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Inter- and Intra-molecular Association of Poly(diorganosiloxane)-αω-diols

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A spectroscopic study has been made of the association of the first three members of the dimethyl, methylvinyl, methylphenyl, and diphenyl series of poly(diorganosiloxane)-αω-diols. A detailed examination of intramolecular hydrogen bonding in the trisiloxane-1,5-diols has provided useful data on the stereochemistry of these compounds. Valency deviation due to the gem-diphenyl groups has been proposed to explain the high intramolecular hydroxyfrequency shift of hexaphenyltrisiloxane-1,5-diol relative to those given by the other trisiloxane-1,5-diols. A second intramolecular band given by hexaphenyltrisiloxane-1,5-diol has been assigned to interaction between the hydroxy-groups and the π -electrons of phenyl substituents.

STUDIES of intramolecular hydrogen bonding in compounds such as the cycloalkane-1,2-diols,^{1,2} polymethylene glycols,³⁻⁵ and ω -methoxyalkanols⁶ have, during the last 15 years, provided much useful stereochemical information. In an earlier investigation,7 intramolecular hydrogen bonding was found in hexaphenyl- and hexamethyl-trisiloxane-1,5-diol and longer chain poly(dimethylsiloxane)-aw-diols. Here a detailed study of association in a series of poly(diorganosiloxane)aw-diols by relative hydroxy-band intensity and frequency-shift measurements is described. The objective was to establish the steric effect of organic substituents and chain length on the molecular geometry of these compounds.

RESULTS AND DISCUSSION

The organosilanols examined were, as in an earlier study,7 prepared by the hydrolysis of organosilicon chlorides in an aqueous solution of ammonium carbonate. An attempt to prepare the second and third members of the poly(methylphenylsiloxane)-aw-diols by the technique developed for the dimethyl and diphenyl series,⁷ was only partly successful. The two isomeric forms of 1,3-dimethyl-1,3-diphenyldisiloxanediol were obtained, but while the fluid also produced almost certainly contained the third member of the series, it could not be isolated. 1,3,5-Trimethyl-1,3,5-triphenyltrisiloxanediol was, however, synthesised, as also were the second and third members of the methylvinyl series, via the corresponding $\alpha \omega$ -dichlorosiloxanes. The second and third members of both the poly(methylphenyland methylvinyl-siloxane)-aw-diol series should exhibit stereoisomerism, but success in separating the isomers has been limited to 1,3-dimethyl-1,3-diphenyldisiloxane-The trisiloxane-1.5-diols have three asymmetric diol. silicon atoms, two of which are identical so that they should give a racemic modification in addition to two *meso*-isomers. However, even after 6 months at -5° no crystalline forms separated from the colourless fluids of these compounds or from 1,3-dimethyl-1,3divinyldisiloxanediol.

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¹ L. P. Kuhn, J. Amer. Chem. Soc., 1954, **76**, 4323; A. R. Cole and P. R. Jefferies, J. Chem. Soc., 1956, 4391; J. S. Brima-combe, A. B. Foster, M. Stacey, and D. H. Whiffen, Tetrahedron, 1958, 4, 351; R. Piccolini and S. Winstein, Tetrahedron Letters, 1959, No. 13, 4; H. Buc, Ann. Chim. (France), 1963, 8, 409.

The results of the i.r. measurements are listed in the Table, while the solution spectra of two diols are given



FIGURE 1 I.r. spectra of (a) tetraphenyldisiloxane-1,3-diol and (b) hexaphenyltrisiloxane-1,5-diol in carbon tetrachloride (A) 0.03м (1 mm. cells); (В) 0.001м (1 cm. cells); and (С) 0.00025м (10 cm. cells)

in Figure 1. The low solubility of the monomer diols in carbon tetrachloride has prevented a complete series

