

Fig. 1.—Log  $[\eta]$  vs.  $\log M_2$  for sodium polyphosphate in: (1) 0.35  $M$  NaBr; (2) 0.415  $M$  NaBr.

When theoretical expressions for  $\beta_{22}$  and  $\beta_{23}$  become available, equation 14 should become useful in relating molecular dimensions to charge and electrolyte concentration.<sup>46</sup>

In the meantime we may look upon equation 11 as an empirical equation which in form reproduces the experimental data. The intercept,  $f$ , which may be considered as a measure of the excluded

(46) The last term in equation 14 can be obtained rigorously from membrane equilibrium data, if  $\beta_{33}$  is known. From literature data (H. S. Harned and C. C. Crawford, *THIS JOURNAL*, **59**, 1903 (1937)),  $(2 + \beta_{33}m_3)$  is found to be equal to 1.85 over the range investigated here. Then, with the membrane equilibrium data, the expression in braces in equation 14 simplifies to  $\{[(i^2 - 0.025)/m_3] + (\beta_{22}/P^2)\}$  for our system. Using a realistic value for  $i$ , e.g., one estimated from electrophoresis results, one finds that the term inside the brackets is an order of magnitude larger than the total experimental value of the expression inside the braces. Thus  $\beta_{22}/P^2$  must be of opposite sign to the first term and also very large. Finally, to account for the slope of the line in Fig. 2 by equation 14, it is necessary that  $\beta_{22}/P^2$  should have a large component which is inversely proportional to  $m_3$ .

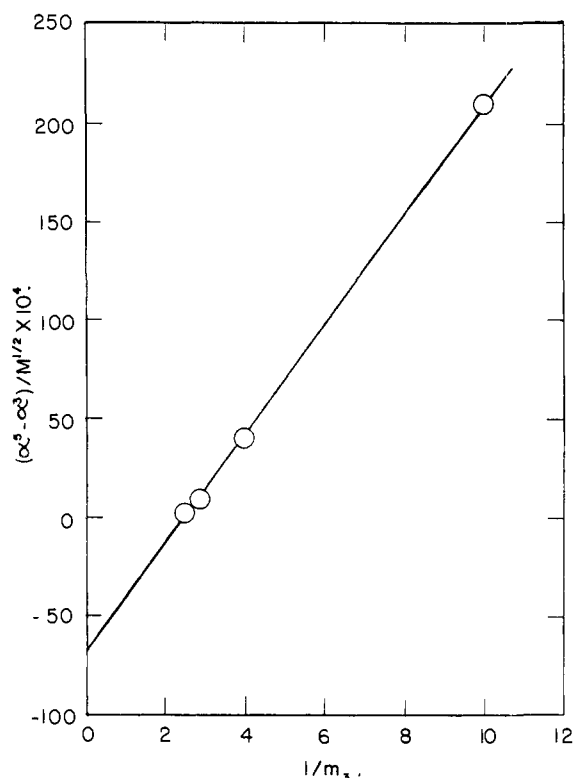


Fig. 2.—Dependence of the molecular expansion coefficient,  $\alpha$ , of sodium polyphosphate (NaPP-7) on the sodium bromide molarity,  $m_3$ .

volume of the hypothetical uncharged polymer, is equal to  $-6.9 \times 10^{-3}$ .<sup>47</sup> This result confirms the solvent incompatibility of associated ( $\text{NaPO}_3$ ) groups which has previously been hypothesized to account for differences in both intrinsic viscosity and salting-out behavior of polyphosphates in the presence of different alkali metal ions.<sup>25</sup>

(47) Such a large negative value so far has been reported only for neutralized polyacrylic acid in solutions of calcium salts (P. J. Flory and J. E. Osterheld, *J. Phys. Chem.*, **58**, 653 (1954)), but not for anionic polyelectrolytes in solutions of sodium salts where the intercept usually is close to zero. This also explains why the difficulty which we encountered in attempting to extrapolate the molecular dimensions to infinite ionic strength has not been observed in other polyelectrolyte-salt systems.

