022. | | | | | | | | | |
| *p*-$MePh_2Si{\cdot}C_6H_4{\cdot}CO_2H$. | | | | | | | | | |
| 2·689 | 0·1833 | 2·694 | 1·999 | 1·487 | 3·125 | 0·1244 | 2·257 | 2·103 | 1·528 |
| 2·865 | 0·1816 | 2·742 | 2·094 | 1·543 | 3·149 | 0·1333 | 2·306 | 2·041 | 1·481 |
| 2·878 | 0·1256 | 2·221 | 2·014 | 1·483 | 3·284 | 0·1326 | 2·345 | 2·126 | 1·532 |
| 3·014 | 0·1250 | 2·249 | 2·077 | 1·518 | | | | | |
| $K = 1{\cdot}510 \times 10^{-6}$; standard deviation ±0·024. | | | | | | | | | |
| *p*-$Ph_3Si{\cdot}C_6H_4{\cdot}CO_2H$. | | | | | | | | | |
| 2·307 | 0·202 | 3·098 | 2·406 | 1·830 | 2·651 | 0·200 | 3·086 | 2·408 | 1·795 |
| 2·444 | 0·201 | 3·088 | 2·404 | 1·813 | 2·858 | 0·200 | 3·102 | 2·438 | 1·797 |
| 2·515 | 0·201 | 3·088 | 2·400 | 1·803 | | | | | |
| $K = 1{\cdot}808 \times 10^{-6}$; standard deviation ±0·014. | | | | | | | | | |

$I$ = Ionic strength of solution; $C_A$ = concentration of weak acid; $K'$ = concentration dissociation constant; $K$ = thermodynamic dissociation constant; $P$ = an experimentally determined quantity calculated as described in ref. 1.

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