

^{29}Si AND ^{13}C -NMR CHEMICAL SHIFTS IN CROWDED BIS(TRIMETHYLSILYL)ETHENES*E. LIPPMAA^a, M. MÄGI^a, V. CHVALOVSKÝ^b and J. SCHRAML^b^a Institute of Cybernetics,

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Received June 15th, 1976

^{29}Si and ^{13}C -NMR chemical shifts are presented for the three isomers of bis(trimethylsilyl)ethene and they are compared with the shifts in vinyltrimethylsilane and in the carbon analogues. Methyl carbon chemical shifts in trimethylsilyl substituted ethenes parallel the trends in the shifts in the carbon analogues and together with the shift of the quaternary carbon in the tert-butyl substituted ethenes they exhibit paramagnetic steric shifts similar to those observed in other compounds containing such substituents in similar sterical arrangement. With the exception of *cis*-1,2-bis(trimethylsilyl)ethene, the silicon chemical shifts vary in trimethylsilyl substituted ethenes as the quaternary carbon shifts in tert-butyl substituted ethenes. In *cis*-1,2-bis(trimethylsilyl)ethene silicon shows diamagnetic steric shift but the silicon in 1,1-bis(trimethylsilyl)ethane is deshielded relative to vinylsilane. Using empirical correlations of olefinic carbon shifts it is demonstrated that both steric and electronic effects are important in bis(trimethylsilyl)ethenes and a consistent interpretation of the observed trends is offered.

Recently we studied¹ the effects of bulky substituents on the shieldings of ^{29}Si and ^{13}C nuclei in *ortho* substituted trimethylsilylbenzenes and found that crowding resulted in a deshielding of these nuclei, the effect being smaller for silicon and larger for carbon nuclei of the trimethylsilyl group. In the crowded molecules, aryl carbons showed¹ deviations from additivity. Since these findings are of considerable importance for stereochemical applications of ^{13}C and ^{29}Si -NMR we decided to investigate other structurally similar organosilicon compounds with the aim to find to what extent are the previously observed deshielding effects general for trimethylsilyl derivatives. Other cases of deshielding of sterically compressed carbons that have been lately reported (see *e.g.* ref.²⁻⁸ and references therein) usually involved the so-called δ (or longer distance) effects of other substituents.

Similarity of spatial relationships between substituents in *ortho* disubstituted benzenes and in *cis*-disubstituted ethenes has been recognized and utilized in NMR for a long time^{9,10}. So it was only natural to choose for the intended study bis(tri-

* Part CXLV in the series Organosilicon Compounds; Part CXLIV: This Journal 41, 2718 (1976).

methylsilyl)ethenes. Their $^1\text{H-NMR}$ spectra were described earlier^{11,12}. Such a study is also of interest in a connection with our current investigation of the spectra of Si-substituted vinylsilanes¹³.

Due to the shorter C—C bond length between olefinic than between aromatic carbon atoms one expects the steric interaction to be more acute in the ethene than in the benzene derivatives.

EXPERIMENTAL

All NMR spectra reported here were measured in neat liquids as described previously¹⁴. The only exception are the spectra of 1,1-bis(trimethylsilyl)ethylene which had to be measured in tetrachloromethane solution using FT mode as described elsewhere¹⁵. Preparation and properties of the studied compounds were described earlier¹¹.

RESULTS AND DISCUSSION

Listed in Table I are the ^{29}Si and ^{13}C chemical shifts in trimethylsilyl substituted ethenes and literature data for analogous carbon compounds.

Olefinic Carbons

In contrast to tert-butyl group, which upon the substitution of ethene increases the shielding of β carbon and decreases that of α carbon, substitution of ethene hydrogen atom by a trimethylsilyl group leads to a deshielding of both α and β carbons, the effect being larger on the α carbon. (This effect, which is apparently due to delocalization of ethene π -electrons onto the trimethylsilyl group, is discussed elsewhere¹³.) In accord with this observation introduction of the second substituent leads to a further deshielding in 1,2-bis(trimethylsilyl)ethenes though the observed shifts deviate considerably from those calculated according to the additivity rule. In 1,2-di-(tert-butyl)ethenes* the olefinic carbons are shielded less than the β carbon and more than the α carbon in the monosubstituted compound; the shift calculated according to the additivity rule agrees better with the shift observed in the *trans* isomer but, even there, the agreement is rather poor. Application of the additivity rule to 1,1-disubstituted ethenes predicts correctly the order of the chemical shifts but the deviations are rather large. It has been commented²⁰ that large deshielding is observed for the carbon bearing two bulky substituents, but as the additivity rule predicts even larger deshielding than observed, the deshielding is obviously not due to the crowding. Accidentally, application of the additivity rule leads to a 0.2 ppm