- ² L. P. Kuhn, J. Amer. Chem. Soc., 1952, 74, 2492.
- ³ L. P. Kuhn, J. Amer. Chem. Soc., 1958, 80, 5950.
- ⁴ P. R. Schleyer, *J. Amer. Chem. Soc.*, 1961, **83**, 1368. ⁵ L. P. Kuhn, P. R. Schleyer, W. F. Baitinger, and L. Eberson, J. Amer. Chem. Soc., 1964, 86, 650.
- ⁶ A. B. Foster, A. H. Haines, and M. Stacey, Tetrahedron, 1961, 16, 177.
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of frequency shifts being obtained for the 0.03M-solutions. The spectra of the trisiloxane-1,5-diols are distinguished from the monomer and dimer diols in two respects. Firstly, by the shape and intensity of the free hydroxy-bands and secondly by the presence of strong intramolecular hydroxy-bands. Even at the relatively low resolution employed in this study the free hydroxybands of the trisiloxane-1,5-diols were found to consist of at least two overlapping absorptions. This difference between the first two and the third member of each series is reflected quantitatively in the three-quarter intensity band widths. The existence of intramolecularly

1.5-diols cannot, unfortunately, be used to calculate the enthalpy of the hydrogen bonds formed. Recent work by Kuhn and Wires⁹ has shown that the Badger-Bauer rule ⁸ does not apply for intramolecular hydrogen bonds. Conclusive evidence indicating a linear relationship between the hydroxy-frequency shifts due to intramolecular hydrogen bonding and the $0 \cdots 0$ distances has, however, been provided by Dearden.¹⁰ This supports the earlier findings of Kuhn,^{2,11} who had derived an empirical formula [equation (1)] relating hydroxy-frequency shifts with H · · · O distances for intramolecular hydrogen bonds. This formula has

		I.r. dat	a				
	Free OH (cm. ⁻¹)			Intermol. bonding		Intramol. bonding	
Siloxane-xw-diols	Freq. major band	Freq. minor band	VĄ	Freq. shift	Free/bonded ext. coeff.	Freq. shift	Free/bonded ext. coeff.
[Me ₂ Si(OH) ₂] Tetramethyldi	3693 3693		19 20	402	0.36		
Hexamethyltri [MeVinylSi(OH) ₂]	3683 3685	3694	30 22	403	0.35	193	1.7
1,3-Dimethyl-1,3-divinyldi 1,3,5-Trimethyl-1,3,5-trivinyltri	3085 3682 3686	3670	24 35 20	350 402	0.49	183	1.8
1,3-Dimethyl-1,3-diphenyldi (meso) 1,3-Dimethyl-1,3-diphenyldi (rac.)	$3684 \\ 3684$		19 20	344	0.76		
1,3,5-Trimethyl-1,3,5-triphenyltri [Ph ₂ Si(OH) ₂	$\begin{array}{c} 3683\\ 3681 \end{array}$	3668 *	38 16	395	0.41	195	1.6
Tetraphenyldi Hexaphenyltri	$3681 \\ 3679$	3670 *	$\begin{array}{c} 20 \\ 42 \end{array}$	$\frac{284}{384}$	$\begin{array}{c} 1 \cdot 34 \\ 0 \cdot 54 \end{array}$	201	$2 \cdot 2$

* Both free hydroxy-bands are of equal intensity.

bonded hydroxy-bands in the solution spectra of the trisiloxane-1,5-diols of the methylvinyl and methylphenyl series is in accord with the results for the poly-(dimethyl- and diphenyl-siloxane)-αω-diols, previously reported.7

