Infrared and Raman Spectra of Cyclic Dimethylsiloxane Oligomers

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Infrared spectra down to 230 cm⁻¹ for the liquid and crystalline state of cyclic dimethylsiloxanes have been compared. Except for the trimer and tetramer, strong conformational selection takes place on crystallization. Useful Raman spectra have been obtained only for the liquid state. Assignments of bands to vibrational types are given; some of these deviate from earlier assignments.

Of the cyclodimethylsiloxanes of general formula (I) only the lowest members $(n=3-6)$ have so far been studied in infrared absorption (above 400 cm^{-1}) and in Raman scattering,[1,2] and a few further members incompletely in the infrared.[3,4]

$$
\left[\begin{array}{c}
CH_3 \\
| \\
-Si-O- \\
| \\
CH_3
\end{array}\right]_n
\tag{I}
$$

The cyclic trimer $(n=3)$ has identical vibrational spectra in the solid, in solution, and in the gas-phase,[1] and these spectra have been interpreted on the basis of a planar ring, although the vibrational assignments may not be final. Vibrational assignments and deduction of conformational symmetry has also been attempted for the cyclic tetramer,[2] but without examining the question of conformational homogeneity.

One objective of the present work was to repeat and extend the infrared spectra for these compounds down to 250 cm^{-1} on a modern grating instrument and to record high-quality Raman spectra on a modern Laser instrument while including the higher members $(n=7-12)$ described in the preceding paper.[9] The lower-frequency part of the spectra might display ring-deformation modes, sensitive to molecular conformations.

The main objective, however, was to record vibrational spectra of the solid state for qualitative comparison with those of the liquid state. This should tell

whether conformational selection by the crystal lattice takes place or not, even when the assignment of the bands to certain vibrational modes is not possible.

Since quite ambitious and more convincing vibrational assignments have subsequently been published [5,6] for the related series of cyclic oligomers of phosphonitrilic fluoride and chloride, it also seemed necessary to critically reconsider in this light the earlier vibrational assignments proposed for the cyclic dimethylsiloxanes.

SPECTROSCOPIC DETAILS

The infrared spectra were recorded for the liquid at room temperature and for the solid in a low-temperature cell, cooled either with liquid nitrogen (estimated temperature $-180°$) or with carbon dioxide-methanol (estimated temperature $-70°$). Only one low temperature spectrum is reproduced for each compound in Fig. 1. For the higher-melting members ($n = 6 - 10$), the spectrum of the crystalline state was obtained with full resolution already with carbon dioxide-methanol cooling, while liquid nitrogen cooling was required for the lower members ($n = 4$ and 5). The actual sample temperature is unknown, since the strong infrared absorption may cause considerable local heating.

Raman spectra of the liquid state were obtained on capillaries, using $He - Ne$ gas laser excitation. The curves are reproduced in the figure together with the infrared spectra to allow easy comparison. No solid state spectra of sufficient quality could be obtained; for the octamer, for example, only a band at 477 cm^{-1} was observed, while the liquid shows its strongest band in this region at 497 cm^{-1}.

Above 1500 cm^{-1}, all spectra are practically identical and uninteresting; this region is therefore not reproduced.

CLASSIFICATION OF OBSERVED BANDS

The infrared and Raman spectra obtained for the liquid cyclosiloxanes are seen to be strikingly similar. Particularly the spectra of the higher oligomers show so little individuality and resemble so strongly the spectra of the polymer that they must represent a very complex mixture of conformers. Obviously, there is no possibility of extracting any information about the conformational situation of the individual rings. The apparent absorption bands are mostly very broad and must rather be called band groups or absorption regions. Most absorption regions split on cooling into several sharp bands, but the complexity is too great to warrant any attempt of detailed band assignments on the basis of assumed conformational symmetries.

