though this correspondence between the two sets of results may be coincidental, the fact that both polymers are polar in nature possibly is significant. These effects of the medium, amounting to 22% in $\langle r^2 \rangle_0$ for PDMS and 15 to 20% for the sulfone, far exceed specific solvent effects observed to date for nonpolar polymers.

The disparity between $\langle r^2 \rangle_0$ and the result calculated for free rotation is considerably smaller than for other polymer chains. The effects of hindrances to free rotation are by no means insignificant, however. They are discussed in detail in the following paper.

Configuration of the Poly-(dimethylsiloxane) Chain. III. Correlation of Theory and Experiment

By P. J. FLORY, V. CRESCENZI,[1] AND J. E. MARK

The characteristic ratio $(r^2)_0/nl^2$ for poly-(dimethylsiloxane) has been calculated by Ising lattice methods using the *trans-gauche* rotational isomeric state model as a convenient device for introducing various bond conformations with appropriate statistical weights. Steric interactions between nonbonded atoms must exclude successive *gauche* rotations of opposite sign for the pair of bonds on either side of a silicon atom; coulombic repulsions of O atoms may largely suppress the similar conformation about O. Bond rotations cannot, therefore, be treated as independent. These inferences from the structure of the siloxane chain are confirmed by experimental values of the characteristic ratio. Owing to the inequality of the bond angles ($\angle$OSiO = 110° and $\angle$SiOSi = 143°), a decrease in the *trans* population increases $\langle r^2 \rangle_0/nl^2$. Hence, the positive temperature coefficient for this ratio denotes a lower energy for the *trans* state by ca. 800 cal. mole^{-1}. This energy is attributed to favorable interaction between CH_3 pairs separated by 3.8 Å. in the planar (*i.e.*, *trans*) conformation. The larger value observed for the ratio in a less polar medium is in the direction predicted for enhanced electrostatic interaction within a chain of partially ionic Si–O bonds.

Bond angles at the oxygen and silicon atoms of the poly-(dimethylsiloxane) chain differ considerably, as we have had occasion to point out in a preceding paper.[2] Whereas $\angle$OSiO is approximately tetrahedral, $\angle$SiOSi is much larger, being in the neighborhood of 143°.[3] It is this alternation in bond angles which marks the point of departure in the analysis of the spatial configuration of the siloxane chain[4] from that of other macromolecules for which successive bond angles are identical, or virtually so.

The significance of this difference is rendered apparent by considering the all-*trans* conformation of the siloxane chain shown by solid lines in Fig. 1 and 2. Owing to the inequality $\theta' < \theta''$, these being the supplements of the bond angles at oxygen and silicon, respectively, the planar conformation generated by assigning all bonds to *trans* rotational "states" consists of a succession of closed figures approximating polygons (the impossibility of superposition of successive polygons being ignored). This is in sharp contrast to chains for which $\theta' = \theta''$; their planar conformations are highly extended, the units being disposed about a rectilinear axis. Rigid adherence to a unique conformation obviously will not prevail except under special circumstances such as those imposed by the crystalline state. Comparison of the two cases considered serves, however, to indicate the profound difference to be expected in the dependence of the chain configuration on $\Delta\epsilon/kT$, where $\Delta\epsilon$ is the difference in energy between the nonplanar and the planar bond conformations. Thus the ratio $(\langle r^2 \rangle_0/nl^2)_{n \to \infty}$ of the unperturbed mean-square end-to-end length of the chain to the product of the number n of bonds and the square of the bond length l, taken in the limit $n = \infty$, increases without limit with $\Delta\epsilon/kT$ for chains having $\theta' = \theta''$. But for $\theta' \neq \theta''$ this ratio must vanish in the limit $\Delta\epsilon/kT = \infty$.