The application of the Badger-Bauer relationship⁸ to the intermolecular hydroxy-frequency shifts given by the diols indicates weaker hydrogen bonding between the disiloxane-1,3-diols than between the trisiloxane-1,5-diols, except in the dimethyl series. The ratios of the extinction coefficients of the free to intermolecularly bonded hydroxy-bands given by the diols are directly related to the bulkiness of the organic substituents. The values decrease for both the disiloxane-1,3-diols and the trisiloxane-1,5-diols in the order $Ph_2 >$ $MeVinyl > MePh > Me_2$, indicating a progressively higher degree of association. The 0.03M-solution of tetraphenyldisiloxane-1,3-diol gives a second welldefined intermolecular band at 3551 cm.⁻¹. The same absorption is also given by the 0.03M-solutions of hexa-1,3,5-trimethyl-1,3,5-triphenyltrisiloxane-1,5-diol, phenyltrisiloxanediol, and the racemic form of 1,3-dimethyl-1,3-diphenyldisiloxanediol as a shoulder on the bonded hydroxy-peak. The bonding responsible for these vibrations will be considered in a later paper.

The hydroxy-frequency shifts resulting from the intramolecular hydrogen bonding in the trisiloxanebeen subject to some criticism,¹² but can be successfully applied to all but the largest frequency shifts.⁴ The

$$\Delta \nu \text{ (cm.}^{-1}) = \frac{250}{\text{H} \cdots \text{O distance (Å)}} - 74 \quad (1)$$

trend in $H \cdots O$ distances obtained when the intramolecular hydroxy-frequency shifts given by the trisiloxane-1,5-diols are substituted in the above equation is $MeVinyl > Me_2 > MePh > Ph_2$. The largest intramolecular hydroxy-frequency shift and consequently the shortest $O \cdots H$ distance is given by hexaphenyltrisiloxane-1,5-diol. The intramolecular frequency shifts are almost in the reverse order of the intermolecular frequency shifts given by the 0.03msolutions of these diols, so that the order of the $H \cdots O$ distances cannot be adequately explained in terms of electronic effects. The shorter $H \cdot \cdot \cdot O$ distance in the chelated form of hexaphenyltrisiloxane-1,5-diol, compared with the other trisiloxane-1,5-diols, is probably due to steric factors. By applying conformational principles and examining molecular models of a trisiloxane-1,5-diol substituted with six identical organic groups, R, there appear to be three very probable conformations [(a), (b), and (c)—Figure 2]. In only one of these, namely conformation (b), are the hydroxy-groups close enough to permit intramolecular hydrogen bonding.

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 ¹¹ L. P. Kuhn, National Meeting American Chemical Society,
- L. L. Ruhn, Varionar meeting Miletenar Chemical Society, Cleveland, Ohio, April 1960, Abstracts, p. 52, section 0.
 ¹³ J. L. Mateos and D. J. Cram, J. Amer. Chem. Soc., 1959, 81, 2756; H. Krieger, Suomen Kem, 1958, B31, B48.

⁸ R. M. Badger and S. H. Bauer, J. Chem. Phys., 1937, 5, 839; R. M. Badger, *ibid.*, 1940, 8, 288. ⁹ L. P. Kuhn and R. A. Wires, J. Amer. Chem. Soc., 1964,

^{86, 2161.}

The eight-membered chelate ring formed in this case is small in terms of polysiloxane chemistry and when, therefore, the organic substituents are large as in hexaphenyltrisiloxane-1,5-diol, then valency deviation (Thorpe-Ingold ¹³) and restriction of rotation ¹⁴ could be important factors. Valency deviation has been proposed by Kuhn³ to explain some of the results obtained in his i.r. study of substituted ethylene glycols. For example, tetra-t-butylethylene glycol which gives an intramolecular hydroxy-frequency shift of 170 cm.⁻¹,



FIGURE 2 Conformations of the trisiloxane-1,5-diols

compared with 32 cm.⁻¹ by ethylene glycol. More recently, Schleyer⁴ in his study of the 2-substituted propane-1,3-diols was able to correlate the spectral shifts with the C-C-C angle.