* In order to stress the similarity of the compounds 3,3-dimethyl-1-butene, 2,2,5,5-tetramethyl-3-hexene, and 2-tert-butyl-3,3-dimethyl-1-butene are called here tert-butylethene, 1,2-di-(tert-butyl)ethene, and 1,1-di(tert-butyl)ethene, resp.

difference between the chemical shifts of olefinic carbons in *trans*-1-trimethylsilyl-2-chloroethene. Such a small difference cannot be utilized for the assignment of the shifts.

In a recent communication²¹ several empirical correlations were described for olefinic carbon chemical shifts in 1,2-disubstituted ethenes. Thus, the differential shielding, $\bar{\Delta}$, between *cis* and *trans* isomers of symmetrically substituted 1,2-disubstituted ethenes can be predicted from the internal shift, Δ , of olefinic carbons in mono-substituted ethene according to the correlation shown on Fig. 1. In this correlation²¹, a positive deviation is observed for bulky tert-butyl group and negative deviations (smaller differential shielding than predicted) are found for substituents the first atoms of which are multiple bonded (CN and COOR groups). As it is apparent from Fig. 1 the point corresponding to the bulky trimethylsilyl group exhibits only a small negative deviation which is almost within the scatter around the correlation line and is definitely not in the same direction as that of tert-butyl group.

Owing to the mentioned spatial similarity, the olefinic carbon chemical shifts in *cis*-1,2-disubstituted ethenes, $\delta(\text{cis})$, correlate very well with the substituted carbon chemical shifts, $\delta(\text{C}_x)$, in *ortho*-disubstituted benzenes²¹. Fig. 2 shows that only the point corresponding to the trimethylsilyl derivative appreciably deviates from the regression line. It should be mentioned, however, that the data for the points corresponding to the substituent with negative deviations in Fig. 1 (CN and COOR) were not available, the point corresponding to the bulky tert-butyl group fits very well the correlation on Fig. 2. Deviations from additivity of the ring carbon chemical

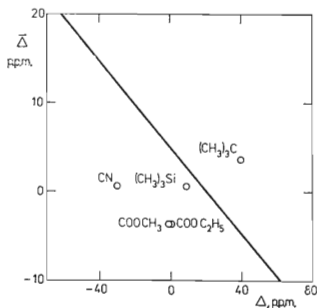


FIG. 1

Linear Correlation of the Differential Shielding, $\bar{\Delta}$, with the Internal Shift, Δ (The correlations taken from ref.²¹)

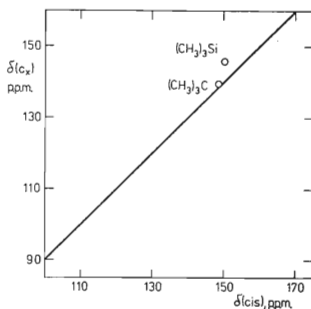


FIG. 2

Linear Correlation of $\delta(\text{cis})$ with $\delta(\text{C}_x)$ (The correlation taken from ref.²¹)

shifts are usually taken as indicating a steric strain in *ortho*-disubstituted benzene derivatives^{22,23}. Such deviations are 0.4 and 1.44 ppm for the substituent bearing carbons ($\delta(C_x)$) in *ortho*-bis(trimethylsilyl) and *ortho*-bis(tert-butyl)benzenes¹, resp. The considerably smaller value found for the trimethylsilyl derivative cannot be explained by longer silicon-aryl bond offsetting the larger van der Waals radius of silicon because in the analogous trimethyl tin compound (with a longer bond length and larger van der Waals radius) the deviation amounts to 1.3 ppm²⁴. Apparently some interplay of steric and electronic factors (and perhaps a ring distortion) compensates the steric shift of this carbon resonance in the trimethylsilyl benzene derivative. The deviation in Fig. 2 indicates that the spatial similarity between the corresponding fragments of *ortho*-disubstituted benzenes and symmetrically 1,2-disubstituted ethenes is distorted in the case of trimethylsilyl derivatives.

