

sponded to monoclinic symmetry only, the platy face (which had been called the (001) by Solly) being the unique (010) plane. Oscillation and Weissenberg photographs confirmed that the symmetry was monoclinic only, though pseudo-orthorhombic, and these, with rotation photographs, showed that the pseudo-orthorhombic cell was *B*-face-centered. The dimensions of the true monoclinic cell chosen were $a = 6.40$, $b = 13.03$, $c = 5.34$ Å., $\beta = 126.5^\circ$. Those of the pseudo-orthorhombic unit cell may be expressed in terms of the above by means of the matrix 100/010/102. Solly's original orthorhombic unit cell vectors are related to the monoclinic vectors by the matrix 100/102/010. All further data are referred to the above monoclinic unit cell; $M = 184.1$, $V = 358.0$ Å.³, d (obsd.) = 1.715. Two molecules in the unit cell would give d (calcd.) = 1.708.

Space-group Determination.—Reflections were observed for $0k0$ only with k even and for $h0l$ only with l even. There were no other systematic extinctions. The class is therefore $2/m$ and the space group is unequivocally determined as $P2_1/c$.

Molecular Symmetry and Configuration.—The two molecules in the unit cell must occupy the spacial positions $0,0,0$, $0, \frac{1}{2}, \frac{1}{2}$, and must be centro-symmetrical. No other twofold symmetry is possible in this space group. It follows therefore that the molecule must have the *trans*-configuration; it must be dihydroxyfumaric acid. The four molecules of water of crystallization occupy general positions. A complete structure analysis is in progress.

Experimental

The preparation of the crystals was as described by Dr. Hartree. They were reasonably stable, although powder lines appeared on X-ray photographs after exposures of several hours. Six diamond-shaped plates were used, measuring about 0.36 mm. (long axis) \times 0.23 mm. (short axis) \times 0.05 mm.

Copper $K\alpha$ radiation was used in taking the oscillation and Weissenberg photographs. In the case of the Laue photographs the radiation was unfiltered and contained white radiation down to $\lambda = 0.4$ Å.

For the space-group determination $0k0$ reflections up to $k = 16$ were observed and $h0l$ reflections as far as 804. Altogether 29 out of a possible 71 $h0l$ reflections were found and 63 out of a possible 85 $0kl$.

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Thermal and Dielectric Study of Octamethylcyclotetrasiloxane

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The dielectric constant and the cooling and warming curves of a purified sample of octamethylcyclotetrasiloxane (hereafter called *cyclic tetramer*) have been investigated in the region 40° to -60° . The temperature measurements were made with an N.B.S. calibrated platinum resistance thermometer, and the dielectric data were obtained at 1, 5 and 10 kc. with a parallel resistance capacity bridge using

a coaxial cell with $14.95 \mu\text{mf.}$ capacitance. The cell was carefully calibrated with standard liquids. Since no dispersion was ever observed, the dielectric data presented here represented the static dielectric constant, ϵ_0 . The dielectric constant data for the liquid, and solid phase just below the freezing point are correct to within at least 0.5%. As is commonly the case for dielectric data obtained with such cells, the observations well below the freezing point and particularly below the transition, are less accurate (probably about 5% low below the transition) owing to the presence of an air-film capacitance. This capacitance is a result of the shrinkage of the solid material between the condenser plates. The data near and below the transition are nonetheless useful in that they show clearly where the transition takes place (see below).

On cooling, cyclic tetramer froze into an α -modification at 17.54° . On further cooling, a new polymorphic form (β) appeared at about -35° . The α -form undoubtedly had supercooled considerably before it finally nucleated. On rewarming after brief storage at -60° , the first-order α - β transition appeared at -16.30° . This transition was accompanied by a latent heat and a sharp break in the dielectric constant curve (Fig. 1). The sample remelted at 17.54° . Analysis of the cooling curve indicated the sample was close to 99.71 mole per cent. pure.¹