Birshtein, Ptitsyn, and Sokolova[4] stressed the importance of bond angle alternation on the configurational characteristics of the siloxane chain. Through misinterpretation of the experimental value of $\langle r^2 \rangle_0/nl^2$, however, they were led to conclude that a satisfactory account of experimental results could be achieved assuming: (a) a threefold rotational hindrance potential symmetric about the *trans* form ($\varphi = 0$), this form being assigned a slightly lower energy than that of the *gauche* forms ($\varphi = \pm120°$); and (b) mutual independence of the hindrance potentials for neighboring bonds. Experimental results gathered in the two preceding papers are irreconcilable with predictions based on the latter assumption, as we shall have occasion to point out. Moreover, examination of structural models of the chain shows this assumption to be untenable. Certain combinations of rotations about two successive bonds give rise to severe interactions; hence, the potential hindering rotation about a given bond must depend on the rotations of its neighbors. The more elaborate mathematical methods appropriate to this latter case must therefore be employed for interpretation of the siloxane chain configuration.

In this paper we undertake to interpret the experimental values of the characteristic ratio $\langle r^2 \rangle_0/nl^2$ and its temperature coefficient for the poly-(dimethylsiloxane) (PDMS) chain in terms of the rotational isomeric chain model.[5-8] Specifically, a threefold potential is assumed, with allowance for interdependence of neighboring bond rotations as indicated by analysis of the molecular geometry.

Theoretical Treatment

The Rotational Isomeric State Approximation.—The barrier height for the potential hindering rotation about the C–O bond of methanol is 1.07 kcal. mole^{-1},[9-11] com-

(1) NATO scholar on leave from Istituto Chimico-Fisica, Naples, academic year, 1962–1963.

(2) J. E. Mark and P. J. Flory, *J. Am. Chem. Soc.*, **86**, 138 (1964).

(3) L. E. Sutton, Ed., "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chemical Society, London, 1958.

(4) T. M. Birshtein, O. B. Ptitsyn, and E. A. Sokolova, *Vysokomolek. Soedin.*, **1**, 852 (1959).

(5) S. Lifson, *J. Chem. Phys.*, **30**, 964 (1959).

(6) K. Nagai, *ibid.*, **31**, 1169 (1959).

(7) T. M. Birshtein and O. B. Ptitsyn, *J. Tech. Phys., U.S.S.R.*, **29**, 1048 (1959); T. M. Birshtein, *High Molec. Compds. (U.S.S.R.)*, **1**, 798, 1086 (1959); O. B. Ptitsyn, *Usp. Fiz. Nauk*, **49**, 371 (1959).

(8) C. A. J. Hoeve, *J. Chem. Phys.*, **32**, 888 (1960).

(9) E. V. Ivash and D. M. Dennison, *ibid.*, **21**, 1804 (1953).

(10) D. R. Hershbach, "Bibliography for Hindered Internal Rotation and

pared with 2.9 kcal. mole^{-1} for the C–C bond in ethane. That for the C–Si bond,[10,11] as manifested in methyl- and ethylsilane, is 1.5 to 2.0 kcal. mole^{-1}.[12] The value for the Si–O bond is not known with certainty. Scott and co-workers[13] concluded from analysis of thermody-namic data for hexamethyldisiloxane that the barrier does not exceed a few hundred cal. mole^{-1}. A barrier of this magnitude would be too small to justify, literally, the rotational isomeric state approximation according to which each bond adopts an angle of rotation close to one of the three minima in the potential barrier. The siloxane chain should in fact be represented by a continuum of rotational states. The rotational potential probably dis-plays no pronounced maxima other than may occur for combinations of rotations of successive bonds giving rise to more or less severe steric conflicts (cf. following).

These considerations would seem to undermine re-liance on methods developed[5–8] for treating chains com-prising bonds each of which has access to a finite number of discrete rotational states. Yet, as a mathematical device, the continuous distribution over rotational angles φ may be approximated by a distribution over a discrete set of values of φ. Let these be s in number. The structure of the siloxane chain requires that the set of angles be symmetrically disposed with respect to the planar, or trans, bond conformation to which we assign the rotation angle $\varphi = 0$. The statistical weights ascribed to these s states must reflect the aver-aged potentials for the ranges of φ which they respec-tively represent. In effect, the actual potential is re-placed by an s-fold potential with unequal values at its various minima. In the special case of equal statis-tical weights for these s states, the result obtained is readily shown to be identical with that for free rota-tion over a continuum of angles. Thus, in this limit-ing case at least, the discrete rotational state model yields the correct result.

