Journal of Organometallic Chemistry, 192 (1980) 319—327
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^{29}Si AND ^{13}C NMR STUDIES OF ORGANOFUNCTIONAL DI- AND TRISILANES

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(Received December 5th, 1979)

Summary

A series of di- and trisilanes of general structure $Ph_3SiSiMe_2R$ and $(Ph_3Si)_2SiR'R''$ were synthesized, and the ^{29}Si and ^{13}C chemical shifts and one-bond silicon—silicon coupling constants ($^1J_{SiSi}$) were measured. The coupling constants of the disilanes were found to be primarily dependent upon the inductive effect of the alkyl group, R, as measured by the Taft σ^* constant. In both series of compounds, increasing alkyl substitution at silicon led to a decrease in $^1J_{SiSi}$.

Although the widespread availability of multinuclei Fourier transform (FT) NMR spectrometers has resulted in a substantial increase in reports of silicon-29 chemical shifts [1], to date there has been only one report of coupling between directly bonded silicon nuclei [2] and only one other report of a longer range silicon—silicon coupling constant [3]. In an earlier paper we studied the effect on $^1J_{SiSi}$ of substituents of widely varying electronegativity by examining a series of substituted disilanes, $Me_3SiSiMe_2X$, as well as some polysilanes [2]. A good correlation was found between $^1J_{SiSi}$ and the sum of the substituent electronegativities in these systems. We now wish to report the synthesis of a series of organo substituted di- and trisilanes which contain no highly electronegative groups, and for which the ^{29}Si and ^{13}C chemical shifts and one bond silicon—silicon coupling constants were measured.

Experimental

All carbon-13 NMR spectra were obtained on a Varian CFT-20 (20 MHz for ^{13}C), FT-80A (20 MHz for ^{13}C) or XL-100-15 NMR spectrometer (25.2 MHz for ^{13}C). Silicon-29 NMR spectra were produced on a Varian XL-100-15 spectrometer operating in the Fourier Transform (FT) mode at 19.9 MHz. All spectra were run with complete proton decoupling except in a few cases where off-resonance decoupling was required to facilitate assignments in the ^{13}C spectra. A small amount of $Cr(acac)_3$ was added to each silicon-29 sample to shorten spin lattice relaxation times (T_1) and partly suppress the negative nuclear Overhauser effect (NOE). Typical parameters for a silicon-29 spectrum included a 1000 Hz spectral width (8 K data points), pulse width corresponding to a 45° flip angle and a total repetition time of 4 s. Deuterated solvents (acetone or chloroform) served as internal lock and Me_4Si as internal standard. All chemical shifts are reported relative to Me_4Si with positive values to lower field.

The compounds used in this study were prepared according to the literature procedure of Gilman et al. [4] in which an equivalent amount of triphenylsilyllithium is added to the appropriate chlorosilane. Satisfactory elemental analysis (C, H, Si) were obtained for all compounds except $Ph_3SiSiMe_2$(n-octyl), $Ph_3SiSiMe_2CH{=}CH_2$ and $Ph_3SiSiMe_2Ph$ whose structures were confirmed by mass spectrometry and their characteristic ^{29}Si NMR spectra. Melting points and analytical data were as follows:

$Ph_3SiSiMe_2$(n-Pr): m.p. 67—68°C. Found: C, 76.3; H, 7.9; Si, 16.0, $C_{23}H_{28}Si_2$ calcd.: C, 76.6; H, 7.8; Si, 15.6%.

$Ph_3SiSiMe_2$(i-Pr), m.p. 46.5—48.0°C; Found: C, 76.4; H, 7.9; Si, 15.8, $C_{23}H_{28}Si_2$ calcd.: C, 76.6; H, 7.8; Si, 15.6%.

$Ph_3SiSiMe_2$(t-Bu), m.p. 82.5—83.0°C, Found: C, 77.0; H, 8.2; Si, 15.2. $C_{24}H_{30}Si_2$ calcd.: C, 76.9; H, 8.1; Si, 15.0%.

$(Ph_3Si)_2SiMe_2$, m.p. 216.0—217.5°C, Found: C, 79.3; H, 6.6; Si, 14.8, $C_{38}H_{36}Si_3$ calcd.: C, 79.1; H, 6.3; Si. 14.6%.