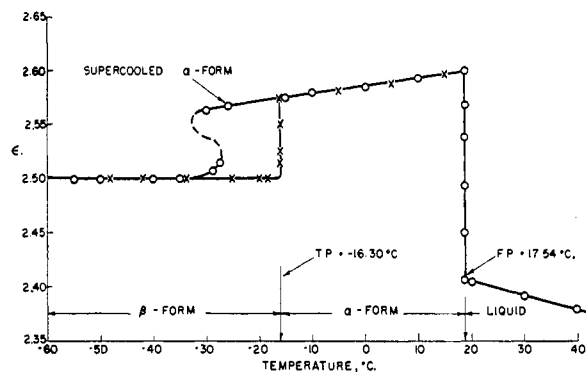


Fig. 1.—Dielectric constant of tetramer as a function of temperature: —○— data obtained with lowering temperature; —X—, rising temperature.

The α - β transition in cyclic tetramer may be the result of the onset of hindered intermolecular rotation which begins at -16.30° . The low heat of fusion² of cyclic tetramer is consistent with the suggestion that there is considerable molecular freedom in the α -form. It is interesting to note that molecules of similar shape (*e.g.*, cyclohexane, chlorocyclohexane and cyclohexanone) also exhibit first-order solid state transitions, low heats of fusion, and dielectric properties which have been interpreted in terms of molecular rotation.³ The rotation in the α -forms of the polar compounds mentioned above should not be considered "free," since the observed dielectric relaxation times are

(1) Drs. R. C. Osthoff and W. T. Grubb of this Laboratory have recently prepared cyclic tetramer, m.p. 17.58° , estimated to be 99.82 mole per cent. pure (to be published).

(2) R. C. Osthoff, W. T. Grubb and C. A. Burkhard, *THIS JOURNAL*, **75**, 2227 (1953).

(3) R. W. Crowe and C. P. Smyth, *ibid.*, **73**, 5406 (1951).

very much longer than would be expected on this basis. It is likely that the molecular motions in the α -forms of cyclic tetramer and cyclohexane are hindered as well. Frenkel's concept of rotational disordering,⁴ which postulates that molecular rotation is hindered both above and below the transition, is probably applicable to the present case. Finally, it should be remarked that rotation of the methyl groups may be involved in the transition at -16.30° .

An effort will now be made to estimate the dipole moment, μ , of cyclic tetramer using data on the liquid in the Onsager equation in the form

$$\frac{4\pi N\mu^2}{9kT} = \frac{M(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{d\epsilon_0(\epsilon_\infty + 2)^2}$$

In this equation N is the Avogadro number, k the Boltzmann constant, T the absolute temperature, M the molecular weight, d the density, and ϵ_∞ that part of the dielectric constant due to atomic and electronic polarization. For cyclic tetramer at 20° , $d = 0.956$, $\epsilon_0 = 2.405$, and $M = 296.51$. It is now necessary to estimate ϵ_∞ . This is usually done by assuming that $\epsilon_\infty \cong n^2$ or $\epsilon_\infty \cong 1.05 n^2$, where n is the index of refraction. As will be demonstrated below, both of these approximations are inadequate for siloxanes. The unusually large discrepancy between ϵ_∞ and n^2 is a result of the strong infrared (atomic) absorption in these substances.^{5,6}

The careful total molar polarization *vs.* temperature data obtained by Di Giacomo and Smyth⁷ on gaseous hexamethyldisiloxane permits an accurate relationship to be found between ϵ_∞ and n^2 for this material. These workers have shown that the total molar polarization of hexamethyldisiloxane is 62.0 cc., and that it is *independent of temperature*. It follows that the dipole moment of this compound is indistinguishable from zero, and that the aforementioned polarization consists entirely of electronic and atomic contributions. The molar electronic polarization, P_e , of hexamethyldisiloxane is only 49.0 cc. (obtained using $n_D^{20} 1.377$ and $d^{20}_4 0.7619$). It is easily deduced from the above that the atomic polarization, P_a , has the value 13.0 cc., and that $\epsilon_\infty = 1.177 n^2$. These data emphasize that it is erroneous to assume that $\epsilon_\infty = n^2$ (or that $P_a = 0$) when calculating solution or Onsager moments of siloxanes. The precise value of ϵ_∞ in terms of n^2 obtained here for hexamethyldisiloxane should apply reasonably well to other siloxanes, although some further enhancement of the atomic polarization is to be expected for compounds containing rings, or with a higher ratio of Si and O to CH_3 .