In the following we explore interpretation of the siloxane chain configuration in terms of three rotational states consisting of the trans state $\varphi = 0$, and two gauche states at $\varphi = \pm 120°$. A threefold model has been chosen partly in deference to convenience, but also in consideration of the likelihood of small potential minima, of origin similar to those in ethane and other hydrocarbons, in the neighborhood of these angles. The choice of 120° is somewhat arbitrary, but not crit-ical, insofar as the numerical calculations are con-cerned. The magnitude of interactions between non-bonded groups considered below depends on the choice of rotational angle for the gauche states, of course, and this must be borne in mind.

Structural Dimensions.—For a wide range of silicate minerals[14] $\angle$ SiOSi $= \pi - \theta'$ averages 140.0°; devia-tions from the average are remarkably small. At the opposite extreme of relevant structures, Aronson, Lord, and Robinson[15] concluded that $\angle$ SiOSi $= 148°$ in gase-ous disilane, their result being based on the moment of inertia about the axis parallel to Si⋯Si as deduced from the far-infrared spectrum. For the hexamethylcyclo-trisiloxane ring, known to be planar,[16] Pyronel[3,17] found $\angle$ SiOSi $= 136°$ ($\pm 0.5°$) from analysis of the X-ray dif-

Figure 1.

Figure 2.

fraction pattern of the crystal.[18] The ring undoubt-edly is strained. This is evidenced by the abnor-mally low $\angle$ OSiO $= 104°$,[17] from which it may be in-ferred that the unstrained $\angle$ SiOSi in higher cyclic homo-logs, and in acyclic analogs, should be at least 140°. This expectation is borne out by the X-ray crystallo-graphic investigation of octamethylcyclotetrasiloxane carried out by Steinfink, Post, and Fankuchen[19] who found $\angle$ SiOSi $= 141.5$ to $143.5°$. The ring is non-planar and therefore free of strain. Larsson[20] found $\angle$ SiOSi $= 145°$ for the analogous cage structure, octa-(methylsilsesquioxane), consisting of six nonplanar rings of eight members each.

In light of these results we consider 37° the best value for θ' (Fig. 1 and 2). Calculations have been per-formed, however, for other values of θ' as well (cf. seq.). The OSiO angle is universally accepted as approxi-mately tetrahedral.[3] Accordingly, we take $\theta'' = 70°$. Distances between nonbonded atoms and groups have been calculated for various conformations using[3] $d_{Si-O} = 1.64$ Å. and $d_{Si-C} = 1.90$ Å.

Statistical Weight Matrices for Bond Rotations.— In the trans (i.e., planar) conformation depicted by solid lines in Fig. 1 the distance between methyl groups attached to neighboring silicon atoms and situated on the same side of the plane is 3.78 Å. This distance is somewhat less than twice the intermolecular van der Waals radius, ca. 2.0 Å., for the methyl group.[21,22] It is considerably greater than the intramolecular methyl-methyl distance, 3.04 Å., in the gauche conformation of n-butane for which the repulsive energy is a mere 800 cal. mole^{-1}. Pitzer and Catalano[23] estimate the difference in electron correlation energies for the gauche and trans conformations of n-butane at -2000 cal mole^{-1}; the repulsive energy is indicated there-

Microwave Spectroscopy," Lawrence Radiation Laboratory, University of California, Berkeley, Calif., 1962.

(11) C. C. Lin and J. D. Swalen, Rev. Mod. Phys., 31, 841 (1959).

(12) R. W. Kilb and L. Pierce, J. Chem. Phys., 27, 108 (1957); D. H. Peterson and L. Pierce, unpublished; see ref. 9.

(13) D. W. Scott, J. F. Messerly, S. S. Todd, G. B. Guthrie, I. A. Hossenlopp, R. T. Moore, A. Osborn, W. T. Berg, and J. P. McCullough, J. Phys. Chem., 65, 1320 (1961).

(14) F. Liebau, Acta Cryst., 14, 1103 (1961).

(15) J. R. Aronson, R. C. Lord, and D. W. Robinson, J. Chem. Phys., 33, 1004 (1960).