$(Ph_3Si)_2SiMe$(n-Pr), m.p. 141.5—143.0°C, Found: C, 79.4; H, 6.7; Si, 14.0, $C_{40}H_{40}Si_3$ calcd.: C, 79.4; H, 6.7; Si, 14.0%.

$(Ph_3Si)_2SiEt_2$, m.p. 151.0—152.5°C, Found: C, 79.2; H, 6.9; Si, 14.2, $C_{40}H_{40}Si_3$ calcd.: C, 79.4; H, 6.7; Si, 14.0%.

$(Ph_3Si)_2Si(CH_2)_4$, m.p. 207.5—208.5°C, Found: C, 79.8; H, 6.3; Si, 13.6, $C_{40}H_{38}Si_3$ calcd.: C, 79; H, 6.3; Si, 14.0%.

$(Ph_3Si)_2Si(CH_2)_5$, m.p. 181.0—182.0°C, Found: C, 79.5; H, 6.8; Si, 13.5, $C_{41}H_{40}Si_3$ calcd.: C, 79.8; H, 6.5; Si, 13.6%.

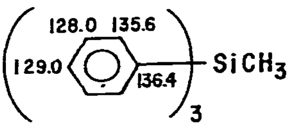
$Ph_3SiSiMe_2Ph$, m.p. 82.5—84.0°C, *m/e* 394 (field desorption mass spectrometry).

$Ph_3SiSiMe_2CH{=}CH_2$, *m/e* 344 (field ionization mass spectrometry)

$Ph_3SiSiMe_2$(n-Oct), *m/e* 431 (chemical ionization mass spectrometry)

Results and discussion

The ^{13}C and ^{29}Si NMR data are collected in Table 1. The ^{13}C chemical shifts of the phenyl ring carbons on Si^A differ by less than 2 ppm for each carbon in the entire series of compounds, and are relatively insensitive to the remote alkyl groups at Si^B. Moreover, the data for a series of phenylsilanes, $PhSiMe_nPh_{3-n}$ have been reported [5], and comparison with the data for the compounds examined in this study shows that no unusual substituent effects occur in the phenyl ring from the silicon—silicon bond. The chemical shifts of methyltriphenylsilane, for example, are very similar to the values found for 1—3.



Assignments of the ^{13}C resonances of the various R groups were made using known alkyl shielding parameters [6] and the off-resonance decoupling technique where necessary. Silicon shieldings of 1b—e were assigned by analogy to 1a; chemical shifts of appropriate model compounds were used to assign 1f and 1g. Compounds in the series 2 and 3 were easily assigned based upon intensity differences (in samples containing $Cr(acac)_3$) of Si^A and Si^B.

The total range of ^{29}Si shifts for Si^A in 1—3 is less than 5 ppm, and is very small (0.4 ppm) within the series 1a—e in which the alkyl substituents comprise the only difference in structure. The substituent effects of R, R′ and R″ are, not surprisingly, much larger at Si^B to which they are directly attached. Several interesting features of the chemical shift changes are apparent. First, replacement of a methyl substituent with a triphenylsilyl group at Si^B has a shielding effect of ca. 18 ppm for the first substituent (1a relative to Me_4Si), and ca. 27 ppm for the second (compare 1a with 2a, and 1b with 2b). These values are very close to those found for successive substitution of a trimethylsilyl group in the series Me_4Si, $(Me_3Si)_2$, $(Me_3Si)_2Si^*Me_2$ (δ_{Si} = 0, —19.6 and —48.5 ppm, respectively), and suggest that the electronic effects of Ph_3Si and Me_3Si are quite similar. This shielding effect at Si^B is accompanied by a corresponding shielding.(ca. 2 ppm) of the alkyl carbons attached to Si^B in 2a and 2b, and a deshielding effect at Si^A (ca. 3 ppm). Secondly, incorporating Si^B into a five-membered ring (3b) has a deshielding effect of 14 ppm relative to δ_{Si^B} in the six-membered homologue 2a. This chemical shift trend, which has been attributed to ring strain, was previously noted by Lauterbur for cyclic siloxanes [7] and is also evident in the data for some five- and six-membered silacyclic compounds examined by Scholl et al. [8]. Finally, the series 1a—e and 2a—c show the effects on the ^{13}C and ^{29}Si chemical shifts of increasing chain length and branching in the alkyl substituents. A progressive deshielding of Si^B occurs from R = Me to R = t-Bu, for which a rather rough correlation ($r = 0.91$) between the Taft polar substituent constants (σ^*) of R and δ_{Si^B} was found (Figure 1). This correlation is found only for the alkyl derivatives, and 1f and 1g, for example, do not fall on the line in Figure 1. The trend noted for 1a—e is repeated in the trisilanes, 2. A shielding effect, however, was found for both δ_C(Me) and δ_{Si^A} (although the t-butyl derivative (1e) was exceptional for both). It is interesting to note that the changes at Si^A and the methyl carbons are parallel to each other, and oppose the changes at Si^B.