NEW BRUNSWICK, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

## The Spectrum and Structure of Disiloxane<sup>1</sup>

BY R. F. CURL, JR.,<sup>2</sup> AND KENNETH S. PITZER

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The infrared absorption spectrum of disiloxane in argon and nitrogen matrices at 20°K. was investigated. The region covered was from 4000 to 600  $\text{cm}^{-1}$ . The band at 764  $\text{cm}^{-1}$  in the gas phase is found to have two components in the matrix. The Raman band at 1009  $\text{cm}^{-1}$  appears in the infrared spectrum of the matrix. A Si-O-Si bond angle of less than 180° is proposed to explain these results. The Si-O-Si bond angle is estimated to be near 155°.

It is now well established that the typical Si-O-Si bond angle is relatively large—near 160° rather

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than the range of 110° characteristic of many systems. The evidence includes the dipole moment measurements on methylsiloxanes by Sauer and Mead<sup>3</sup> and the crystal structure studies of crys-

(3) R. O. Sauer and D. J. Mead, *THIS JOURNAL*, **68**, 1794 (1946).

tobalite by Nieuwenkamp.<sup>4</sup> These investigations obtained the values  $160 \pm 15^\circ$  and  $150^\circ$ , respectively. Also the study of octamethylspiro(5.5)-pentasiloxane by Roth and Harker<sup>5</sup> indicates that the unstrained Si-O-Si angle must be equal to or greater than the  $130^\circ$  value found in the planar rings of this compound.

While these values are all substantially less than  $180^\circ$ , Lord, Robinson and Schumb<sup>6</sup> conclude that their spectral studies of disiloxane are compatible with a strictly linear Si-O-Si structure and they advance qualitative arguments that the deviation from linearity, if any, must be small. In contrast, Emeleus, MacDiarmid and Maddock<sup>7</sup> concluded from the absence of resolvable structure in the  $957 \text{ cm}^{-1}$  band of disiloxane that the molecule was significantly bent.

There is no significant disagreement between the spectra found by the two groups of investigators, and indeed our results agree also; nevertheless, the conclusions disagree sharply. We have sought to resolve this question by measurements of the spectrum of disiloxane in inert matrices at  $20^\circ \text{K}$ ., where the bands are much sharper. The results indicate a bent Si-O-Si structure.

### Experimental

A sample of disiloxane was prepared by the method used by Lord, *et al.*,<sup>6</sup> except that  $\text{SiH}_3\text{Br}$  rather than  $\text{SiH}_3\text{Cl}$  was the intermediate. The gas phase infrared spectrum of the sample in the sodium chloride region agreed with the gas phase spectrum given by Lord, *et al.*<sup>6</sup> The melting point of the sample was  $-144^\circ$ . The melting point reported by Stock, Somieski and Wintgen<sup>8</sup> is  $-144.1^\circ$ .

The matrix isolation technique employed was developed in this Laboratory by Pimentel and Becker.<sup>9</sup> A gaseous mixture of disiloxane and argon was prepared with a mole ratio of 1 to 830, respectively. One hundredth of a mole of the mixture was sprayed onto a CsBr window maintained at  $20^\circ \text{K}$ . by liquid hydrogen. The spray-on time was 30 minutes. In a similar experiment with a nitrogen matrix, the ratio of moles of nitrogen to moles of disiloxane was 990; the amount of 0.01 mole; and the time of spray on was 1 hr. and 14 minutes. The matrix spectra are shown in Fig. 1. The inconsistency between extinction coefficients, say of the  $1100 \text{ cm}^{-1}$  band, calculated from the two

spectra probably is due to a change of orientation of the spray-on tip with consequent different distributions of sample thickness. The frequencies of the bands observed in the gas phase and in both matrices are listed in Table I.

TABLE I  
INFRARED SPECTRA OF DISILOXANE  
(Absorption maxima,  $\text{cm}^{-1}$ )

| Gas phase       | A Matrix | N <sub>2</sub> Matrix | Intensity |
|-----------------|----------|-----------------------|-----------|
| ..              | 714 (?)  | ..                    | vvw       |
| 764             | 748      | 746                   | vs        |
|                 | 759      | 762                   | vs        |
| 957             | 943      | 947                   | vvs       |
|                 | 964      | 958                   | vvs       |
| .. <sup>a</sup> | 1011     | 1007                  | w         |
| 1107            | 1119     | 1104                  | vs        |
| 1220            | ..       | ..                    | w (?)     |
| 1700            | 1711     | ..                    | vw        |
| 2180            | 2211     | 2213                  | vs        |
| ..              | 2338 (?) | ..                    | vvw       |

<sup>a</sup> There is a Raman band at 1009.

