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Spectroscopic and AM1 semiempirical studies of vibrations of tris(trimethylsilyl)silane derivatives, $(Me_3Si)_3SiX$ ($X = H, Cl, OH, OD, Me, OMe, SiMe_3$)

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Abstract

The title compounds were synthesized and characterized. The vibrational frequencies of $(Me_3Si)_3SiX$ ($X = H, Cl, OH, OD, Me, OMe, SiMe_3$) were determined by means of IR and Raman spectroscopy. Based on our AM1 semiempirical calculation and the literature group frequencies of CH_3, Me_3Si, $SiSi_3$, SiX ($X = H, Cl, OH, OD, CH_3, OCH_3$) have been assigned. The intensities of the Raman lines of the stretching vibrations of $(Me_3Si)_3Si{-}X$ ($X = Cl, OH, OMe$) and $(Me_3Si)_3SiO{-}H$ are very low compared with those of the IR lines. This indicates that the bonds have a strong ionic nature.

Introduction

Silanols have been the subjects of a number of theoretical [1,2] and experimental [3,4] investigations. The simplest silanol H_3SiOH, silicon analog of methanol is unstable toward disproportionation and has never been isolated [5], but the molecule has been investigated by *ab initio* methods [1,2]. The polysilanol compound $(Me_3Si)_3SiOH$, ≡SiOH (note that the sign ≡ means $(Me_3Si)_3$) is, however, quite stable since the molecule contains three large trimethylsilyl groups. This compound was reported to be synthesized earlier by Gilman and Harrell [3]. Using the reported method [3], the hydrolysis of ≡SiCl with aqueous tetrahydrofuran, the conversion of ≡SiCl to ≡SiOH was not possible in our laboratory [6*]. Also,

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* Reference number with an asterisk indicates a note in the list of references.

Table 1

Vibrational frequencies (cm^{-1}) for $(Me_3Si)_3SiH$ derived by the AM1 method and measured by IR and Raman

Approximate type of mode	AM1 [a]	This work		Literature [b]	
		IR	Raman	IR	Raman
CH_3 str.	3170	2955(vs)	2948(vs)	2956(s)	2951(vs)
	3069	2893(s)	2892(vs)	2900(m)	2897(vs)
Si–H str.	2212	2052(s)	2048(s)	2051(s)	2049(vs)
CH_3 deform.	1397	1439(m)	1434(vw)	1443(m)	1443(vw)
		1404(m)	1404(w)	1400(w)	1402(m)
	1373	1259(w)	1258(w)	1245(vs)	1254(w)
		1250(vs)	1242(w)	–	1239(m)
CH_3 rock	863	841(br, vs)	868(w)	838(vs)	865(w)
	810	– [c]	838(w)		833(m)
	787	752(s)	744(m)	745(m)	743(m)
SiC_3 str.	652	691(s)	686(m)	686(s)	685(s)
	576	613(s)	624(vs)	636(w)	623(vs)
					611(sh)
Si–H bending	518	–	–	–	–
	440	450(m)	444(w)	445(s)	444(m)
$SiSi_3$ str.	357	– [d]	358(s)	357(m)	357(vs)

[a] The calculated frequencies shown here are the values giving the maximum transition dipole for the specific modes. [b] Ref. 8. [c] The broad peak of 841 cm^{-1} covers this frequency range. [d] FT-IR absorption data in the vibrational range (< 400 cm^{-1}) are not available using our FTIR instrument.

spectroscopic evidence for the production of ≡SiOH in the synthesis [3] has not been reported in the literature, to our knowledge.

Here, we report a modified method for the synthesis of ≡SiOH(D) and spectroscopic data of ≡SiOH(D). In an attempt to reliably assign the vibrational modes of the specific groups in the polysilanol, we have also synthesized a series of polysilanes, ≡SiX (X = H, Cl, CH_3, OCH_3, $SiMe_3$), similar to ≡SiOH in structure, and then compared the spectroscopic data with those of ≡SiOH. Also we carried out the AM1 [7] semiempirical calculation on the vibrations of ≡SiH, ≡SiOH and ≡SiOD. Since the AM1 calculations on several silicon compounds are in good agreement with experiments [7] and our AM1 calculations on the vibrational frequencies and the mode assignments are quite consistent with the previous study [8], the AM1 calculations could help determine the mode assignments of the observed vibrational absorptions in the IR and Raman spectra of the title polysilanes.