Variations in alkyl groups have been examined for their effect on silicon chemical shifts in trialkylsilanes (R_3SiH) [10] and tin chemical shifts in hexaorganoditin and octaorganotritin compounds [11]. In each study, δ_M (M = Si or Sn) did not vary monotonically with increasing chain length of R, but oscillated about a particular value. This alternation in chemical shift change decreased with increasing chain length in the straight chain alkyl groups, and no correlation with alkyl group electronegativity (as measured by σ^*) was noted. In both of these studies, however, three alkyl groups at M were varied simultaneously, whereas in the disilanes examined here only one alkyl group was varied. The variations in δ_{Si^B} for 1a—e are not inconsistent with the observation that alkyl shielding parameters similar to those proposed for ^{13}C shifts may be useful for predicting silicon shieldings [10]. We are currently preparing some triphenyl trialkyl disilanes (Ph_3SiSiR_3) to determine the extent

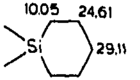
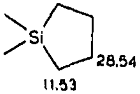
(Continued on p. 324)

TABLE 1

^{13}C AND ^{29}Si CHEMICAL SHIFTS AND SILICON—SILICON COUPLING CONSTANTS FOR SOME DI- AND TRISILANES [a]

$Ph_3Si^ASi^BMe_2R$ (1)	δ_{Si}		$^1J_{SiSi}$	$\delta_C(C_6H_5)$				δ_C(Other)	
R	A	B		C_i	C_o	C_m	C_p	CH_3	R
a) Me [b]	−20.22	−18.37	86.5	136.40	136.40	128.80	129.88	−0.87	
b) n-Pr	−20.36	−17.05	85.3	135.66	135.24	127.89	128.91	−2.79	$\delta_1 = 17.77$ [c] $\delta_2 = 18.17$ $\delta_3 = 18.25$
c) n-Oct	−20.51	−16.81	84.5	135.79	136.03	127.94	128.93	−2.68	$\delta_1 = 16.77$ [c] $\delta_2 = 24.43$ $\delta_3 = 33.65$ $\delta_4 = \delta_5 = 29.26$ $\delta_6 = 32.00$ $\delta_7 = 22.71$ $\delta_8 = 14.11$
d) i-Pr	−20.60	−11.92	81.5	136.01	136.01	127.88	128.90	−4.51	14.00 (CH) 18.60 (CH_3)
e) t-Bu	−20.37	−7.95	80.0	135.84	136.08	127.73	128.79	−3.91	18.34 (C) 28.06 (CH_3)
f) $CH{=}CH_2$	−21.28	−24.70	86.2	135.04	135.71	127.66	128.80	−3.12	138.09 (=CH) 132.08 (=CH_2)
g) Ph	−21.41 [d]	−21.84 [d]	[e]	135.04	136.08	127.88	129.05	−2.25	138.33 (C_i) 134.38 (C_o) 127.68 (C_m) 128.66 (C_p)

$(Ph_3Si^A)_2Si^BR'R''$ (2)		δ_{Si}		$^1J_{SiSi}$	$\delta_C(C_6H_5)$				δ_C(Other)	
R′	R″	A	B		C_i	C_o	C_m	C_p	R′	R″
a) Me	Me	−17.02	−45.90	74.5	136.54	136.32	128.99	127.85	−2.02	
b) Me	n-Pr	−17.60	−42.71	72.2	134.50	135.55	127.50	128.72	−5.28	$\delta_1 = 15.81$ [c] $\delta_2 = 18.84$ $\delta_3 = 18.15$
c) Et	Et	−18.10	−34.14	70.3	135.51	136.40	127.78	128.88		4.66 (CH_2) 10.09 (CH_3)