A considerable amount of independent evidence can be cited which suggests that the gem-diphenyl groups in polysiloxanes do influence bond angles in such a way as to favour the formation of ring rather than openchain polymers. The thermal condensation of diphenylsilanediol,^{15,16} even in the absence of solvents, yields the cyclic trimer and tetramer as the principle products, not the expected open-chain polysiloxane. The cyclic trimer and tetramer are also formed almost exclusively by the condensation of diphenylsilanediol in alcohol solutions containing a few drops of strong acid or alkali, respectively.¹⁶ Another example is provided by the difficulties encountered in attempting to prepare open-chain polydiphenylsiloxanes by the alkali-catalysed re-arrangement of hexaphenylcyclotrisiloxane or octaphenylcyclotetrasiloxane. Despite the advantages to be expected in respect to thermal stability and irradiation resistance, all reported attempts ¹⁷ to make high molecular weight polymers of this type have failed. Useful polymers have been prepared only when at least one out of every eight phenyl groups has been replaced by a smaller group. The highly phenylated linear polysiloxanes synthesised from methylheptaphenylcyclotetrasiloxane and vinylheptaphenylcyclotetrasiloxane have, consequently, been the subject of patent applications.¹⁸ The relative values for the $H \cdot \cdot \cdot O$ distances given by the other three trisiloxane-1,5-diols appear to be dependent on electronic effects.

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The population of intramolecularly hydrogen bonded to open-chain molecules depends on the configuration and conformation of the molecules, the strain within the chelate rings, and the strength of the intramolecular hydrogen bonds. All these factors will be influenced to varying degrees by the steric and electronic effects of the organic substituents, so that the intensity ratios of the free to bonded hydroxy-bands for the trisiloxane-1,5-diols require careful analysis. In organic compounds the strain factor becomes more favourable to closure as the ring size increases from three to sixmembered rings. This is exemplified by the intramolecular hydrogen bonding in the polymethylene glycols² and their monomethyl ethers.⁶ The hydroxyfrequency shift increases with the greater ring size. By contrast, the percentage of molecules in the chelated form, as indicated by the intensity ratios, decreases progressively with ring size due to the decreasing probability of molecules adopting a conformation suitable for the formation of an intramolecular bond. The free to bonded hydroxy-intensity ratios for the trisiloxane-1,5-diols indicate that a high proportion of the molecules are, in each case, in the gauche conformation. In addition, the four trisiloxane-1,5-diols as well as octamethyltetrasiloxane-1,7-diol and decamethylpentasiloxane-1,9-diol⁷ give intramolecular hydroxy-frequency shifts of the same order of magnitude which suggests that the rings contain sufficient atoms to be strain-free.

A more detailed examination of the differences in the free to bonded intensity ratios found for the trisiloxane-1.5-diols of the dimethyl, methylvinyl, and methylphenyl series indicates that they follow the order given by the intramolecular frequency shifts. The population of internally bonded molecules, therefore, appears to be influenced by the relative strengths of the proton donating and accepting properties of these diols. The position of hexaphenyltrisiloxane-1,5-diol appears at first sight to be anomalous, but an explanation can be offered after an examination of a molecular model of this The gem-diphenyl groups cause a recompound. striction of rotation about the siloxane bonds x and yin (I), thus reducing the entropy of the open structure



but only slightly influencing the chelated form, which, by its nature, has a much lower degree of freedom. The

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¹³ R. M. Beesley, C. K. Ingold, and J. F. Thorpe, J. Chem. Soc.,
1915, 107, 1080; C. K. Ingold, *ibid.*, 1921, 119, 305.
¹⁴ G. S. Hammond in 'Steric Effects in Organic Chemistry,'
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Pardwall, C. F. Oshorn and R. D. Chapman, L. Amer, Chem. Bordwell, C. E. Osborn, and R. D. Chapman, *J. Amer. Chem. Soc.*, 1959, **81**, 2698; N. L. Allinger and V. Zalkow, *J. Org.* Chem., 1960, 25, 701.

