

## TRANSMISSION OF SUBSTITUENT EFFECTS THROUGH THE Ge–Ge BOND

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### Summary

A series of digermanes of type  $\text{XMe}_2\text{GeGeMe}_3$ , where  $\text{X} = \text{CH}_3, \text{Cl}, \text{Br}, \text{CN}$ , and  $\text{OC}_2\text{H}_5$ , have been prepared and their  $^{13}\text{C}$ – $^1\text{H}$  coupling constants and  $^{13}\text{C}$  and  $^1\text{H}$  chemical shifts were measured. Correlations of the coupling constants with a variety of inductive parameters were performed. Comparisons with the carbon and silicon analogs showed that the Ge–Ge linkage is a slightly better transmitter of substituent effects than the Si–Si linkage but not as good as the C–C bond. The relative transmitting abilities can be rationalized by a combination of inductive and electrostatic field effects.

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In contrast to the wealth of information about the effect of substituents across carbon skeletons, there is very little known about the ability of other homocatenated linkages to transmit electronic effects. In a previous study we have investigated the relative sensitivity of the silicon–silicon and carbon–carbon bonds to substituent effects by monitoring  $^{13}\text{C}$ – $^1\text{H}$  coupling constants and  $^{13}\text{C}$  chemical shifts in compounds of the type  $\text{XMe}_2\text{MMMe}_3$  ( $\text{M} = \text{C}$  and  $\text{Si}$ ) and the basicities of the amine derivatives  $\text{XMe}_2\text{MMMe}_2\text{NMe}_2$  [1]. The significantly depressed transmitting ability of the silicon–silicon bond relative to the carbon–carbon bond can be readily explained by the shorter substituent–“reaction site” distance and consequent greater electrostatic field effects in the carbon system.

We report here the results of our extension of this investigation to the digermanes,  $\text{XMe}_2\text{GeGeMe}_3$ . Because of the slightly larger size of germanium the transmission of substituent effects would be expected to be lower in the digermanes if the electrostatic field effect predominates. On the other hand, the greater polarizability of germanium could produce a greater through-bonds inductive effect. Although stronger ( $p$ – $d$ ) $\pi$  interactions in the silicon system could diminish the transmitting ability of this linkage, the previously observed [1] good correlation with inductive parameters suggests that recourse to this model is unnecessary.

## Experimental

All operations were carried out in a nitrogen atmosphere using dry reagents and glassware. Trimethylchlorogermane was prepared by the method of Mironov and Kravchenko [2] in 80–90% yield and then converted to hexamethyldigermane in a two-step reaction. Considerable difficulty was experienced in obtaining good yields in this conversion. The procedure given below produced the best results.

Hexamethyldigermane [3]. Trimethylchlorogermane (8 ml, 0.065 mol) was added dropwise to 5.1 g (0.13 mol) molten potassium metal which was rapidly dispersed by mechanical stirring in refluxing cyclohexane. After the addition, the red-brown mixture was stirred for 15 minutes and 8 ml of trimethylchlorogermane were added dropwise. After cooling, the pyrophoric solid was separated from the mixture by suction filtration. Fractional distillation under aspirator pressure through an 8 cm Vigreux column resulted in a 50% yield of the product boiling at 40°C/28 Torr.

Following the procedure of Bulten and Noltes [4] hexamethyldigermane was treated with  $\text{SnCl}_4$  to give chloropentamethyldigermane in 80% yield. This derivative was then treated with NaBr and AgCN following the procedure of Andy and Thayer on a micro scale to form the bromo and cyano derivatives [5]. The ethoxy derivative (b.p. 40°C/23 Torr) was obtained by reaction of the chloro derivative with dry ethanol in the presence of triethylamine (equimolar ratios) in hexane. The proton chemical shifts of all products agreed with those reported by Andy and Thayer [5].

NMR spectra were obtained on a JEOL FX-90Q operating at 22.49 MHz for carbon. Coupling constants were measured from the non-decoupled  $^{13}\text{C}$  spectrum and based on the reproducibility of the measurements are assumed to be correct to within 0.2 Hz. The  $\alpha$  and  $\beta$  carbons were assigned both on the basis of the coupling constants and the long-range coupling in the non-decoupled quartets.

## Results and discussion

Table 1 presents the  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts and  $^{13}\text{C}$ - $^1\text{H}$  coupling constants for the digermane derivatives and, for purposes of comparison, the values for the disilane analogs. Although the proton and carbon chemical shifts do not correlate well with measures of substituent effects, it is clear that there is a relationship between the coupling constants and the inductive effect of the substituent. It has been amply documented that the theoretical relationship between the  $^{13}\text{C}$ - $^1\text{H}$  coupling constant and *s*-character and effective nuclear charge [6] does in general lead to good Hammett-type correlations [7].

Correlations between a variety of substituent effect parameters [8] and the coupling constants are shown in Table 2. The inductive parameters clearly produce the best correlations. Of greatest interest to this investigation is the slope ( $\rho$ ) of these correlations for the disilane, digermane, and ethane series. The correlations are given for the same set of substituents and are in the order  $\text{C}-\text{C} > \text{Ge}-\text{Ge} > \text{Si}-\text{Si}$ . The same order was obtained for correlations of other sets of substituents; for example, exclusion of the  $\text{OC}_2\text{H}_5$  derivative increases  $R$  to 0.99 for the digermanes but results in similar slopes:  $M = \text{Ge}, 2.9; \text{Si}, 2.0; \text{C}, 3.4$ .

