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 Smyth[7] 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 $n^{20}\text{D}$ 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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(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.

The Synthesis of 4,5-Diamino-*n*-eicosane and of 2-Methyl-3,4-diamino-*n*-nonadecane[1]

BY MIYOSHI IKAWA AND CARL NIEMANN[2]

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It has been shown[3] 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 $CH_3(CH_2)_{14}CH(NH_2)CH(NH_2)C_3H_7$. 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*-C_{20}-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

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(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).

of nitrogen, 500 ml. of dry xylene and 23 g. of sodium. The flask and its contents were heated in an oil-bath maintained at 110°, until all of the sodium was well dispersed whereupon a mixture of 68 g. (0.25 mole) of methyl palmitate and 25 g. (0.25 mole) of methyl butyrate was slowly added during the course of 45 minutes. Stirring was continued for an additional 15 minutes, the oil-bath removed and 25 ml. of methanol slowly added to the viscous reaction mixture. When all of the sodium had disappeared 500 ml. of water was slowly added to the now fluid reaction mixture, the residual solid collected by centrifugation, washed several times with benzene, and the washings added to the xylene layer. This latter solution was washed with water until neutral, then with dilute hydrochloric acid, and finally with water. Fractional distillation gave 26.6 g. (34%) of a *n*-C_{20}-acyloin fraction, b.p. 170–180° (1.5 mm.). To 3.12 g. of this product, dissolved in 25 ml. of ethanol, was added 4.3 g. of phenylhydrazine and 3 ml. of acetic acid, the solution heated on a steam-bath for a few minutes, and sufficient water added to produce a slight turbidity. As the heating was continued the reaction mixture became more turbid and from time to time sufficient ethanol was added to restore the reaction mixture to its original state. When heating no longer led to an increased turbidity of the reaction mixture, it was cooled, the oil that formed induced to crystallize by scratching and the solid so obtained recrystallized from aqueous ethanol to give 2.9 g. (59%) of the phenylosazone of 4,5-*n*-eicosandione, m.p. 71–73°.

Anal. Calcd. for $C_{32}H_{50}N_4$ (490.8): C, 78.4; H, 10.3. Found: C, 78.5; H, 10.4.

4,5-*n*-Eicosandione.—To 10 g. of the *n*-C_{20}-acyloin fraction in 100 ml. of chloroform was added 50 ml. of a 1.05 *M* solution of iodine monochloride in glacial acetic acid[7] and the mixture allowed to stand at 25° for two days. To this solution was added 200 ml. of water and then solid sodium thiosulfate, in small portions, until the aqueous phase remained colorless after shaking. The chloroform layer was then washed with dilute aqueous sodium thiosulfate, evaporated to dryness, and the residue recrystallized from ethanol to give 6.34 g. (64%) of 4,5-*n*-eicosandione, m.p. 56.5–57.5°.

Anal. Calcd. for $C_{20}H_{38}O_2$ (310.5): C, 77.4; H, 12.3. Found: C, 77.5; H, 12.3.

Dioxime of 4,5-*n*-Eicosandione.—To a solution of 4.65 g. of 4,5-*n*-eicosandione in 75 ml. of ethanol was added a solution of 2.4 g. of sodium hydroxide and 6.3 g. of hydroxylamine hydrochloride in 30 ml. of water, and the mixture heated, under refluxing conditions, for one hour with the addition of sufficient ethanol to prevent the formation of a precipitate. The mixture was then cooled, the crystalline precipitate collected, washed with water and recrystallized from aqueous ethanol to give 4.25 g. (83%) of the dioxime, m.p. 135.5–137.5°. A second recrystallization from the same solvent gave a product, m.p. 136.5–137.5°.

Anal. Calcd. for $C_{20}H_{40}O_2N_2$ (340.5): C, 70.5; H, 11.8; N, 8.2. Found: C, 70.7; H, 11.7; N, 8.1.

4,5-Diamino-*n*-eicosane Dihydrochloride.—A solution of 1.02 g. of the dioxime of 4,5-*n*-eicosandione in 100 ml. of absolute ethanol and 1.5 ml. of concentrated hydrochloric acid was hydrogenated, under one atmosphere of hydrogen and over 0.40 g. of platinic oxide, for four hours at 25°. The solution was then freed of catalyst, evaporated to a small volume, the residue dissolved in water, the solution extracted with ether, the aqueous phase made alkaline with aqueous sodium hydroxide, extracted with ether and the ethereal extract dried over anhydrous sodium sulfate. Dry hydrogen chloride was passed into the dry ethereal extract to give a precipitate which was collected and recrystallized twice from water to give 0.385 g. of 4,5-diamino-*n*-eicosane dihydrochloride, colorless glistening plates.

Anal. Calcd. for $C_{20}H_{46}N_2Cl_2$ (385.5): C, 62.3; H, 12.0; N, 7.3. Found: C, 62.6; H, 12.2; N, 7.2.