An inconclusive effort was made to find the low frequency Si-O-Si bending mode. If the band is above  $165 \text{ cm}^{-1}$ , it must be very weak, since no distinct absorption band was observed with a 70 cm. cell at 41 mm. pressure. Our search at longer wave lengths (down to  $40 \text{ cm}^{-1}$ ) was less complete but no positive evidence was obtained. Some absorptions were noted at very low frequency, but we felt they were too narrow to be the Si-O-Si bending motion.

The search at longer wave lengths was made possible by the very kind cooperation of Mr. Robert Ohlmann of the Physics Department. He carried out the search on a grating instrument which he has constructed.

### Discussion

It is quite clear that most features of the disiloxane spectrum may be explained on the basis of a linear,  $D_{3d}$ , model. However, most of the features of the spectrum of dimethyl ether<sup>10</sup> also can be explained on such a basis even though the C-O-C bond angle is  $111^\circ$ . The two spectra are very similar in the small number of strong bands—a feature which indicates high symmetry. Thus, if the Si-O-Si bond angle is near  $150^\circ$  as indicated in other studies, the spectrum of disiloxane can be expected to differ only very slightly from that for the linear model.

Two features appeared in the matrix spectra of disiloxane which conflict with the linear model. The band at  $764 \text{ cm}^{-1}$  in the gas phase is assigned to the  $E_u$  degenerate  $\text{SiH}_3$  rocking motion. The narrowing of the bands in the matrix shows this to be two separate bands separated by about  $10 \text{ cm}^{-1}$ . One is to be assigned to the in-plane motion and the other to the out-of-plane motion where the plane is defined by the non-linear Si-O-Si structure.

The other feature is the appearance of the weak band at  $1010 \text{ cm}^{-1}$ . This is the totally symmetric  $\text{SiH}_3$  deformation frequency which appears strongly in the Raman spectrum. In the gas phase infrared spectrum the very strong  $957 \text{ cm}^{-1}$  band is broad enough to conceal a weak band at  $1010 \text{ cm}^{-1}$ . However, the matrix spectra show it unmistakably. Since gas phase selection rules do not hold rigorously in condensed phases, the appearance of this band is contributory evidence rather than proof that the Si-O-Si linkage is non-linear.

(10) B. L. Crawford and L. Joyce, *ibid.*, **7**, 307 (1939).

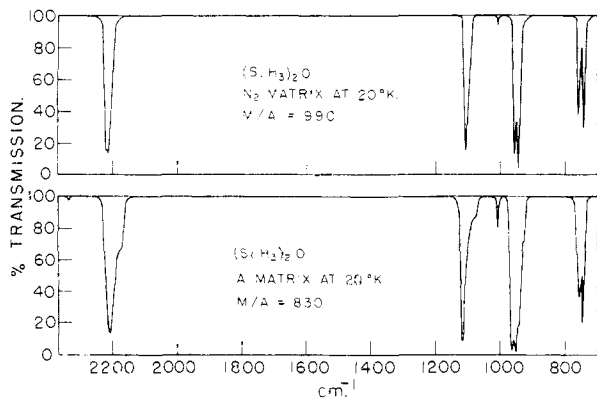


Fig. 1.

- (4) W. Nieuwenkamp, *Z. Krist.*, **92**, 82 (1935); **96**, 454 (1948).  
 (5) W. L. Roth and D. Harker, *Acta Cryst.*, **1**, 34 (1948).  
 (6) R. C. Lord, D. W. Robinson and W. C. Schumb, *THIS JOURNAL*, **78**, 1327 (1956).  
 (7) H. J. Emeleus, A. G. MacDiarmid and A. G. Maddock, *J. Inorg. Nucl. Chem.*, **1**, 194 (1955).  
 (8) A. Stock, C. Somieski and R. Wintgen, *Ber.*, **50**, 1754 (1917).  
 (9) E. Becker and G. C. Pimentel, *J. Chem. Phys.*, **25**, 224 (1956).