(16) E. H. Aggarwal and S. H. Bauer, ibid., 18, 42 (1950).

(17) G. Pyronel, Atti Accad. naz. Lincei, Rend., 16, 231 (1954).

(18) These results are confirmed by the X-ray crystallographic distances for octamethylspiro-5:5-pentasiloxane, consisting of two six-membered rings, and investigated by W. L. Roth and D. Harker, Acta Cryst., 1, 34 (1948); see ref. 3, p. M220.

(19) H. Steinfink, B. Post, and I. Fankuchen, Acta Cryst., 8, 420 (1955).

(20) K. Larsson, Arkiv Kemi, 16, 203 (1960).

(21) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954.

(22) L. Pauling, "The Nature of the Chemical Bond," Third Ed., Cornell U iversity Press, Ithaca, N. Y., 1960.

(23) K. S. Pitzer and E. Catalano, J. Am. Chem. Soc., 78, 4844 (1956).

fore to be about 2500 to 3000 cal. mole^{-1} (positive). Without entering into discussion of the reasons for the empirically evident disparity between the inter- and intramolecular van der Waals radii, we note that the magnitude of the correlation energy calculated by Pitzer and Catalano[23] for interactions between atoms of the methyl groups in the *gauche* form of butane is much greater than the energy of attraction, -600 cal. mole^{-1}, at the minimum in the Lennard-Jones intermolecular potential for methane.[21] This difference is consistent with the smaller distances between methyl groups noted above.

In light of these considerations, an interaction energy in the range of -500 to -1000 cal. mole^{-1} (attractive) could be anticipated for closest pairs of methyl groups attached to neighboring silicon atoms of the siloxane chain. Methyl groups situated on opposite sides of the plane of the chain backbone are 4.88 Å. apart, a distance beyond the range of significant interaction.

Gauche rotations about bond i-1 and about bond i in Fig. 1 place the outer Si atoms in positions out of the plane of these bonds. These positions are indicated by heavy dashed lines. A rotation about the bond i of Fig. 1 to one of the *gauche* states with $\varphi_i = \pm120°$ eliminates one of the two near-neighbor pairs of CH_3 groups attached to the Si atoms separated by chain bonds i and i + 1. This pair is replaced by a $CH_3 \cdots O$ pair at a similar distance apart (*ca.* 3.78 Å.). The interaction of the latter pair may be presumed negligible at this distance owing to the smaller domain of the O atom.

As a further consequence of rotation about bond i, the distance between the oxygen atom on the left and the silicon atom on the right in Fig. 1 is diminished from 4.32 to 3.76 Å. If, on the basis of Liebau's[14] value of 0.37 for the partial ionic character of the Si–O bond, formal charges of this magnitude are assigned to the chain atoms and a dielectric constant of 2.5 is assumed, the change in coulombic energy associated with the indicated decrease in nonbonded Si$\cdots$O distance is calculated to be around -500 cal. mole^{-1}. This change in the energy attributable to the polarity of the Si–O bond may be calculated alternatively as the difference in dipole–dipole interaction energies for the two relevant bonds when in the planar and in the *gauche* conformations. Taking the Si–O bond dipole moment to be 2.8×10^{-18} e.s.u.,[24] which accords very well with the moment calculated from the degree of ionic character quoted above, we arrive at approximately the same result for the energy decrease.

These estimates of the coulombic energy associated with a *gauche* rotation are subject to large error. Moreover, the rotation under consideration simultaneously brings closer together pairs of atoms of *like* polarity and separated by four (instead of three) bonds. The energy is thereby increased. We conclude that the coulombic contribution to the change in energy for a rotation from *trans* to *gauche* probably is negative and therefore opposite in sign to the increase in energy predicted for the concurrent elimination of a $CH_3 \cdots CH_3$ close neighbor pair, but that the magnitude of the coulombic contribution is comparatively small.