Nevertheless, a broad classification of the band groups seems justified. One approach may be to adopt the more rigorous assignments for the simplest model substances, such as tetramethyldisiloxanes,[7] and assume that further mechanical coupling between such units is relatively weak. This is the idea behind earlier assignments for the cyclic dimethylsiloxane trimer [1] and tetramer,[2] and for the linear dimethylsiloxane oligomers.[8] The second approach is
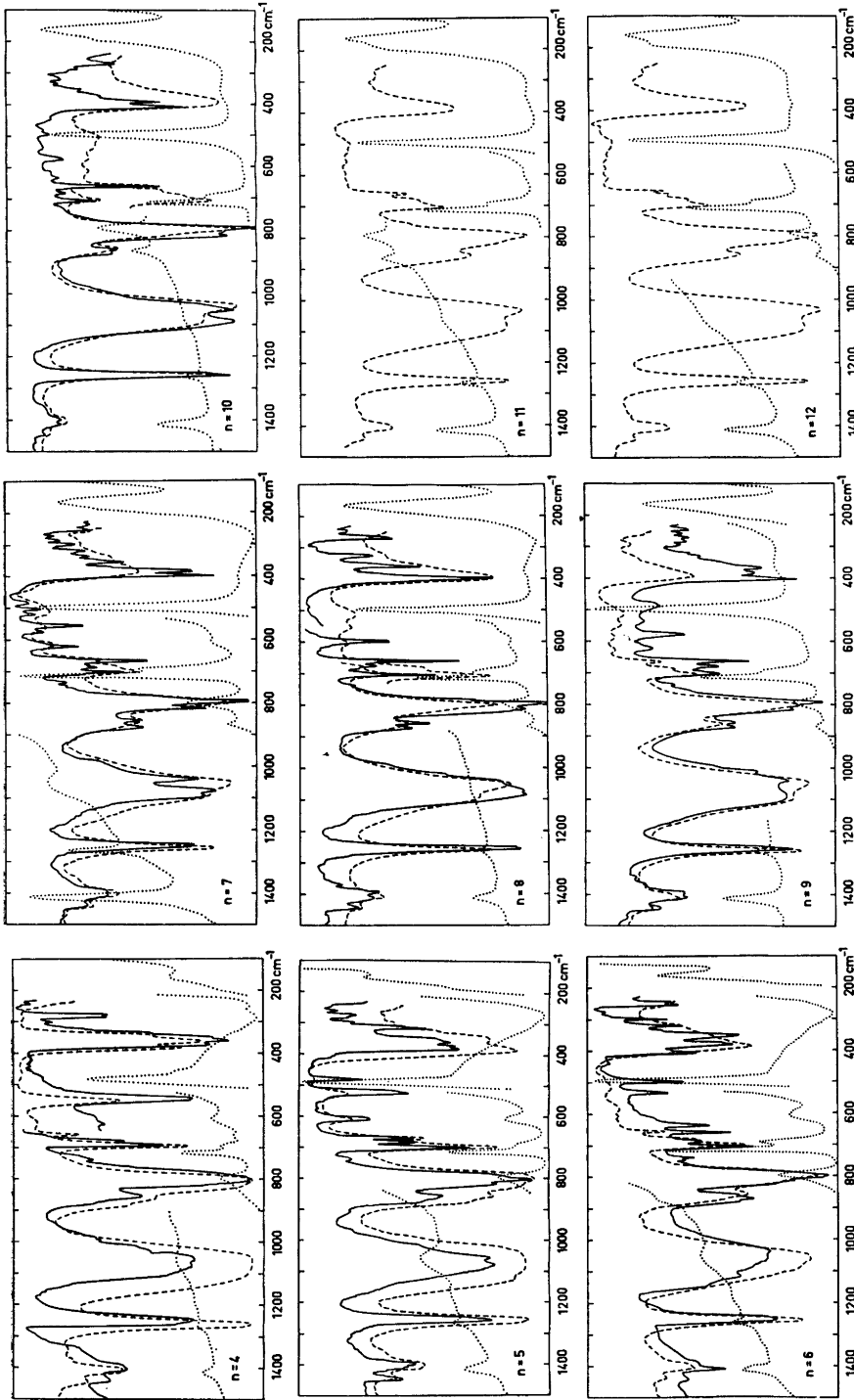
Fig. 1. Infrared and Raman spectra of cyclic dimethylsiloxanes (I). Full line, infrared spectra of solids at low temperature. Broken line, infrared spectra of liquids at room temperature. Dotted line, Raman spectra of liquids at room temperature. The low-temperature spectra presented were obtained for $n = 4 - 7$ with liquid nitrogen cooling; for $n = 8 - 10$ with carbon dioxide/methanol cooling.

to assume strong mechanical coupling of all vibrations of the ring skeleton and relatively weaker coupling only of the vibrations of the substituents. Normal coordinate calculations of the ring vibrations of trimeric phosphonitrilic halides reveal [6] that the splitting of the PN stretching frequencies gives about the same pattern as when the masses are equal, and one gets, as in the familiar benzene case, a low-lying pulsation, and the remaining modes at much higher frequencies.