The above dihydrochloride was converted into the dipicrate, m.p. 138–140.5° after two recrystallizations from aqueous ethanol.

Anal. Calcd. for $C_{32}H_{50}O_{14}N_8$ (770.8): C, 49.9; H, 6.5; N, 14.5. Found: C, 50.2; H, 6.5; N, 14.6.

The ethereal solution remaining after the collection of the ether-insoluble dihydrochloride was evaporated to dryness and the residue recrystallized from ethyl acetate containing a small amount of absolute ethanol to give 0.332 g. of a second 4,5-diamino-*n*-eicosane dihydrochloride.

Anal. Calcd. for $C_{20}H_{46}N_2Cl_2$ (385.5): C, 62.3; H, 12.0; N, 7.3. Found: C, 62.6; H, 12.0; N, 7.2.

In contrast to the ether-insoluble dihydrochloride, the ether-soluble dihydrochloride was appreciably soluble in cold water. All attempts to prepare a dipicrate from the latter compound failed in that only oils were obtained.

Mixed Iso-C_{20}-acyloins.—The acyloin condensation of methyl palmitate and methyl isobutyrate, conducted as described above, gave 36% of an iso-C_{20}-acyloin fraction, b.p. 175–190° (2 mm.).

2-Methyl-3,4-*n*-nonadecandione.—The oxidation of 17.7 g. of the iso-C_{20}-acyloin fraction, dissolved in 100 ml. of chloroform, with 87 ml. of 1.05 *M* iodine monochloride in glacial acetic acid gave after fractional distillation 13.4 g. (76%) of crude 2-methyl-3,4-nonadecandione, b.p. 140–145° (0.1 mm.), m.p. 18–20°, and a small amount, *i.e.*, 0.48 g., of an unidentified product, m.p. 58–61°.

Dioxime of 2-Methyl-3,4-*n*-nonadecandione.—To a solution of 4.65 g. of the crude diketone in 75 ml. of ethanol was added a solution of 6.3 g. of hydroxylamine hydrochloride and 2.4 g. of sodium hydroxide in 30 ml. of water and the reaction conducted as previously described for the corresponding derivative of *n*-eicosane. The solid which was obtained was recrystallized from ethanol to give 4.5 g. of an impure product, m.p. 60–90°. On further recrystallization from ethanol a product, m.p. 113–115°, was obtained.

Anal. Calcd. for $C_{20}H_{40}O_2N_2$ (340.5): C, 70.5; H, 11.8; N, 8.2. Found: C, 71.6; H, 11.8; N, 7.6.

2-Methyl-3,4-diamino-*n*-nonadecane Dihydrochloride.—A solution of 0.80 g. of the crude dioxime, m.p. 60–90°, in 80 ml. of absolute ethanol and 1.5 ml. of concentrated hydrochloric acid was hydrogenated as before using 0.3 g. of platinic oxide. After removal of the catalyst the filtrate was evaporated to dryness, the residue dissolved in water, the solution extracted with ether, the aqueous phase made alkaline with aqueous sodium hydroxide, extracted with ether, the ethereal solution acidified with methanolic hydrogen chloride and evaporated to dryness. The residue was extracted with dry ether to give an ether-soluble and an ether-insoluble fraction. The ether-insoluble fraction was recrystallized from ethanol to give 0.173 g. of a 2-methyl-3,4-diamino-*n*-nonadecane dihydrochloride.

Anal. Calcd. for $C_{20}H_{46}N_2Cl_2$ (385.5): C, 62.3; H, 12.0; N, 7.3. Found: C, 62.4; H, 11.9; N, 7.4.

The ether-soluble fraction was evaporated to dryness to give a partially crystalline sirup which was triturated and washed with ethyl acetate and then recrystallized from ethyl acetate to give 0.065 g. of a second 2-methyl-3,4-diamino-*n*-nonadecane dihydrochloride.

Anal. Calcd. for $C_{20}H_{46}N_2Cl_2$ (385.5): C, 62.3; H, 12.0; N, 7.3. Found: C, 62.2; H, 12.1; N, 7.2.

All attempts to prepare the dipicrates from the above two diamine dihydrochlorides gave only oils.

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Correlation of Entropies of Transition and Fusion

BY GEORGE C. HOOD

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Certain molecules which approach spherical symmetry possess the ability to rotate in the solid phase. In general, the very existence and entropy change of a transition believed to indicate the onset of molecular rotation in a crystal must be determined experimentally. Similarly, the entropy change of a fusion is difficult to estimate. However, with the aid of the external symmetry number (σ), certain correlations and predictions can be made for members of a substitution series, such as CX_4, CX_3Y . . ., CY_4.

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[7] V. L. Hansley, THIS JOURNAL, 57, 2305 (1935).