Results and discussion

As shown in Table 1, our IR and Raman data for ≡SiH are in excellent agreement with the reported values [8]. It is also shown that the vibrational frequencies and mode assignments for ≡SiH determined by the AM1 method are generally consistent with the previous study [8]. Also it was found in our laboratory that the AM1 calculation on the vibrational frequencies for ≡SiH is superior to the MNDO [9] and MINDO/3 [10] calculations.

Table 2

Vibrational frequencies (cm^{-1}) for $(Me_3Si)_3SiOH$ derived by the AM1 method and measured by IR and Raman

Approximate type of mode	AM1	IR	Raman
O–H str.	3578	3661(s)	3664(vw), 3646(vw)
CH_3 str.	3168	2955(vs)	2936(s)
	3067	2893(s)	2880(vs)
CH_3 deform.	1393	1435(w)	1420(vw)
		1400(m)	1390(w)
		1308(w)	
	1372	1259(s),	1244(m),
		1250(vs)	1222(m)
O–H bending	1142	1049(br, s)	–
CH_3 rock	863	841(br, vs)	854(m)
	808		816(w)
	789	748(vs)	722(m)
Si–O str. + $SiSi_3$ bending + O–H bending	819	1080(br, s)	–
SiC_3 str.	653	691(s)	666(s)
	570	625(s)	602(vs)
$SiSi_3$ str. + Si–O bending	455		
		471(m)	440(m)
$SiSi_3$ str. + Si–O bending + O–H bending	452		
$SiSi_3$ str.	363	–[a]	344(s)

[a] IR absorption data in the vibrational range (< 400 cm^{-1}) are not available using our FTIR instrument.

Tables 1, 2 and 3 compare the AM1 results and the experimental data. Based on our AM1 semiempirical calculations on ≡SiH (Table 1), ≡SiOH (Table 2) and ≡SiOD (Table 3) and the literature [8,11], we have characterized the vibrational frequencies in ≡SiX (X = H, Cl, OH, OD, Me, OMe, $SiMe_3$) corresponding to the symmetric and non-symmetric stretching and deformation of the CH_3 group, the rocking of the CH_3, and the symmetric and non-symmetric stretching of the SiC_3 and $SiSi_3$ groups. Table 4 lists the spectral data for the vibrations observed commonly in the title polysilanes. It is also evidenced in Table 4 that the vibrational frequencies due to the $SiMe_3$ group are relatively insensitive to the rest of the molecule.

By changing the substituent on the silyl group, we have also assigned the characteristic group frequencies due to the Si–X stretching where X = H, C, O, Cl and SiO–X where X = H, D. Variation of the stretching frequencies with groups is shown in Table 5.

The absorptions for the symmetric and non-symmetric stretches of CH_3–Si are observed in the same regions for those of CH_3–C. However, the symmetric deformations of CH_3–Si are observed in a much lower frequency region, near 1241 cm^{-1}, than those for CH_3–C. Note that the absorption for the symmetric deformation of CH_3–C usually occurs near 1375 cm^{-1} [11]. This frequency shift is caused

Table 3

Vibrational frequencies (cm^{-1}) for $(Me_3Si)_3SiOD$ derived by the AM1 method and measured by IR and Raman

Approximate type of mode	AM1	IR	Raman
CH_3 str.	3168	2928(vs)	2890(m)
	3067	2852(s)	2832(s)
O–D str.	2604	2680(m)	2646(vw)
CH_3 deform.	1393	1390(m), 1432(m)	1340(vw)
	1372	1254(sh, m), 1242(vs)	1174(w), 1192(w)
CH_3 rock	863	840(br, vs)	808(w)
	811		766(vw)
	789	745(vs), 760(vs) 770(sh, m)	736(vw)
O–D bending	849	– [a]	–
Si–O str. + C–H bending	811	1044(br, m)	–
SiC_3 str.	653	688(vs)	618(s), 678(w)
	570	– [b]	554(vs)
$SiSi_3$ str. + Si–O bending	455	– [b]	
$SiSi_3$ str. + Si–O bending + O–D bending	450	– [b]	396(br, w)
$SiSi_3$ str.	361	– [b]	

[a] The absorption peak may be hidden in the broad and strong band near 840 cm^{-1}. [b] IR absorption data in the vibrational range (< 650 cm^{-1}) are not available using our normal IR instrument.

by change in the bending force constants. For a similar reason, the absorptions for the CH_3–Si rocking are observed at lower frequencies than those for CH_3–C.