$(Ph_3Si^A)_2\overline{Si^B(CH_2)_n}$ (3)	δ_{Si}		$^1J_{SiSi}$	$\delta_C(C_6H_5)$				δ_C(Other)
	A	B		C_i	C_o	C_m	C_p	
a) $n = 5$	−18.40	−48.63	70.8	135.31	136.47	127.77	128.93	
b) $n = 4$	−16.79	−34.84	69.8	135.07	136.35	127.81	129.01	

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[a] Chemical shifts are given in ppm (±0.05) relative to Me_4Si. Positive values are downfield. Coupling constants are in Hz (±0.3). Data for **1a** and **1f** were obtained in acetone-d_6, the rest were obtained in $CDCl_3$. [b] Ref. 2. [c] The numbering starts at the carbon atom directly attached to silicon. [d] May be reversed. [e] Obscured.

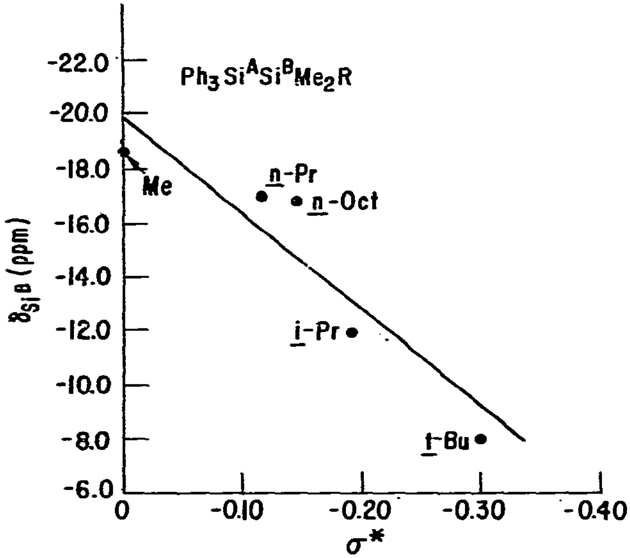

Fig. 1. Plot of δ_{Si^B} vs σ^* of R for 1a—e. Values of σ^* were taken from ref. 9. The value for R = n-heptyl was used for R = n-octyl.

of the correlation between δ_{Si^B} and σ^*.

None of the compounds examined in this study gave first-order silicon spectra. One bond silicon—silicon coupling constants were determined from all four ^{29}Si satellites of the AB pattern except for compounds 1b and 1c which gave spectra with only the inner two satellites visible. The coupling constants of 1—3 cover a relatively small range (ca. 18 Hz).

The effects on $^1J_{SiSi}$ of both vinyl and phenyl substituents appear to be approximately the same as that of methyl. Although $^1J_{SiSi}$ of 1a was obscured, the values for 1f (86.2 Hz), Ph$_3$SiSiMe(CH=CH$_2$)(Ph) (86.7 Hz, ref. 12) and Me$_3$SiSiMe$_2$Ph (86.1 Hz, ref. 2) are very close. Likewise, the values for 3a and 3b are quite close which indicates that there is no major effect on $^1J_{SiSi}$ from incorporating one silicon atom in a 5-membered ring. $^1J_{SiSi}$ of 1a—e gave a rough correlation (r = 0.92) with σ^* (Figure 2), with the trisilanes (2) also following this trend (see insert in Figure 2). A much better correlation (r = 0.98) between $^1J_{SiSi}$ and δ_{Si^B} in 1a—e was found, however (Figure 3). This is in contrast to prior studies which showed a very poor correlation between $^1J_{SiC}$ and δ_{Si} in trimethylsilyl compounds [13], and no correlation between $^1J_{SiSi}$ and δ_{Si^A} or δ_{Si^B} in pentamethyldisilanyl compounds [2]. Both of these studies involved substituents covering a wide range of electronegativities. Apparently, within the closely related series 1a—e, both $^1J_{SiSi}$ and δ_{Si^B} are responding to the same factors which may be roughly approximated by σ^* (the inductive effect of R). These results closely parallel those obtained by Mitchell and Walter [11] for $^1J_{Sn_nSn}$ in distannanes. A value of σ^* for Ph$_3$Si (—0.55) may be extrapolated from Figure 2 using $^1J_{SiSi}$ for 2a. If this value is used to calculate σ^* for 2b and 2c, the plot shown in Figure 4 may be drawn.