overall effect of replacing all the methyl by phenyl groups in a trisiloxane-1,5-diol should, therefore, be to cause the equilibrium to move in favour of the chelated form, since the entropy change is reduced. The fact that this view is not supported by a stronger intra-molecular bonded hydroxy-band is, at least partly, explained by the existence of a competing intramolecular interaction. A second intramolecular band is given by this diol at 3616 cm.⁻¹ which has also been reported, but not assigned, in the spectra of octaphenyltetrasiloxane-1,7-diol.¹⁹ This may be due in both compounds to internal hydrogen bonding between the hydroxy-groups and the π -electrons of phenyl substituents [see (II)]. The hydroxy-frequency shift due to this proposed interaction is 65 cm.⁻¹ for hexaphenyltrisiloxane-1,5-diol, which is of the same order as that found by West and Baney²⁰ for the intermolecular interaction of some triorganosilanols with the π -base, mesitylene. Trimethyl-, triethyl-, and triphenyl-silanol gave frequency shifts of 71,62, and 79 cm.⁻¹, respectively. The interaction of phenol with a series of aromatic π -bases also gives many frequency shifts in this range,²¹ while with various phenyl-substituted disiloxanes, shifts of 51-55 cm.⁻¹ are reported.22

EXPERIMENTAL

Materials.—The dimethyl and diphenyl series of poly-(diorganosiloxane)- $\alpha\omega$ -diols examined were prepared by the procedures previously reported.⁷

Methylvinylsilanediol.—This was prepared as white plates [m.p. 69.5° (from pentane-diethyl ether)], by the method used for dimethylsilanediol in an earlier investigation,⁷ except that diethyl ether was also present in the hydrolysis system in sufficient quantity to give theoretically a 10% solution of diol in this phase on completion of the hydrolysis.

Methylphenylsilanediol.—This compound, m.p. 85° (from pentane-diethyl ether), was prepared in a similar fashion to the preceding one.

meso- and rac-1,3-Dimethyl-1,3-diphenyldisiloxanediol.— Dichloromethylphenylsilane (1.0 mole) was added during 2.5 hr. to ammonium carbonate (1.4 moles), diethyl ether (1946 ml.), and water (1.5 moles), stirred at 0°, by the method previously described.⁷ After the mixture had been stirred for a further hour, more water (0.5 mole) was added; the hydrolysate isolated on evaporation of the dried ethereal solution consisted of the mixed isomers of 1,3-dimethyl-1,3-diphenyldisiloxanediol (white solid) together with a colourless fluid. The latter was extracted with cold, light petroleum (b.p. 40—60°), while the racemic isomer dissolved in cold benzene to leave the *meso*-form. The racemic isomer was recrystallised from benzenelight petroleum (b.p. 60—80°) to give white needles, m.p.

¹⁹ A. W. Jarvie, A. Holt, and J. Thompson, *J. Organometallic Chem.*, 1968, **11**, 623.

²⁰ R. West and R. H. Baney, J. Amer. Chem. Soc., 1959, 81, 6145.

²¹ R. West, J. Amer. Chem. Soc., 1959, **81**, 1614; R. West and C. S. Kraighanzee, *ibid.*, 1961, **83**, 765; Z. Yoshida and E. Osawa, *ibid.*, 1965, **87**, 1467; 1966, **88**, 4019. 120° (lit.,^{23,24} m.p. 110°) and the *meso*-form was fractionally recrystallised from light petroleum (b.p. 60-80°) to give an amorphous white solid, m.p. 89.5° (lit.,²³ m.p. $82-84^{\circ}$, lit.,²⁴ 100°). Attempts to separate higher members of the homologous series by fractional distillation of the fluid (92.5 g.) (Found: Si, 18.9; OH, 5.3%) resulted in thermal decomposition.