An estimate of the probable minimum bond angle may be obtained by comparing the intensity of the 1010  $\text{cm}^{-1}$  band to that of the out-of-phase symmetrical  $\text{SiH}_3$  deformation. For if one assumes that the dipoles generated at each  $\text{SiH}_3$  group have the same magnitude in the in-phase and out-of-phase modes, then

$$\frac{I_i}{I_o} = \cot^2 \left( \frac{\alpha}{2} \right)$$

where

- $\alpha$  = the Si-O-Si bond angle
- $I_i$  = intensity of the in-phase deformation
- $I_o$  = intensity of the out-of-phase deformation

Both the out-of-phase symmetrical deformation and the out-of-phase unsymmetrical deformation were assigned by Lord, *et al.*, to the gas phase band at 957  $\text{cm}^{-1}$ . In the matrix this band is found to be split into a doublet. Which component of this doublet should be identified with the out-of-phase symmetrical deformation has not been determined. Therefore, in order to estimate the minimum bond angle the less intense component (964  $\text{cm}^{-1}$  in argon) was chosen. The estimate of the minimum bond angle obtained is 152° in argon, 158° in nitrogen. The peak intensity was used in the estimate rather than the integrated intensity. This, together with other approximations already mentioned, limits the accuracy of these values.

It should be noted that the band at 1220  $\text{cm}^{-1}$  in the gas phase is not observed in the matrix spectrum. In our opinion no really satisfactory explanation of this band has been found. We, therefore, shall not discuss its disappearance.

It is possible to estimate the Si-O-Si bond angle from the splitting of the 764  $\text{cm}^{-1}$   $\text{SiH}_3$  wagging frequency if certain simplifying assumptions are made.

When the molecule is linear the F and G (potential energy and reciprocal kinetic energy) matrices may be factored into several blocks corresponding to the representations of the  $D_{3d}$  group. The two components of the  $\text{SiH}_3$   $E_u$  wag are in two separate identical blocks. As the molecule is bent off-diagonal elements appear in both the F and G matrices which connect certain blocks. There still remain, however, two separate blocks by symmetry, of which one contains one component of the 764  $\text{cm}^{-1}$  band and the other block contains the other component. It is assumed that the off-diagonal elements which might appear in the F matrix when the molecule is bent are zero since the forces which would yield such elements are expected to be very small. Some of the corresponding elements in the G matrix are non-zero and are

considered. The effect of these off-diagonal elements in the G matrix is calculated by use of second-order perturbation. There are also first order perturbation elements in both the F and G matrices which can be included. The H-H repulsion between silyl groups is a first-order perturbation in the F matrix. It is estimated by using the potential function developed by Hirschfelder and Linnett<sup>11</sup> for the triplet state of hydrogen. This is divided by two as required by valence bond theory. Also the effect of any mixing of the  $\text{SiH}_3$  wag with the E  $\text{SiH}_3$  deformation is neglected.

The bond angle calculated from the splitting in this manner is 157° in the case of argon and 150° in the case of nitrogen. Thus we have a reversal between the estimates based upon the argon and nitrogen matrix data from this splitting as compared to the estimate of the bond angle obtained from the intensity of the 1009  $\text{cm}^{-1}$  band. The estimate of the bond angle obtained from the splitting of the 764  $\text{cm}^{-1}$  band can be called neither an upper or lower limit to the bond angle since the effects of the neglected force constants depend upon their sign. Nevertheless, the various estimates fall in the range 150–158°.

These results apply directly to the disiloxane molecule in the matrix whereas other data refer to the gas molecule. One may ask whether the matrix bends the molecule. If the matrix is crystalline, with cubic closest packing, linear cavities appear to be easiest to form. Thus a straightening of the molecule seems more likely than a bending. If the matrix is glassy, broadening of the bands and not splitting is expected in analogy to liquid solution. Thus we believe there is evidence for a non-linear Si-O-Si structure in the free molecules as well as in the matrices.

The matrix isolation method promises to be a valuable tool for determination of vibrational assignments. The experiment described here is one of the first applications of the matrix isolation method for this purpose. At the dilution employed interactions between the solute molecules should be quite small, and it is hoped that the solute molecules behave as a non-rotating gas at liquid hydrogen temperature in so far as their infrared spectrum is concerned. Thus vibrational bands are very sharp and overlapping bands may be resolved where they could not be in the gas phase. Nevertheless the possible effects of solute-matrix interactions must be kept in mind.

BERKELEY 4, CALIF.

(11) J. O. Hirschfelder and J. W. Linnett, *J. Chem. Phys.*, **18**, 130 (1951).