In the IR spectra, we have observed the absorptions due to the O–H stretching at 3660 cm^{-1} and in the region 3240–3600 cm^{-1}, which may be attributable to the free and H bonded O–H stretchings, respectively. When a deuterium atom replaces the H position of the OH group in the molecule, the free O–D and the D-bonded O–D stretches are observed as expected at 2680 cm^{-1} and in the region 2320–2640 cm^{-1}, respectively. Also in the Raman spectrum of ≡SiOD, the weak absorption of the free SiO–D stretch is observed at 2646 cm^{-1}. This correctly reflects the isotope effect.

Similar behaviors are also observed in triphenylsilanol. In the IR spectrum of triphenylsilanol, broad absorptions due to the H-bonded O–H vibrations occur in the range 2400–3520 cm^{-1}. In ≡SiOH, we have also observed the absorptions at 1049 and 1080 cm^{-1} presumably due to the O–H bending and the combination bands of Si–O stretches, O–H bending and Si–Si_3 stretches, respectively. The value of 1049 cm^{-1} of the O–H bending in the IR spectrum of ≡SiOH is lower than that of the calculation, 1142 cm^{-1}, which may reflect the intermolecular H-bonding of the Si–O bond.

In an attempt to help identify the mode assignment for the free Si–O stretch, we have obtained the IR and Raman spectra of octamethylcyclotetrasiloxane,

Table 4

IR and Raman frequencies (cm^{-1}) observed commonly in polysilanes $(Me_3Si)_3SiX$ (X = H, Cl, OH, OD, Me, OMe, $SiMe_3$)

Approximate type of mode	Selected value [a] of frequency	Infrared	Raman
CH_3 non-sym. str.	2949(4) [b]	2954.4(1.2)(vs)	2943(4)(s)
CH_3 sym. str.	2891(5)	2894.5(2.0)(s)	2886(4)(vs)
CH_3 non-sym. deform.	1433(9)	1436.2(5.1)(w)	1429(7)(vw)
	1399(5)	1400.9(1.6)(m)	1397(5)(w)
CH_3 sym. deform.	1256(5)	1259.3(1.6)(w)	1252(5)(m)
	1241(6)	1249.3(1.6)(vs)	1233(6)(m)
CH_3 rock	861(5)		861(5)(m)
		838.4(3.2)(br, vs)	
	827(8)		827(8)(w)
	740(8)	747.4(4.1)(vs)	733(7)(m)
SiC_3 non-sym. str.	684(9)	691.8(5.3)(s)	676(7)(s)
SiC_3 sym. str.	618(8)	621.7(4.5)(s)	613(7)(vs)
$SiSi_3$ str.	349(13)	357 [c]	340(13)(s)

[a] Selected value of frequency: the average value of the IR and Raman frequencies for the specific mode. The IR and Raman vibrational values listed here are the average values of the vibrational frequencies of the seven compounds examined. Since the IR absorptions due to the CH_3 rock ($\lambda_{max} = 838$ cm^{-1}) occur in the range 769–940 cm^{-1} as the broad peaks, the Raman values, 861 and 827 cm^{-1} were selected. [b] Values in parentheses indicate one standard deviation (σ) of the spectral variation with the chemical environments of the polysilanes. [c] The value is from ref. [8].

$(Me_2Si{-}O)_4$ in which we have observed a broad intense peak at 1067 cm^{-1} in the IR spectrum and a broad weak signal at 1036 cm^{-1} in the Raman spectrum. In the similar vibrational region, we have also observed the Si–O stretching vibrational absorptions ($\lambda_{max} = 1076$ cm^{-1}) in both the IR and Raman spectra of $\equiv SiOCH_3$. The IR peak is sharp and intense while the Raman signal is very weak. These indicate that the Si–O bond is a very polar bond as reflected in the large electronegativity difference between silicon and oxygen.