The decrease in coupling constant with increasing electron releasing ability of the alkyl group suggests that the effective nuclear charge at silicon is the

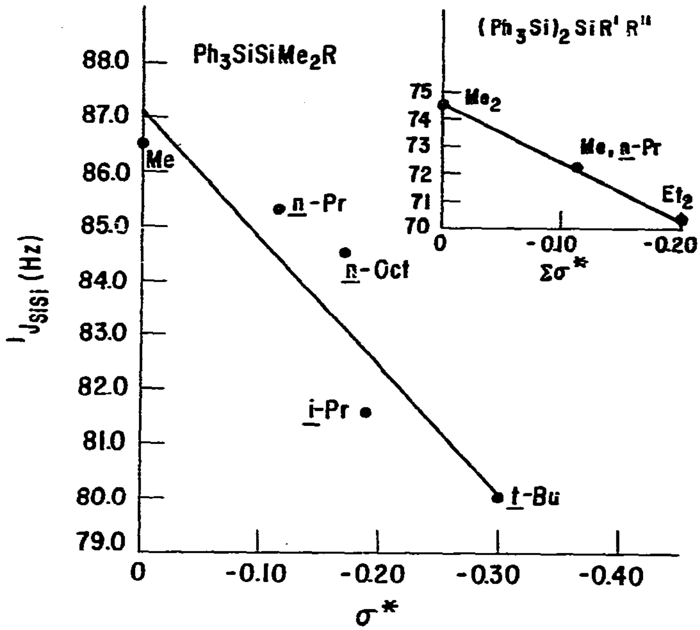

Fig. 2. Plot of ${}^1J_{SiSi}$ vs. σ* for 1a—e and 2 (insert).

main factor in determining ${}^1J_{SiSi}$ in these compounds. This is consistent with the assumption of dominance of the Fermi contact term in the theoretical expression for silicon—silicon coupling constants. Although substituents of widely varying electronegativity produce little or no correlation between

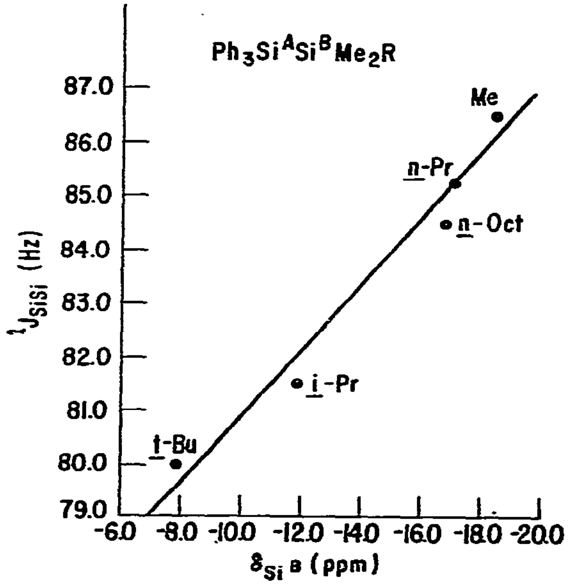

Fig. 3. Plot of ${}^1J_{SiSi}$ vs. δ_{SiB} for 1a—e.