If the revised approximation $\epsilon_\infty = 1.177 n^2$ is used in the Onsager equation with the other data for cyclic tetramer, it is found that μ is $0.4 D$. This value of μ is certainly more reliable than the value of 1.1 Debye calculated using the approximation

$\epsilon_\infty = n^2$. The present estimate of $\mu = 0.4$ Debye probably represents an upper limit for the dipole moment since it is likely that the amount of atomic polarization has been somewhat underestimated for this ring compound (see above). A dipole moment might arise in this material if some of the molecules in the liquid existed in a "crown" form with silicon and oxygen atoms occupying separate and parallel planes, provided that an accidental cancellation of bond moments did not occur.

Finally, it is of interest to attempt to calculate the increase of density at the freezing point for cyclic tetramer using only the dielectric constant of the liquid and solid at the freezing point, and to compare this with the increase of density as measured directly. Using $P_{e,a}(\text{liq}) = P_{e,a}(\text{s})$ where $P_{e,a} \equiv (\epsilon_0 - 1)M/(\epsilon_0 + 2)d$, it is found that $d(\text{solid})/d(\text{liquid}) = 1.090$. The above calculation assumes (a) the electronic and atomic polarization does not change appreciably with change of state and (b) orientation (dipole) polarization is negligibly small. It is found by direct measurement that $d(\text{solid})/d(\text{liquid}) = 1.095$.

The change of ϵ_0 which appears at the solid state transition temperature is a result of the material expanding and again coming into contact with the condenser plates. Thus, while the abrupt change of ϵ_0 at -16.30° clearly denotes the α - β transition, it is not possible to obtain an accurate estimate of the density change accompanying the transition.

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The Synthesis of 4,5-Diamino-*n*-eicosane and of 2-Methyl-3,4-diamino-*n*-nonadecane¹

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It has been shown³ that the phospholipide moiety of a complex polysaccharide obtained from cultures of *E. coli* contains, as one of its nitrogenous components, a base which has been named necrosamine, and to which has been assigned the provisional formula $\text{CH}_3(\text{CH}_2)_{14}\text{CH}(\text{NH}_2)\text{CH}(\text{NH}_2)\text{C}_2\text{H}_7$. Since it appears that necrosamine is one of the isomers of 4,5-diamino-*n*-eicosane, or of 2-methyl-3,4-diamino-*n*-nonadecane, we have investigated the synthesis of each of these two diamines and have obtained each diamine in the form of two diastereoisomeric dihydrochlorides. Preliminary experiments have suggested that necrosamine dihydrochloride may be one of the optical isomers of the more soluble 4,5-diamino-*n*-eicosane dihydrochloride.

Experimental^{4,5}

Mixed *n*-C₂₀-Acyloins.⁶—To a 2-liter 3-necked flask, equipped with a stirrer, reflux condenser, dropping funnel, nitrogen inlet and thermometer, was added, in an atmosphere

(4) J. Frenkel, "Kinetic Theory of Liquids," Oxford University Press, 1946, pp. 488. See pp. 88-92.

(5) N. Wright and M. J. Hunter, *THIS JOURNAL*, **69**, 803 (1947).

(6) E. B. Baker, A. J. Barry and M. J. Hunter, *Ind. Eng. Chem.*, **38**, 1117 (1946).

(7) A. Di Giacomo and C. P. Smyth (to be published). The author is indebted to Professor Smyth and Dr. Di Giacomo for the use of their data prior to publication.

(1) Supported in part by a grant from the National Cancer Institute of the U. S. Public Health Service.

(2) To whom inquiries regarding this article should be sent.

(3) M. Ikawa, J. B. Koepfli, S. G. Mudd and C. Niemann, *THIS JOURNAL*, **75**, 3439 (1953).

(4) All melting points are corrected.

(5) All microanalyses by Dr. A. Elek.

(6) S. M. McElvain, *Org. Reactions*, **4**, 267 (1948).