Surprisingly in $\equiv SiOH$, the IR bands, $\lambda_{max} = 3443$, 1080 and 1049 cm^{-1} which we have attributed to the H-bonded O–H stretch, Si–O stretch and O–H bending, respectively, are not observed in the Raman spectra. These behaviors are also

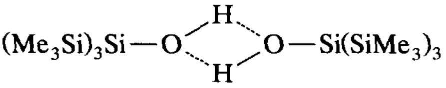
Table 5

Characteristic group frequencies (cm^{-1})

Group	Bond-stretching vibration
$\equiv SiO{-}H$	3663
$\equiv SiO{-}D$	2663
$\equiv Si{-}H$	2050
$Et_3Si{-}H$	2114
$\equiv Si{-}OH$ [a]	1080
$\equiv Si{-}OCH_3$ [b]	1076
$\equiv Si{-}CH_3$	656
$\equiv Si{-}Cl$	480
$Me_3Si{-}Cl$	472

[a] $SiSi_3$ bending and O–H bending included. [b] $SiSi_3$ bending, O–C bending and C–H bending included.

observed in the deuteriated analog ≡SiOD. These drastic spectral changes may be due to the change of the symmetry upon formation of the silanol dimer.



$$(Me_3Si)_3Si{-}O\overset{H}{\underset{H}{\leftrightharpoons}}O{-}Si(SiMe_3)_3$$

In the dimer molecule, the Raman lines of the H (D)-bonded O–H (D) and Si–O stretches and the H-bonded O–H (D) bending could be too low to appear since the vibrational bands of the stretches are very broad, and could be split due to the centrosymmetric properties of the dimer molecules. In the centrosymmetric molecules, the absorption due to the antisymmetric stretching vibrations could not occur in the Raman spectra. Thus the absorptions at 3240–3600 and at 1049–1080 cm^{-1} could more or less involve the anti-symmetric stretches of the O–H and Si–O bonds, respectively. This could reduce the intensities of the Raman lines.

A piece of evidence is shown in the IR and Raman spectra of $\equiv SiOCH_3$ in which the Si–O stretching bands are clearly observed in both IR [1080.1 cm^{-1} (vs)] and Raman [1072 cm^{-1} (vw)] since the molecules can not undergo intra- and inter-molecular hydrogen bondings.

The addition of small amount of CH_3OD to ≡SiOH in C_6D_6 solution (mole ratio of CH_3OD and ≡SiOH is 31 : 1) changes the NMR spectrum in which a sharp singlet signal at $\delta = 1.55$ ppm almost diminishes and a broad new peak at $\delta = 2.08$ appears. This peak corresponds to the OH proton peak in CH_3OH formed by the exchange of H and D. This is confirmed by the following isotope exchange reactions. When the mixture of ≡SiOH and CH_3OD (mole ratio of ≡SiOH and $CH_3OD = 1.0:10.0$) is allowed to react for 24 hours, complete H/D exchange is observed [12*].

When we add a small amount of CH_3OD to the silanol sample, the free O–H stretching peak due to ≡SiO–H disappears and the H-bonded O–H stretching signal is red-shifted by 80 cm^{-1}. This indicates that the dimer dissociates into the corresponding monomers which then react with CH_3OD giving rise to the fast exchange of H and D. Thus we presume that the broad peak in the region 3100–3600 cm^{-1} ($\lambda_{max} = 3300$ cm^{-1}) is due to the H-bonded $CH_3O{-}H$ stretching.

From the spectral data, the stretching force constants for the characteristic bonds are derived: $k_{SiO-H} = 7.5 \times 10^2$, $k_{Si-H} = 2.45 \times 10^2$, both in N/m. The value for the stretching force constant of the SiO–H single bond is compared with the reported value of the force constant of O–H bond in alcohols, $k_{O-H} = 7.66 \times 10^2$ N/m [13]. This indicates that the O–H bond in ≡SiOH has an alcoholic OH character. Comparison of these force constants and the peak intensities of the IR and Raman spectra throws light on the nature of the forces holding silicon and other atoms together and on the electronic structures of the molecules, and also provides information about the affinities of silicon for oxygen and chlorine, *etc.*