Pursuant to formulation of matrices by means of which to generate statistical weights for rotational configurations of the chain as a whole, we consider rotations about the pair of bonds i-1 and i in Fig. 1. For convenience, bonds i-1 and i are pictured as remaining in the plane of the figure, rotations about them being accommodated by displacing adjoining sections of the chain out of the plane. Bonds for the planar, all-*trans*, conformation are shown by solid lines; the Si–O bonds of the chain skeleton are represented by heavy

(24) R. S. Holland and C. P. Smyth, *J. Am. Chem. Soc.*, **77**, 268 (1955).

solid lines, and bonds to the pendant methyl groups lying above and below the plane of the skeleton by light solid lines. *Gauche* rotations about bonds i-1 and i place the outer Si atoms in Fig. 1 in positions above and below the plane of these bonds, as indicated by heavy dashed lines labeled g$^+$ and g$^-$.

We first consider rotational states about bond i when its predecessor is in the *trans* (t_{i-1}) state. Bond i + 1 may, if desired, be regarded tentatively to be *trans* also; consequences of rotation from the *trans* state for bond i + 1 (Fig. 1) will be dealt with subsequently as we proceed along the chain from left to right. A (conditional) statistical weight of unity is arbitrarily assigned to t_i preceded by t_{i-1}; *i.e.*, to t_i in the sequence $t_{i-1}t_i$. Symmetry requires assignment of equal statistical weights σ to the *gauche* states in the sequences $t_{i-1}g^+_i$ and $t_{i-1}g^-_i$. The analysis offered above suggests a value of σ less than unity. Commitment to this conjecture is not required, however.

If the bond i − 1 is in the g$^+$ state (the consequences thereof with respect to preceding bonds and their pendant groups having been taken into account in the previous step of the analysis), the statistical weight for $g^+_{i-1}t_i$ should be assigned the same value (unity) as for $t_{i-1}t_i$, inasmuch as interactions dependent upon φ_i are the same in the two cases. Transition to g^+_i or to g_i^- eliminates one $CH_3 \cdots CH_3$ near-neighbor pair, as previously found for t_{i-1}. Simultaneously, the outer Si atoms of Fig. 1 are placed in close proximity in out-of-plane *gauche* positions indicated by dashed lines. In the former conformation, $g^+_{i-1}g^+_i$, the Si atoms occur on *opposite* sides of the plane at a distance of 4.62 Å.; in the latter, $g^+_{i-1}g^-_i$, they are on the *same* side of the plane with $d_{Si\cdots Si} = 4.29$ Å. Strict adherence to bond dimensions and rotation angles would place methyl groups at the uncomfortable distance of 2.77 Å. in the $g^+_{i-1}g^+_i$ conformation. This conflict is rather easily alleviated by relaxation of the rigid structural stipulations, however. According to examination of models, compromise of the two rotation angles ($\pm120°$) is particularly effective in this regard. The severe conflicts encountered in the $g^+_{i-1}g^-_i$ conformation, for which the Si atoms occur on the same side of the plane, are not readily alleviated by structural adjustments. We therefore assign a weight of zero to $g^+_{i-1}g_i^-$, and to $g^+_{i-1}g^+_i$ a weight of σ' which may be less than σ to the extent that conflicts between substituents on the two Si atoms are effective in suppressing this conformation.

Symmetry requires corresponding statistical weights for conformations involving g^-_{i-1}. Hence, we arrive at the matrix

$$U' = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma' & 0 \\ 1 & 0 & \sigma' \end{bmatrix} \tag{1}$$

for rotations about Si–O bond i, states of O–Si bond i − 1 being given by row indices and those of i by column indices.

Turning to bond i + 1 of the chain (Fig. 2), consistency with the foregoing account requires a weight of unity for t_it_{i+1}. Rotations to $t_ig^+_{i+1}$ and to $t_ig^-_{i+1}$ again involve "rupture" of one nearest Me$\cdots$Me pair, and the simultaneous decrease of $d_{Si\cdots O}$ for the Si on the left and the O on the right in Fig. 2. Hence, the appropriate statistical weight is σ for each of these equivalent "transitions."