Intuitively, one feels that the second approach is well justified for the cyclic trimer which is a rigid planar molecule with SiOSi angles not very much wider than the OSiO angles. The larger rings, however, are generally non-planar, and so much evidence suggests the relatively independent mobility of each monomer unit,[9] that the first approach would seem acceptable. Support for the idea of incomplete mechanical coupling may be found in the observation that although the SiO stretching in hexamethyldisiloxane is very strongly split [8] into the symmetric and asymmetric mode (520 and 1055 cm^{-1}), the SiF stretching in difluorodimethylsilane [10] is only weakly split (828 and 952 cm^{-1}). The reason for the strong splitting in the former case may be in part the more linear structure [1] around oxygen (140°), and in part the movement of one light atom between the two relatively heavy silicon atoms,* while the weaker splitting in the latter case is related with the narrow angle at silicon (110°) and weaker interaction between two light atoms through the heavy silicon atom.*

Having both viewpoints in mind, we shall try to find a band classification that is most satisfactory and coherent both for the liquid conformer mixtures of the higher cyclic oligomers and for the single crystal conformer of the cyclic tetramer.

CH$_3$-deformation. The symmetric mode (umbrella-opening) comes at 1270 cm^{-1} and the asymmetric mode at 1410 cm^{-1}, and both are seen in both the infrared and Raman. These vibrations must be rather internal in type,[12] but some broadening would nevertheless be expected due to geminal coupling [12] and differences in conformational environment.

CH$_3$-rocking. This vibration is much more external in type,[12] and geminal coupling produces a symmetric and an asymmetric mode which most likely corresponds to the bands at 870 and 800 cm^{-1}, respectively, seen in both spectra. Further splitting into in-plane and out-of-plane modes, and differences due to the conformational environment would be expected. We think that these are the reasons for the broadness and structure of the infrared bands, rather than an underlying absorption due to the asymmetric SiC stretching [1,2] (see below).

SiO-stretching. If the strong primary splitting takes place within the SiOSi unit, and only weak secondary interaction through silicon is assumed, one would expect two absorption regions of comparable width [1,2] around 500 cm^{-1} (symmetric modes) and 1050 cm^{-1} (asymmetric modes), respectively. The strong and broad infrared absorption at 1000 — 1150 cm^{-1} could fit such a

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* *Cf.* the stronger splitting of the stretching vibration of CS$_2$ (656 and 1523 cm^{-1}, ratio 2.22) than of CO$_2$ ($\sim$1340 and 2350 cm^{-1}, ratio 1.75) and HgCl$_2$ (320 and 415 cm^{-1}, ratio 1.30), all linear molecules, and the markedly weaker splitting in the bent molecules NO$_2$ (1930 and 1615 cm^{-1}, ratio 1.18) and SO$_2$ (1334 and 1145 cm^{-1}, ratio 1.17).[1]

picture, but the sharpness of the strong Raman band at 500 cm^{-1} and its invariability with ring size would rather suggest that this is the ring pulsation mode, so that all other modes are to be found in the 1000 – 1150 cm^{-1} region. This is what one expects if extensive coupling in the ring takes place and compares well with the situation in the phosphonitrilic halides.[6] For the higher cyclosiloxanes (Fig. 1), a subdivision into infrared band groups at 1030 and 1100 cm^{-1}, and a Raman band group at 1050 cm^{-1} is visible. The weak infrared bands between 450 and 650 cm^{-1} have earlier [1,2] been assigned to symmetrical SiO stretching modes, but must now be otherwise interpreted. We are going to show below that these fit in most naturally as symmetrical SiC stretching modes.

Ring deformation. There are two distinct band groups which must be attributed to ring deformations: strong infrared-active bands at 300 – 400 cm^{-1} and weaker bands at 200 – 300 cm^{-1}, both with little distinct Raman counterparts. It is tempting to assign the higher-frequency group to deformations in a rough molecular plane, and the lower-frequency group to deformations perpendicular to that plane, although admittedly such a distinction is very arbitrary in molecules that are not rigorously planar. The strong Raman band at 150 – 200 cm^{-1}, which may or may not have an infrared counterpart, occupies a more narrow frequency region, and may therefore not be a ring deformation, but rather the SiC$_2$ deformation, which for difluorodimethylsilane comes at 213 cm^{-1}.[10]

