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NOTE

Anomalous hydrogen bonding in polyphenylsiloxane-α,ω-diols

A previous study of a series of poly(dimethyl- and diphenylsiloxane)-α,ω-diols showed that these compounds are strongly hydrogen bonded both in the solid state and in solution[1].

It has been shown that the silanols are much more strongly acidic than the carbinols and of comparative basicity[2], it is therefore reasonable to infer that the strong hydrogen bond formation observed in these compounds is due to interaction of the terminal OH groups and there is no evidence for any interaction of the terminal OH groups with the much less basic oxygen of the siloxane linkage.

In the previous work quoted above the study of the diols was continued in the methyl series as far as the decamethylpentasiloxane-1,9-diol but in the phenyl series the largest molecule examined was the hexaphenyltrisiloxane-1,5-diol. Having prepared octaphenyltetrasiloxane-1,7-diol as a starting material for another study, we determined its infrared spectrum merely for analytical purposes but were somewhat surprised to observe that films of the material showed a single sharp band at 3600 cm^{-1} and that there was no indication whatsoever of either inter- or intramolecular hydrogen bonding of the type observed in the other diols of the series. In contrast solution spectra of the octaphenyltetrasiloxane-1,7-diol in carbon tetrachloride showed four bands in the OH stretching frequency region at 3680, 3620, 3450 and 3290 cm^{-1}. In the case of the hexaphenyltrisiloxane-1,5-diol Harris observed bands at 3674, 3464 and 3290 cm^{-1}. He assigns the band at 3674 cm^{-1} to the monomeric OH and the bands at 3464 and 3290 cm^{-1} to the intra- and intermoleculary hydrogen-bonded species respectively. In the solution spectra there is also a weak band at 3610 cm^{-1} which is not recorded by Harris. Determination of the acidity and basicity of the octaphenyltetrasiloxane-1,7-diol by Kuhn's infrared procedure[3] reveals that the proton-donating power and the proton-accepting power of this molecule do not differ greatly from that of the other members of the series. It would seem therefore that the very weak band at 3680 cm^{-1}, in the solution spectra of octaphenyltetrasiloxane-1,7-diol can be assigned to the monomeric OH and those at 3450 and 3290 to the intra- and intermoleculary bonded hydrogen-bonded species respectively. The band at 3600 cm^{-1} which is the only observable band in the film spectra and which occurs rather more weakly at 3620 cm^{-1} in the solution spectra would appear both from its shape and position to be due to some very weak hydrogen-bonding interaction. Dilution experiments indicate that this bonding is intramolecular.

In the crystal, the molecule is probably held in one particular conformation which is favourable to this interaction, whereas in solution where the molecule is more mobile it can adopt various conformations and normal strong hydrogen bonding is observed.

There are several possible explanations for this weak interaction in octaphenyltetrasiloxane-1,7-diol; it could be due to interaction of the silanol OH with the phenyl groups. The shift is comparable in magnitude with that observed when phenol interacts with phenylsiloxanes, and it has been postulated that this small shift (55 cm^{-1}) of the OH band of the phenol is due to hydrogen bonding with the phenyl groups[4].

The OH group of the phenyl silanols is only slightly more acidic than that of phenol and one might expect a similar shift for the interaction of this type of OH group with a phenyl group. Using Courtaulds models it is impossible to make a conformation in which the protons of the OH group lie on or near the six-fold axis of the benzene ring, invariably the protons lie on twofold axes. One would not expect an interaction of the type observed with this type of molecular geometry.

Another possibility is that the oxygen of the silanol group is interacting with the electropositive silicon atoms in the chain and that this interaction is decreasing the force constant of the OH bond and lowering the stretching frequency. Models show that there is considerable crowding around the silicon atoms in this molecule and such an interaction would appear to be unlikely.

The most probable explanation is that hydrogen bonding occurs with the oxygens of the siloxane linkages. It is possible to assemble several conformations of this molecule in which this type of interaction would be favoured.

It is rather difficult to understand why this weak type of bonding is preferred in the crystals of octaphenyltetrasiloxane-1,7-diol because although it would appear that there is steric hindrance to intermolecular hydrogen bonding it is possible to construct structures in which the more normal type of intramolecular bonding is no more hindered than it is in the hexaphenyltrisiloxane-1,5-diol.

As has previously been observed[5] with regard to the crystal structures in general "... only in very exceptional cases does a hydrogen atom bonded to nitrogen or oxygen occupy a position such that hydrogen-bond formation is impossible".

Experimental

Octaphenyltetrasiloxane-1,7-diol. The diol was prepared by the method of Kipping and Robison[6]. Crystallisation from chloroform and light petroleum (30–90°) gave needle-like crystals, m.p. 128.5°.

Infrared Spectra were recorded using a Perkin Elmer Infracord 237 infrared spectrophotometer. Solution spectra were recorded in carbon tetrachloride as solvent at concentrations varying from 0.001 to 0.03 *M*. Solid spectra were taken, using KBr discs and mulls in hexachlorobutadiene.

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