1,3,5-Trimethyl-1,3,5-triphenyltrisiloxanediol.— Dichloro-1,3,5-trimethyl-1,3,5-triphenyltrisiloxane, b.p. $182^{\circ}/0.2$ mm., prepared by application of the partial hydrolysis technique,²⁵ was hydrolysed to give 1,3,5-trimethyl-1,3,5-triphenyltrisiloxanediol as a viscous liquid, $n_{\rm D}^{25}$ 1.5399 (Found: C, 59.4; Si, 19.6; OH, 7.9. C₂₁H₂₆O₄Si₃ requires C, 59.1; Si, 19.75; OH, 8.0%).

1,3-Dimethyl-1,3-divinyldisiloxanediol and 1,3,5-Trimethyl-1,3,5-trivinyltrisiloxanediol.-Water (2.25 moles) in dioxan (40.5 ml.) was added to dichloromethylvinylsilane (3.0 mole) in diethyl ether (400 ml.) by the literature procedure,²⁵ to give a mixture of $\alpha\omega$ -dichlorosiloxanes from which 1,3-dichloro-1,3-dimethyl-1,3-divinyldisiloxane (30 g., 8.8%), b.p. 61-63°/0.9 mm. (Found: Si, 24.9; Cl, 30.5. C₆H₁₂Cl₂OSi₂ requires Si, 24.7; Cl, 31.2%), and dichloro-1,3,5-trimethyl-1,3,5-trivinyltrisiloxane (117 g., 37%), b.p. 71-73°/1.0 mm. (Found: Si, 27.1; Cl, 21.9. C₉H₁₈Cl₂- O_2Si_3 requires Si, 26.9; Cl, 22.6%), were isolated. 1,3-Di-methyl-1,3-divinyldisiloxanediol, n_D^{25} 1.4391 (Found: Si, 29.4; OH, 17.5. C₆H₁₄O₃Si₂ requires Si, 29.5; OH, 17.9%), and 1,3,5-trimethyl-1,3,5-trivinyltrisiloxanediol, n_D^{25} 1.4383 (Found: Si, 30.3; OH, 11.9. $C_9H_{20}O_4Si_3$ requires Si, 30.5; OH, 12.3%), were prepared by hydrolysis of the $\alpha\omega$ -dichlorosiloxanes, as outlined above.

Anhydrous Chemicals.—The carbon tetrachloride (spectroscopic grade) was dried over calcium hydride and fractionated immediately before use. The organosilanols were handled as in a previous study.⁷

Infrared Spectra.—The spectra were examined with a Unicam SP 700 double-beam spectrometer and grating with Infrasil cells of 1-mm., 1-cm., and 10-cm. path-length.

Solutions of the diols in carbon tetrachloride were examined at concentrations of 0.03M in 1-mm. cells, 0.001m in 1-cm. cells, and 0.00025m in 10-cm. cells. The frequencies of the bands due to intermolecular hydrogen bonding were taken at 0.03M when solubility permitted. The doublet character of the free hydroxy-bands of the trisiloxane-1,5-diols and the three-quarter intensity band widths, as well as the bands due to intramolecular hydrogen bonding were studied by examining 0.00025M-solutions in the 10-cm. path-length cells with the instrument controls set at resolution 4, scan speed 4, and damping 3. The spectra were automatically drawn on a Honeywell recorder set at a running speed of 40 in./hr. The free/bonded intensity ratios for the inter- and intra-molecular hydrogen bonding studies were obtained by measuring the relative extinction coefficients given by the 0.03M- and 0.00025Msolutions, respectively. All the spectra were recorded at a temperature of $20 \pm 2^{\circ}$. The sharp free hydroxybands were reproduced within an accuracy of ± 1 cm.⁻¹

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²⁴ H. J. Hickton, A. Holt, J. Homer, and A. W. Jarvie, J. Chem. Soc. (C), 1966, 149.
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and the frequencies were corrected against the free hydroxyband of phenol, which was taken as 3609 cm.⁻¹. The frequency shifts due to inter- and intra-molecular hydrogen bonding were reproducible within an accuracy of ± 3 and ± 2 cm⁻¹, respectively, and the intensity ratios within 5%.

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