Experimental

General data

^1H NMR spectra were recorded on a Bruker AC-80 FT spectrometer. Gas chromatograph-mass spectra (GC-MS) were recorded on a Shimadzu GCMS-QP1000 operating at an ionization voltage of 70 eV. Normal IR and FT-IR spectra were recorded on a Jasco A-1 model and on a Dicilled FTS-80, respectively using a KBr pellet containing the pure isolated polysilane compounds. The Raman measurement system has been described in detail elsewhere [14]. A Spectra-Physics 165 Ar^+ ion laser was used for sample excitation. The Raman scattering was collected at 90° from the sample excitation beam. A 1-m Jovin-Yvon Raman U-1000 double monochromator and a Hamamatsu C1230 photon counter/ discriminator were used for the Raman signal detection. The Raman absorptions were measured using the conventional NMR tube (length *ca.* 10 cm) containing the pure liquid polysilane samples.

Materials

Preparation of tetrakis(trimethylsilyl)silane. Synthesized by the method of Gilman and Smith [15]. FT-IR (cm^{-1}) (relative intensity): 2954.9(s), 2893.2(m), 1442.0(w), 1400.0(m), 1257.6(sh, m), 1246.0(vs), 833.2(vs), 750.0(m), 686.7(s), 621.1(s), 460.0(w). Raman (cm^{-1}) (relative intensity): 2942(vs), 2886(vs), 1424(vw), 1394(w), 1252(w), 1232(m), 866(w), 826(m), 734(m), 674(s), 616(vs), 544(w), 442(m), 326(w), 224(vw), 168(vs).

Preparation of ≡SiH. Synthesized by the method of Gilman, Holmes, and Smith [16]. FT-IR (cm^{-1}) (relative intensity): 2954.9(vs), 2893.2(s), 2052.3(s), 1438.9(m), 1404.2(m), 1259.0(sh, w), 1249.9(vs), 841.0(vs), 752.2(s), 690.5(s), 613.4(s), 450.0(m). Raman (cm^{-1}) (relative intensity): 2948(vs), 2892(vs), 2048(s), 1434(vw), 1404(w), 1258(w), 1242(w), 868(w), 838(w), 744(w), 686(m), 624(vs), 444(w), 358(s), 274(w), 218(m).

Preparation of ≡SiCl. Synthesized by the method of Gilman and Harrell [3]. FT-IR (cm^{-1}) (relative intensity): 2954.9(vs), 2897.1(vs), 1435.0(m), 1435.0(m), 1400.3(vs), 1262.0(m), 1249.9(vs), 837.1(vs), 744.5(s), 690.5(vs), 624.9(vs), 486.1(vs). Raman (cm^{-1}) (relative intensity): 2946(vs), 2886(vs), 1426(vw), 1396(w), 1250(m), 1232(m), 858(w), 826(w), 734(m), 678(s), 614(vs), 474(m), 454(m), 324(s), 248(w), 224(m), 218(m), 160(vs).

Preparation of ≡SiOH. A 100 ml three necked, round-bottomed flask containing 5.0 g (0.018 mole) of ≡SiCl and 15 ml pentane was fitted with a reflux condenser and a pressure-equalizing dropping funnel. In the dropping funnel was placed 10 ml of distilled water and 15 ml triethylamine. Nitrogen gas was blown through the reaction flask *via* the dropping funnel. To the reaction mixture was added slowly 25 ml of the solution. The reaction mixture was stirred vigorously overnight at room temperature. The organic phase was separated and dried with sodium sulfate. The solvent was removed under reduced pressure to afford 3.74 g (0.0142 mole) of ≡SiOH (yield = 79%), b.p. 76–77°C/3 mmHg (lit. 81°C/1.5 mmHg [3]). ≡SiOD was synthesized in the same manner using D_2O. The product ≡SiOH was identified from ^1H NMR, mass, IR, and Raman spectra.