If bond i occurs in the g$^+$ state by previous assignment, the number of nearest $CH_3 \cdots CH_3$ pairs has already been reduced to one. (Methyl groups are omitted in Fig. 2.) A g$^+$ rotation about bond i + 1 eliminates the one remaining $CH_3 \cdots CH_3$ pair separated by bonds i and i + 1, and replaces it by another $CH_3 \cdots O$

pair (see above); the oxygen atoms, at positions on opposite sides of the plane as shown by dashed lines in Fig. 2 for $g^{+}{}_{i}g^{+}{}_{i+1}$, are well separated by a distance of 4.57 Å.—only a little closer than the 5.10 Å. for $g_{i}{}^{+}t_{i+1}$. The consequences of the $g^{+}{}_{i+1}$ assignment appear to be similar to those for the $t_{i}g^{+}{}_{i+1}$ transition. Hence, we assign a statistical weight σ (not σ') to $g^{+}{}_{i}g^{+}{}_{i+1}$. The conformation $g^{+}{}_{i}g^{-}{}_{i+1}$, while retaining one $CH_3\cdots CH_3$ pair at close range, reduces the distance between the outer pair of oxygen atoms in Fig. 2 from 5.10 Å. for $g_{i}{}^{+}t_{i+1}$, to 3.69 Å. for $g_{i}{}^{+}g^{-}{}_{i+1}$, these oxygen atoms then being on the same side of the plane as indicated by the appropriate pair of dashed lines in Fig. 2. The estimated increase in coulombic repulsion is of the order of 1000 cal. mole^{-1}. We therefore represent this transition by a statistical weight δ, which is expected to be small. The statistical weight matrix for rotations about O–Si bond $i + 1$ therefore takes the form

$$U'' = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \delta \\ 1 & \delta & \sigma \end{bmatrix} \qquad (2)$$

Statistical weights for configurations of the chain as a whole may be generated by raising the product $U'U''$ to a power corresponding to the degree of polymerization, and the partition function can be extracted from this product in the usual manner.[25]

Formulation of $\langle r^2 \rangle_0/nl^2$ for Chains of Alternating Bonds.—The characteristic ratio of the mean-square end-to-end length of the chain can be expressed, with neglect of terms of order $1/n$, as

$$\langle r^2 \rangle_0/nl^2 = 1 + \sum_{1}^{\infty} (P_k' + P_k'') \qquad (3)$$

where P_k' is the statistical mechanical average projection on an Si–O bond of a unit vector attached to the kth succeeding bond in the chain, proceeding from left to right; P_k'' is the corresponding average for an O–Si bond. For the evaluation of these average projections we employ the methodology for treating the Ising model[25] in one dimension as adapted to the treatment of chain molecule configurations by Lifson,[5] Nagai,[6] Ptitsyn and Birshtein,[7] and Hoeve.[8]

Let a right-handed cartesian coordinate system be defined for each bond i of the chain, with the x_i-axis taken in the direction of the bond and the y_i-axis in the plane of bonds $i - 1$ and i, its direction forming an acute angle with bond $i - 1$. Transformation from the coordinate system $i + 1$ to i is effected by

$$T(\theta_i, \varphi_i) = \begin{bmatrix} \cos \theta_i & \sin \theta_i & 0 \\ \sin \theta_i \cos \varphi_i & -\cos \theta_i \cos \varphi_i & \sin \varphi_i \\ \sin \theta_i \sin \varphi_i & -\cos \theta_i \sin \varphi_i & -\cos \varphi_i \end{bmatrix} \qquad (4)$$

where θ_i is the angle between bonds $i + 1$ and i, and φ_i is the angle of rotation about bond i measured from the *trans* (planar) conformation. Further, let $T' = T(\theta', \varphi')$ denote the transformation from the reference frame for an O–Si bond to that for the preceding Si–O bond; e.g., from the coordinate system for bond $i + 1$ to that for i in Fig. 1. Similarly, let $T'' = T(\theta'', \varphi'')$ represent transformation from the reference frame affixed in the foregoing manner to an Si–O bond to its predecessor in the chain, φ'' being the angle of rotation about the latter (e.g., about bond $i + 1$ or bond $i - 1$ in Fig. 1).

By successive applications of these transformations, a bond may be projected on its kth predecessor, as required for evaluation of P_k' and P_k''. If, for example, k is odd

$$P_k' = [1\ 0\ 0]\ \langle T_i' T''_{i+1} \cdots T'_{i+k-1} \rangle \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \qquad (5)$$

where the required average of the matrix product, indicated by angle brackets, is to be taken over all configurations of the chain.