The largest deviations are also found for the trimethylsilyl derivatives in the correlation²¹ between the shifts of olefinic carbons in *cis*, $\delta(cis)$, and *trans*, $\delta(trans)$, isomers of 1,2-disubstituted ethenes (Fig. 3) and in the correlations²¹ of these shifts with the α carbon shifts in monosubstituted ethenes (Figs 4 and 5). In the latter case (Figs 4 and 5) again the deviations are in the same direction as those for carboxy and cyano derivatives but in the former one (Fig. 3) the deviation for the trimethylsilyl compounds is in the same direction as that of tert-butyl compounds, the two deviations being the only deviations noticeable in Fig. 3 (carboxy and cyano derivatives fit the regression line well).

If one assumes that the described deviations of the tert-butyl derivatives are due to the sterical crowding and those of the cyano or carboxy derivatives are caused by electronic interactions of ethene π electrons with substituents multiple bonds then the directions of the deviations can be interpreted as follows. Correlation of $\delta(trans)$ versus $\delta(cis)$ (Fig. 3) is insensitive to the electronic effects (which are,

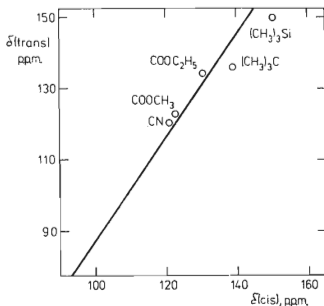


FIG. 3

Linear Correlation of $\delta(trans)$ with $\delta(cis)$ (The correlation taken from ref. 21)

perhaps, of similar magnitude in the two isomers) and hence, the deviation of the point corresponding to the tert-butyl derivatives is caused by a steric paramagnetic shift in the *cis* derivative and similarly is paramagnetically shifted the olefinic carbon in *cis*-1,2-bis(trimethylsilyl)ethene. The correlations on Figs 4 and 5 are apparently more sensitive to the electronic than to sterical effects, the deshielding of olefinic carbons in 1,2-dicyano and 1,2-dicarboxy substituted ethenes below the shift that should be observed in these compounds according to the regression line could be explained by a delocalization of ethene π electrons, resulting in an additional decrease of electron density below that corresponding to additive substituent effects. Similar deviations of trimethylsilyl derivatives can then be ascribed to a delocalization of the electrons either into the vacant $3d$ silicon orbitals or to other low-lying unoccupied orbitals. In the case of the correlation sensitive to both effects (Fig. 1), the electronic effects appear to dominate the shifts of olefinic carbons in bis(trimethylsilyl)derivatives which fact is in accord with larger magnitude of the deviations assigned to this effect (compare the deviations on Figs 4 and 5 with those in Fig. 3).

The correlations with the Q parameter²¹ yield different Q values for the trimethylsilyl group depending upon which of the chemical shift correlations²¹ is employed (*i.e.* Q values of 0.2 and 1.0 are obtained from the correlations²¹ of $\delta(\textit{cis})$ and $\delta(\textit{trans})$, resp., values 1.7 and 3.6 follow from carbon chemical shifts in monosubstituted ethene while the proton shifts^{9,25} yield the value 2.9). Such a spread of Q values is observed²¹ also for CN, COCH₃, CHO and NO₂ groups and is to be expected¹⁰ for substituents lacking quasicylindrical symmetry when conformational effects are important.

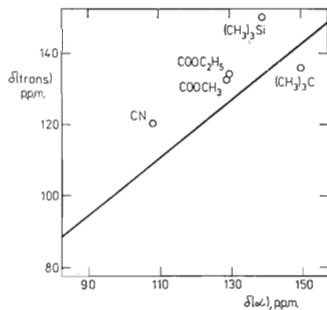


FIG. 4

Linear Correlation of $\delta(\textit{trans})$ with $\delta(\alpha)$
(The correlation taken from ref.²¹)

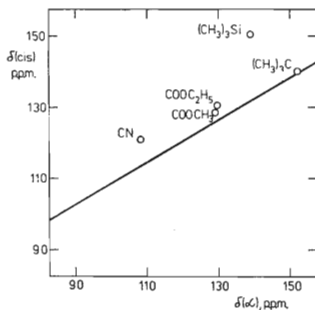
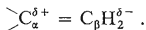


FIG. 5

Linear Correlation of $\delta(\textit{cis})$ with $\delta(\alpha)$ (The correlation taken from ref.²¹)

The internal chemical shift $\Delta = \delta(C_\alpha) - \delta(C_\beta)$ was suggested²⁶ as a measure of a double bond polarization in the sense