At least three factors can be used to rationalize the transmitting ability of a linkage: (1) the electrostatic field effect which depends upon the distance between the substituent and "reaction site", (2) the inductive effect which depends at least in

part on the polarizabilities of the intervening bonds, and (3) the interaction of substituents with silicon and germanium through ( $p-d$ ) $\pi$  bonding. This latter effect can operate when the substituent contains a lone pair of electrons and is generally thought to be more effective for silicon than germanium. The donation of electron density from a substituent such as chlorine to silicon would diminish the expected electron-withdrawing effect of the chlorine and result in an apparently decreased ability of silicon to transmit electrical effects. If these ( $p-d$ ) $\pi$  interactions were constant or proportional to the inductive effect of the substituent, they would not, however, result in a diminution of transmitting ability. On the other hand, if the ( $p-d$ ) $\pi$  interactions were not proportional to the inductive effect of the substituent, correlations with parameters such as  $\sigma$ , would not be good. Hence we are forced to conclude that on the basis of a somewhat limited set of substituents these interactions are not responsible for the observed order of transmitivities.

We can conclude, therefore, that silicon behaves as a poorer transmitter of electronic effects than carbon because of its greater size and decreased electrostatic field effects, whereas germanium is a better transmitter than silicon due to its greater polarizability and only slightly longer bond lengths [9].

TABLE 1  
CHEMICAL SHIFTS AND  $^{13}\text{C}$ - $^1\text{H}$  COUPLING CONSTANTS FOR  $(\text{CH}_3)_3\text{MM}(\text{CH}_3)_2\text{X}$

| X                              | $\delta(^1\text{H})$ (ppm) <sup>a</sup> |                                   | $\delta(^{13}\text{C})$ (ppm) <sup>a</sup> |                                   | $J(^{13}\text{C}-^1\text{H})$ , (Hz $\pm$ 0.2) |                                   |
|--------------------------------|---|-----------------------------------|--|-----------------------------------|--|-----------------------------------|
|                                | $(\text{CH}_3)_3\text{M}$               | $\text{M}(\text{CH}_3)_2\text{X}$ | $(\text{CH}_3)_3\text{M}$                  | $\text{M}(\text{CH}_3)_2\text{X}$ | $(\text{CH}_3)_3\text{M}$                      | $\text{M}(\text{CH}_3)_2\text{X}$ |
| <i>M = Ge</i>                  |   |                                   |  |                                   |  |                                   |
| CH <sub>3</sub>                | 0.21                                    | 0.21                              | -2.60                                      | -2.60                             | 125.7  | 125.7                             |
| Cl                             | 0.40                                    | 0.74                              | -2.49                                      | 4.49                              | 127.1  | 128.8                             |
| Br                             | 0.42                                    | 0.90                              | -2.30                                      | 4.55                              | 126.5  | 129.4                             |
| CN                             | 0.48                                    | 0.60                              | -2.30                                      | -3.33                             | 127.4  | 129.7                             |
| OC <sub>2</sub> H <sub>5</sub> | 0.30                                    | 0.37                              | -2.12                                      | 0.00                              | 126.5  | 126.5                             |
| <i>M = Si<sup>b</sup></i>      |   |                                   |  |                                   |  |                                   |
| CH <sub>3</sub>                | 0.02                                    | 0.02                              | -2.39                                      | -2.39                             | 119.5  | 119.5                             |
| Cl                             | 0.13                                    | 0.42                              | -2.92                                      | 2.12                              | 120.4  | 121.4                             |
| Br                             | 0.15                                    | 0.58                              | -2.98                                      | 1.93                              | 120.5  | 121.9                             |
| CN                             | 0.25                                    | 0.38                              | -  | -                                 | 120.7  | 122.8                             |
| OC <sub>2</sub> H <sub>5</sub> | 0.04                                    | 0.13                              | -2.01                                      | -0.76                             | 119.8  | 118.8                             |

<sup>a</sup> ppm from TMS, neat liquids for  $^1\text{H}$ , ca. 30% solutions in  $\text{CDCl}_3$  for  $^{13}\text{C}$ . <sup>b</sup> From ref. 1.

TABLE 2  
 $J(^{13}\text{C}-^1\text{H})$ ,  $\text{M}(\text{CH}_3)_3$ -INDUCTIVE PARAMETER CORRELATIONS<sup>a</sup>

|       | $\sigma_i$ |      | $\sigma^*$ |      | F      |      | $\sigma_m$ |      | $\sigma_p$ |      | $\sigma_R$ |      |
|-------|------------|------|------------|------|--------|------|------------|------|------------|------|------------|------|
|       | $\rho$     | R    | $\rho$     | R    | $\rho$ | R    | $\rho$     | R    | $\rho$     | R    | $\rho$     | R    |
| C-C   | 3.35       | 0.94 | 0.60       | 0.97 | 3.60   | 0.93 | 2.81       | 0.91 | 1.50       | 0.75 | 1.11       | 0.40 |
| Si-Si | 2.22       | 0.96 | 0.34       | 0.97 | 2.43   | 0.97 | 1.91       | 0.99 | 0.96       | 0.91 | 1.18       | 0.75 |
| Ge-Ge | 2.57       | 0.91 | 0.42       | 0.91 | 2.55   | 0.87 | 2.21       | 0.85 | 1.31       | 0.73 | 1.10       | 0.38 |

<sup>a</sup> Substituent constants taken from "best values" in ref. 7;  $\rho$  = slope of  $J = \rho\sigma + C$  line; R = correlation coefficient.

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