Following the procedures of Lifson[5] and Nagai,[6] we define matrices $\mathbf{U}'$ and $\mathbf{U}''$ of order $(3s, 3s)$ as the direct products of the identity matrix E of order 3 with U' and U'', respectively. Thus

$$\mathbf{U}' = E \times U' = \begin{bmatrix} U' & 0 & 0 \\ 0 & U' & 0 \\ 0 & 0 & U' \end{bmatrix} \qquad (6)$$

where 0 denotes the null matrix of order s. Let $t'_{ij;1} \cdots t'_{ij;s}$ represent values of element ij of matrix T' for the respective rotational states $\varphi_1' \cdots \varphi_s'$, and let the diagonal matrix comprising these elements be denoted by T_{ij}'. Finally, let these matrices supply the elements for the matrix

$$\mathbf{T}' = \|T_{ij}'\| \qquad (7)$$

of order $(3s, 3s)$. The matrix $\mathbf{T}''$ is analogously defined. With these definitions the required statistical mechanical average in eq. 5 is given by[5-8,25]

$$\langle T_i' T''_{i+1} \cdots T'_{i+k-1} \rangle = \mathbf{B}(\mathbf{U}'\mathbf{T}'\mathbf{U}''\mathbf{T}'')^{(k-1)/2}\mathbf{U}'\mathbf{T}'\mathbf{U}''\mathbf{A}\lambda^{-k-1} \qquad (8)$$

where $\mathbf{A}$ and $\mathbf{B}$ of order $(3s, 3)$ and $(3, 3s)$, respectively, are defined as follows in terms of the mutually normalized eigencolumn A and eigenrow B of $U'U''$ corresponding to the largest eigenvalue λ^2 of $U'U''$

$$\mathbf{A} = E \times A; \quad \mathbf{B} = E \times B \qquad (9)$$

the $\times$ sign signifying the direct product as above. Corresponding expressions for averages of the various matrix products yield

$$\left.\begin{array}{l} P_k' = \mathbf{B}_1\mathbf{S}^{k+1}\mathbf{T}''^{-1}\mathbf{A}_1 \\ P_k'' = \mathbf{B}_1\mathbf{T}''\mathbf{S}^{k-1}\mathbf{A}_1 \end{array}\right\}\ k\ \text{odd}$$

$$\left.\begin{array}{l} P_k' = \mathbf{B}_1\mathbf{S}^k\mathbf{A}_1 \\ P_k'' = \mathbf{B}_1\mathbf{T}''\mathbf{S}^k\mathbf{T}''^{-1}\mathbf{A}_1 \end{array}\right\}\ k\ \text{even} \qquad (10)$$

where

$$\mathbf{S}^2 = \mathbf{U}'\mathbf{T}'\mathbf{U}''\mathbf{T}''/\lambda^2 \qquad (11)$$

and $\mathbf{A}_1$ and $\mathbf{B}_1$ are the column $(3s, 1)$ and row $(1, 3s)$ vectors

$$\mathbf{A}_1 = \mathbf{A} \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} A \\ 0 \\ 0 \end{bmatrix}$$

$$\mathbf{B}_1 = \mathbf{B}\ [1\ 0\ 0]$$

Thus, $\mathbf{A}_1$ is the vector comprising the column of elements $a_1 \cdots a_s$ of A followed by $2s$ zeros, and $\mathbf{B}_1$ is correspondingly constituted in row form from the elements of B.