Assuming that other factors remain constant, increased polarization should increase the Δ value²⁶. It might be argued, in view of the detailed study¹⁷ of the relationship between the carbon chemical shifts and electronic densities in monosubstituted ethenes, that the suggestion²⁶ is oversimplifying (especially if the substituents are σ electron acceptors and at the same time π electron donors). Despite this reservation, a comparison of the internal chemical shifts caused by tert-butyl and trimethylsilyl groups shows different effects of these groups. Thus the first tert-butyl group causes the internal shift of 40.0 ppm in tert-butyl ethene (as compared to null internal shift in ethene), the second tert-butyl group in 1,1-di(tert-butyl) ethene enhances this internal shift to 55.2 p.p.m., the sign of the internal shifts being in accord with the inductive effect of tert-butyl group (electron donation). In trimethylsilylethene the internal shift is much smaller, 9.1 ppm, and of the same sign as that of tert-butyl group; with two trimethylsilyl groups in 1,1-bis(trimethylsilyl)ethene the internal shift becomes even smaller, only 5.3 ppm (the same sign). One can speculate that in trimethylsilylethene the inductive effect of silicon is partially compensated by π electron withdrawal and that such a compensation is even more effective in 1,1-bis(trimethyl)silylethene. The difference between the internal chemical shifts of silicon and analogous carbon compounds are too large to be caused by sterical effects.

Interpretation of ¹H-NMR spectra^{11,12,27} of bis(trimethylsilyl)ethenes encountered with a difficulty because additivity was well observed in these spectra. It was not clear²⁷ how can each of the two trimethylsilyl groups have the same effect as the single group has upon the olefinic proton shielding in trimethylvinylsilane²⁵ in which the deshielding was ascribed²⁵ to a transfer of π electrons into silicon 3d orbitals. Apparently carbon shieldings are more sensitive to these effects as in their spectra the deviations from additivity are large. It is worth mentioning, however, that the observed carbon shifts are more paramagnetic than calculated (in 1,2-derivatives). This fact would imply enhanced delocalization in 1,2-disubstituted ethenes relative to the monosubstituted ethene.

Methyl Carbons

Methyl carbons are, next to methyl protons, most exposed to the sterical crowding. In disubstituted ethenes the crowding increases in the order *trans*-1,2- \ll *cis*-1,2- $<$ $<$ 1,1-isomer. In parallel to the increasing crowding we see increasing deshielding of the methyl carbons both in tert-butyl ($\delta = 30.0, 32.46$ and 32.5 , resp.) and trimethylsilyl ($\delta = -1.7, -0.7$, and -0.26 resp.) substituted ethenes, but the difference between *cis* and *gem* isomers is small. In ¹H-NMR spectra, however, the

deshielding of methyl protons increases in the series¹¹ *trans*-1,2 < 1,1- < *cis*-1,2. As the methyl carbon chemical shift in *trans*-1,2-bis(trimethylsilyl)ethene differs only by 0.1 ppm from the shift of the corresponding carbon in *trans*-1-trimethylsilyl-2-chloroethene and by 0.5 from the shift in trimethylsilylethene this carbon appears insensitive to substituent effects and it seems that the deshielding of the *cis* isomer relative to the *trans* isomer is almost entirely due to the steric effect. The same cannot be ascertained for the deshielding observed in 1,1-derivatives. In our studies^{14,28-31} we saw that the methyl carbon shifts varied only little in fragments (CH₃)₃SiCH₂Y (for 1 = CH₃, C₆H₅, OH, Cl, NH₂, and F the total range of δ was from -3.0 to -4.4) but in the present work we are concerned with a transmission over a *sp*² carbon atom. Bartuska and Maciel³² reported a variation of 8.4 ppm for the methyl carbon chemical shift in a series of H₂C=C(X)CH₃ compounds with a number of substituents X. Though the variation of the shifts in compounds considered here would certainly be smaller, contributions of other than steric effects cannot be estimated.

Silicon and Quarternary Carbon

As it is apparent from Table I the shielding of the quarternary carbon is remarkably decreased only in geminal isomer. It has been show here that in the last mentioned