SiC-stretching. It is generally agreed that the symmetric mode should be lower in frequency [10] and couple more strongly through the ring bonds than the asymmetric mode. The actual earlier assignment [1,2] of the band group at 650 – 720 cm^{-1} in the infrared and the doublet at 700 cm^{-1} in the Raman to symmetric SiC stretching, and the background infrared absorption at 780 – 830 cm^{-1} (underneath the asymmetric CH$_3$-rocking) to asymmetric SiC-stretching does not seem quite convincing. The corresponding frequency regions for symmetric and asymmetric PF-stretching in the related cyclic oligomeric phosphonitrilic fluorides [5,6] are much broader (600 – 900 cm^{-1} and 900 – 1000 cm^{-1}, respectively). Furthermore, the weak but characteristic infrared bands at 450 – 650 cm^{-1}, whose interpretation as SiO-stretching modes has been rejected above, would fit very well in the role of coupled symmetric SiC stretching bands. This leaves the band group at 650 – 720 cm^{-1} as the only candidate for coupled asymmetric SiC-stretching vibrations.

CONCLUSIONS FROM INDIVIDUAL SPECTRA

For a detailed discussion of each ring, it seems most practical to start with the largest rings, as the smallest rings must be expected to show most pronounced individual character.

n = 11 and 12. The smoothness of the band envelopes and the similarity of the liquid spectra for these two rings indicate a very complex conformer mixture. Only the SiC stretching bands give some individual structure to the infrared spectra. Since the observed entropies of melting are very low, it follows that even the solid state must here contain a conformer mixture.

$n = 10$. The liquid spectra show only slightly more individuality. The infrared spectrum of the solid is considerably different, particularly in the SiC stretching region, where much fewer and sharper bands occur. This is indicative of strong conformational selection on crystallization, in agreement with the large observed melting entropy. The spectra suggest that the crystal conformer(s) may not at all be predominant in the liquid.

$n = 9$. The situation resembles that of the decamer, but the infrared spectral changes on crystallization are less marked, since the liquid shows somewhat more spectral structure and the solid definitely more sharp lines. This is in accord with a smaller observed entropy of melting, but it cannot be decided whether the high number of infrared bands in the solid is due to a lower symmetry of the crystal conformer(s) or to a larger number of crystal conformers.

$n = 8$. The spectra of the liquid octamer are very similar to those of the liquid higher oligomers, so that there is no indication whatsoever of a higher conformational homogeneity for this member than for higher homologues. The spectrum of the solid is on the other hand particularly simple with few and sharp bands. This is to be expected on the basis of the observed highest entropy of fusion of the series, indicating strong conformational selection, and from our independent knowledge [13] that only one highly symmetric conformation exists in the crystal lattice. The splitting of all CH_3-group vibrations into clear doublets may be connected with the existence of two non-equivalent $Si(CH_3)_2$ groups in the established crystal conformation.

$n = 7$. The spectra of the liquid heptamer are slightly more specific than those of the higher members. On the other hand, the solid shows even more sharp infrared bands than does the solid nonamer. Unlike the higher members, the liquid spectrum can now be roughly reproduced by simply broadening all the sharp bands of the solid. It therefore seems as if the crystal contains a number of conformers, and that these same are also the most preponderant in the liquid. This is in agreement with the small observed entropy of melting.

$n = 6$. The situation for the hexamer resembles quite much the situation for the octamer. The higher number of bands in the spectrum of the solid might indicate a lower symmetry. That the entropy of melting is much lower than for the octamer might of course indicate the existence of a mixture of conformers in the solid, but it is more likely due to a smaller number of liquid conformers for this smaller ring.

$n = 5$. Since the infrared spectrum of the liquid pentamer can be reproduced quite well by broadening the sharp bands of the solid, and since the number of bands in the solid is quite modest for a molecule having little possibility of adopting a conformation of high symmetry (see earlier), it seems that we must now be approaching a situation with conformational homogeneity. The numerical value of the entropy of melting is acceptable for such a case.

$n = 4$. All the main features of the spectra of the tetramer suggest that the same conformation is present in the liquid as in the solid. Extra infrared bands appear at 280 and 740 cm^{-1}, not in the liquid but in the solid. They have therefore to be explained as a sharpening of broad absorption in the liquid or relaxation of selection rules by packing deformation to a lower symmetry in the crystal lattice.

EXPERIMENTAL

The infrared spectra were recorded on a Perkin-Elmer model 225 spectrometer. For the spectra of the crystals, a low-temperature cell from RIIC was used. Raman spectra were recorded on a Cary model 81 spectrometer, equipped with a Spectra Physics model 125 helium-neon laser.

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