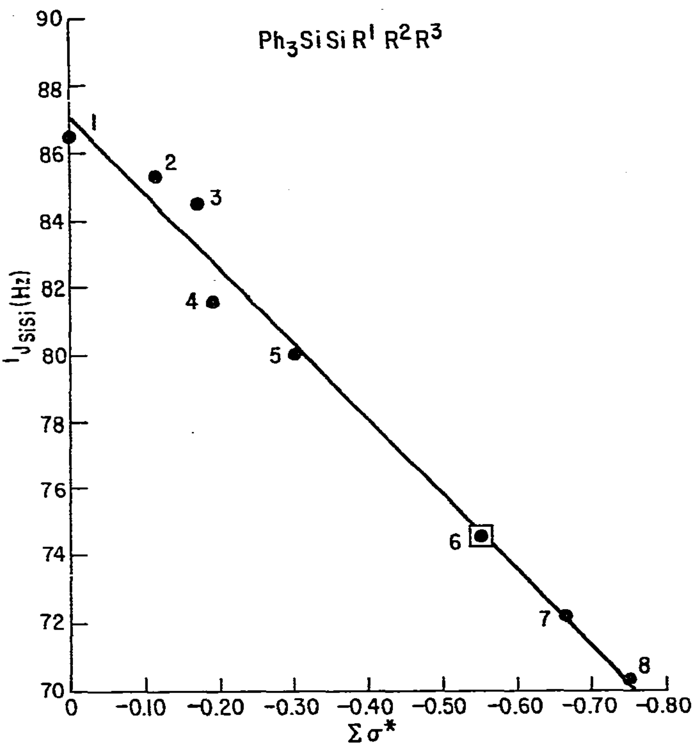

Fig. 4. Plot of $^1J_{SiSi}$ vs. σ^* for 1a—e and 2. The value of σ^* for $Si(C_6H_5)$ was extrapolated from Figure 2 (see text). The numbers are: 1, $R^1 = R^2 = R^3$ = Me (1a); 2, $R^1 = R^2$ = Me, R^3 = n-Pr (1b); 3, $R^1 = R^2$ = Me, R^3 = n-Oct (1c); 4, $R^1 = R^2$ = Me, R^3 = i-Pr (1d); 5, $R^1 = R^2$ = Me, R^3 = t-Bu (1e); 6, $R^1 = R^2$ = Me, R^3 = $SiPh_3$ (2a); 7, R^1 = Me, R^2 = n-Pr, R^3 = $SiPh_3$ (2b); 8, $R^1 = R^2$ = Et, R^3 = $SiPh_3$ (2c).

$^1J_{SiSi}$ and δ_{Si}, within a series of compounds limited to changes only in alkyl substituents a good linear relationship was observed. The general trends observed for $^1J_{SiSi}$ parallel those observed for $^1J_{SnSn}$ in analogous stannanes [11].

Acknowledgment

The authors wish to thank Ms. Marsha Thigpen for preparing some of the disilanes used in this study. We also thank Dr. W.V. Ligon, Mr. H. Grade and Mrs. N. Marotta for the mass spectra and elemental analyses.

References

1 J. Schraml and J.M. Bellama in F.C. Nachod, J.J. Zuckerman and E.W. Randall (Eds.), Determination of Organic Structure by Physical Methods, Vol. 6, Academic Press, New York, 1976, Chapter 4; R.K. Harris, "NMR and the Periodic Table", R.K. Harris and B.E. Mann, Eds., Academic Press, New York, 1978, pp. 309—340; E.A. Williams and J.D. Cargioli in Annual Reports on NMR Spectroscopy, G.A. Webb, (Ed.), Vol. 9, Academic Press, London, 1979, pp. 221—318.
2 K.G. Sharp, P.A. Sutor, E.A. Williams, J.D. Cargioli, T.C. Farrer and K. Ishibitsu, J. Amer. Chem. Soc., 98 (1976) 1977.
3 R.K. Harris and B.J. Kimber, J. Magn. Reson., 17 (1975) 174.
4 H. Gilman, D.J. Peterson and D. Wittenberg, Chem. and Ind., (1958) 1479.

5 Nguyen-Duc-Chuy, V. Chvalovsky, J. Schraml, M. Magi and E. Lippmaa, Coll. Czech. Chem. Commun., 40 (1975) 875.
6 J.B. Stothers, Carbon-13 NMR Spectroscopy, Academic Press, New York, 1972, p. 58.
7 P.C. Lauterbur in G.C. Nachod and W.D. Phillips (Eds.), Determination of Organic Structure by Physical Methods, Vol. 2, p. 465, Academic Press, New York, 1962.
8 R.G. Scholl, G.E. Maciel and W.K. Musker, J. Amer. Chem. Soc., 94 (1972) 6376.
9 L.S. Levitt and H.F. Widing, Prog. Phys. Org. Chem., 12 (1976) 119.
10 R.K. Harris and B.J. Kimber, Adv. Mol. Relax. Proc., 8 (1976) 17.
11 T.N. Mitchell and G. Walter, J. Chem. Soc., Perkin II, (1977) 1842.
12 E.A. Williams, J.D. Cargioli and P.E. Donahue, unpublished results, 1978.
13 R.K. Harris and B.J. Kimber, J. Magn. Reson., 17 (1975) 174.