TABLE I
²⁹Si and ¹³C-NMR Chemical Shifts in Ethene Derivatives^a

| Substituent | $\delta(^{29}\text{Si})$ | $\delta(^{13}\text{C})$ | | | | | |
|---|--------------------------|-------------------------|-----------|--------------------|-------------------------|--------------------|-------------------------|
| | | CH ₃ | C (quart) | C-1 (obs) | C-1 (calc) ^b | C-2 (obs) | C-2 (calc) ^b |
| — | — | — | — | 122.8 ^c | — | 122.8 ^c | — |
| 1-Si(CH ₃) ₃ | - 7.6 | -2.2 | — | 139.0 | — | 129.9 | — |
| <i>trans</i> -1,2-(Si(CH ₃) ₃) ₂ | - 8.9 | -1.7 | — | 150.0 | 146.1 | 150.0 | 146.1 |
| <i>cis</i> -1,2-(Si(CH ₃) ₃) ₂ | - 11.8 | -0.7 | — | 150.5 | 146.1 | 150.5 | 146.1 |
| 1,1-(Si(CH ₃) ₃) ₂ | - 3.11 | -0.26 | — | 145.03 | 155.2 | 139.71 | 137.0 |
| 1-Si(CH ₃) ₃ , 2-Cl | - 6.9 | -1.8 | — | 138.3 ^d | 132.5 ^e | 132.2 ^d | 132.3 ^e |
| 1-(C(CH ₃) ₃) ^f | — | 28.7 | 33.0 | 148.9 | — | 108.5 | — |
| <i>trans</i> -1,2-(C(CH ₃) ₃) ^g | — | 30.00 | 32.34 | 135.78 | 134.6 | 135.78 | 134.6 |
| <i>cis</i> -1,2-(C(CH ₃) ₃) ^g | — | 32.46 | 32.76 | 139.35 | 134.6 | 139.35 | 134.6 |
| 1,1-(C(CH ₃) ₃) ₂ ^h | — | 32.5 | 37.5 | 163.8 | 175.0 | 108.6 | 94.2 |

^a All chemical shifts are in δ scale (*i.e.* in p.p.m. relative to tetramethylsilane, positive values for paramagnetic shifts); ^b values calculated according to the direct additivity rule; ^c value taken from ref. ¹⁶; ^d assignment uncertain; ^e calculated using the data of ref. ¹⁷; ^f values converted from ref. ¹⁸ using $\delta(\text{CS}_2) = 193.1$; ^g values taken from ref. ¹⁹; ^h values taken from ref. ²⁰.

isomer large deviations from additivity occurred for olefinic carbons. It seems very likely that in this compound the steric strain is relieved by some deformations which effect most the shift of olefinic and quaternary carbons, while those of methyl group are affected only little. (For comparison, quaternary carbons in neopentane and 2,2,4,4-tetra-methylpentane occur at $\delta = 28.0$ and 32.4 , resp.³³.)

While the trends in methyl carbon shifts in trimethylsilyl derivatives of ethene paralleled the trends of corresponding carbons in tert-butyl derivatives and while in benzene derivatives also the trends in the silicon shielding paralleled those of corresponding quaternary carbons¹, in ethene derivatives silicon behaves differently. In *trans*-1,2-bis(trimethylsilyl)-ethene silicon is more shielded than in vinyltrimethylsilane. Such an increase in the shielding is in harmony with the simultaneous decrease of olefinic carbon shielding discussed above. But as there is no practical change in olefinic carbon shielding when going from the *trans* to the *cis* isomer the large increase in the silicon shielding in the *cis* isomer seems to be due to steric effect.

Diamagnetic steric shift of silicon in the *cis* isomer is difficult to understand in view of the paramagnetic steric shifts in benzene *ortho* derivative but the structural distortions indicated above by the deviation in Fig. 2 offer a possible interpretation.

In 1,1-bis(trimethylsilyl)ethene the silicon is shielded even less than in vinyltrimethylsilane as if the crowding led to a deshielding of the silicon similarly as it does in benzene derivatives¹ or of carbons in carbon analogues. Obviously, electronic interactions are also important in this case. As in bis(trimethylsilyl)methane the silicon is only slightly deshielded³⁴ (by 0.5 ppm) relatively to tetramethylsilane, the large deshielding in 1,1-bis(trimethylsilyl)ethane involves interactions with ethene electrons. It is assumed¹³, and the present results seem to support such a view, that the silicon shielding in silylethenes is due to the delocalization of ethene electrons towards the silicon atom. It would seem rather unlikely that the charge supplied to each of the two silicon atoms attached to the same carbon atom is equal to that supplied to one silicon atom in vinyltrimethylsilane.

The above considerations are, of course, of speculative nature, they should be supported by precise molecular structure determinations which are not available now. Unfortunately, the study³⁵ of other spectra and properties of these compounds did not provide data for all the isomers.

The authors are grateful to Dr G. Engelhardt, Academy of Science, DDR Berlin, for the measurements of 1,1-bis(trimethylsilyl)ethene.

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Translated by the author (J. S.).