≡SiOH: ^1H NMR (80 MHz, C_6D_6): δ 1.55 (OH, sharp singlet, 1H), δ 0.21 (CH_3, sharp singlet, 27H). ^1H NMR (80 MHz, $CDCl_3$): δ 1.38 (broad singlet, 1H, OH), δ 0.21 (sharp singlet, 27H, CH_3). ^1H NMR (80 MHz, $C_6D_6 + CH_3OD$, mole ratio of CH_3OD and ≡SiOH = 31 : 1): δ 2.08 (broad singlet, OH), δ 1.55 (sharp singlet, OH) {1H}, δ 0.27 (sharp singlet, 27H, CH_3). Note that the peak area of $\delta = 1.55$ is about 1/13 that of $\delta = 2.08$. Mass spectrum m/z (relative intensity): 264 (M^+, 12), 249 (28), 248 (38), 233 (46), 189 (72), 175 (67), 174 (50), 159 (79), 131 (60), 129 (34), 73 (100). FT-IR (cm^{-1}) (relative intensity): 3661(s), 3443(br, s), 2955(vs), 2893(s), 1435(w), 1400(m), 1308(w), 1250(s), 1049(br, s), 841(vs), 748(vs), 691(s), 625(s), 567(w), 471(m). Raman (cm^{-1}) (relative intensity): 3664(vw), 3646(vw), 2936(s), 2880(vs), 1420(vw), 1390(w), 1244(w), 1222(w), 854(w), 816(w), 722(w), 666(s), 602(vs), 440(w), 344(w), 266(w), 214(m), 160(vs).

≡SiOD: IR (cm^{-1}): 2928(vs), 2852(s), 2680(m), 2540(s), 1432(m), 1390(m), 1302(w), 1254(sh, m), 1242(vs), 1044(m, br), 840(br, vs), 770(sh, m), 760(sh, m), 745(vs), 688(s). Raman (cm^{-1}) (relative intensity): 2890(s), 2832(vs), 2646(vw), 1340(vw), 1192(w), 1174(w), 808(w), 766(vw), 736(vw), 678(w), 618(s), 554(vs), 396(w), 280(vs), 196(w).

Preparation of $\equiv SiCH_3$. Synthesized by the method of Barton [17*]. FT-IR (cm^{-1}) (relative intensity): 2951.1(vs), 2893.2(s), 2816.1(w), 1427.3(m), 1400.3(m), 1249.9(vs), 837.1(vs), 783.1(vs), 740.7(m), 690.5(s), 621.1(s), 486.1(s). Raman (cm^{-1}) (relative intensity): 2944(vs), 2886(vs), 1430(vw), 1400(w), 1254(w), 1234(m), 862(w), 832(w), 736(m), 678(s), 656(s), 612(vs), 444(m), 344(w), 262(w), 216(m), 168(vs).

Preparation of $\equiv SiOCH_3$. This material was synthesized by a modification of the procedure of Chen and Gaspar [18]. A 100 ml three necked, round-bottomed flask containing 8.0 g (28 mmole) of ≡SiCl and 20 ml pentane was fitted with a reflux condenser and a pressure equalizing dropping funnel. In the dropping funnel was placed excess methanol and triethylamine. Nitrogen gas was blown through the reaction flask *via* the dropping funnel. To the reaction mixture the solution was added slowly. The reaction mixture was stirred vigorously overnight at room temperature. Appreciable amounts of insoluble salts were formed. The salts were removed by filtration. The excess solvent was removed under reduced pressure. The residue was fractionated under reduced pressure to afford 6.1 g (22 mmole) of $\equiv SiOCH_3$ (yield = 79%), bp 85–95°C/1 mm (lit. 63°C/0.5 mm) [19]. The product was identified from ^1H NMR, mass, IR, and Raman spectra. ^1H NMR spectrum shows only two peaks as follows: ^1H NMR (80 MHz, $CDCl_3$) δ 0.02 (s, 27H, Si–CH_3), 3.22 (s, 3H, O–CH_3). Mass m/z (relative intensity) 278 (M^+, 15), 263 (100), 248 (6), 233 (8), 205 (40), 189 (36), 175 (65), 147 (13), 131 (36), 117 (21), 101 (5), 73 (67), 59 (15), 45 (7). FT-IR (cm^{-1}) (relative intensity): 2954.9(vs), 2897.1(s), 2819.9(s), 1438.9(m), 1400.3(m), 1259.0(w), 1249.9(vs), 1080.1(vs), 841.0(vs), 748.5(w), 702.1(vs), 624.9(s), 474.5(m). Raman (cm^{-1}) (relative intensity): 2942(s), 2884(vs), 2812(sh, w), 1440(vw), 1398(w), 1252(w), 1234(w), 1072(vw), 858(w), 824(w), 730(w), 696(w), 674(m), 608(vs), 466(w), 452(w), 344(s), 298(w), 212(w), 162(vs).

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