Insertion of these results in eq. 3 yields

$$\langle r^2 \rangle_0/nl^2 = \mathbf{B}_1 (\mathbf{E} + \mathbf{T}'') \sum_{m=0}^{\infty} (\mathbf{S}^2)^m (\mathbf{E} + \mathbf{S}^2\mathbf{T}''^{-1})\mathbf{A}_1$$

where $\mathbf{E}$ is the identity matrix of order $3s$. Thus

$$\langle r^2 \rangle_0/nl^2 = \mathbf{B}_1(\mathbf{E} + \mathbf{T}'')(\mathbf{E} - \mathbf{S}^2)^{-1}(\mathbf{E} + \mathbf{S}^2\mathbf{T}''^{-1})\mathbf{A}_1 \quad (12)$$

or, by rearrangement

$$\langle r^2 \rangle_0/nl^2 = \mathbf{B}_1(\mathbf{S}^2 + \mathbf{T}'')(\mathbf{E} - \mathbf{S}^2)^{-1}(\mathbf{E} + \mathbf{T}''^{-1})\mathbf{A}_1 \quad (12')$$

These alternative expressions for a chain of alternating bonds may be shown to be equivalent to Hoeve's result[8] obtained using a different, but related, matrix scheme.

In the special case

$$U' = U'' = U \qquad (13)$$

eq. 12 simplifies to

$$\langle r^2 \rangle_0/nl^2 = \mathbf{B}_1(\mathbf{E} + \mathbf{T}'')(\mathbf{E} - \mathbf{S}^2)^{-1}(\mathbf{E} + \mathbf{T}')\mathbf{A}_1 \quad (14)$$

If the rotational potential for each bond is independent of the rotational states of its neighbors, the matrix U may be replaced by a vector of *a priori* statistical

(25) H. A. Kramers and G. H. Wannier, *Phys. Rev.*, **60**, 252 (1941); G. F. Newell and E. W. Montroll, *Rev. Mod. Phys.*, **25**, 353 (1953).
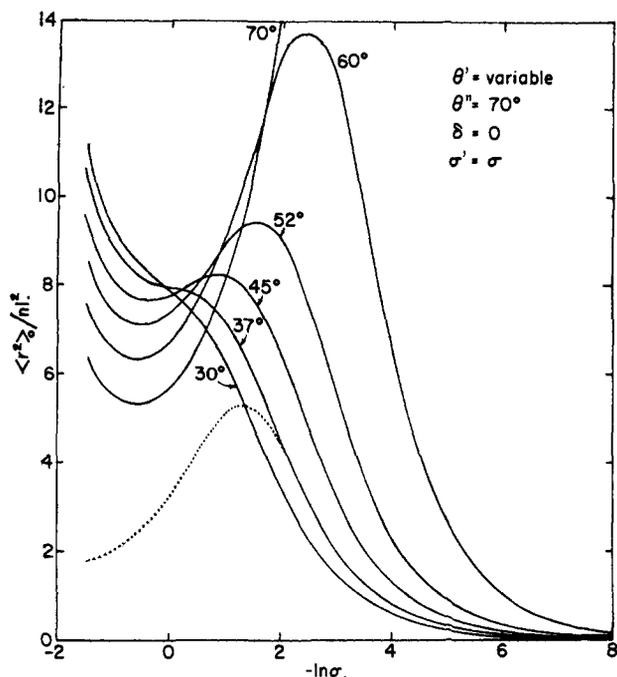
Fig. 3.—The characteristic ratio as a function of $-\ln \sigma$ for various angles θ'; other parameters as indicated. The dotted curve is calculated for independent bond rotations (eq. 16 and 17) and $\theta' = 37°$, $\theta'' = 70°$.

weights, the transformation matrices T may be averaged independently, and the averages of matrix products required for evaluation of the P_k's (see eq. 5) can be replaced by products of averages, e.g.

$$P_k' = [1\ 0\ 0]\langle T_i'\rangle(T''_{i+1})\cdots(T'_{i+k-1})\begin{bmatrix}1\\0\\0\end{bmatrix}$$

Substituting the appropriate P_k's in this form in eq. 3 as before, we find

$$\langle r^2\rangle_0/nl^2 = [1\ 0\ 0][(E +$$
$$(T''))(E - (T')(T''))^{-1}(E + \langle T'\rangle)]\begin{bmatrix}1\\0\\0\end{bmatrix} \quad (15)$$

The condition expressed by eq. 13 is necessarily fulfilled in this case. If the potential is symmetric about $\varphi = 0$, then $\langle \sin \varphi\rangle = 0$, and expansion of eq. 15 yields

$$\langle r^2\rangle_0/nl^2 = \frac{(1 + \eta^2)(1 + \cos \theta')(1 + \cos \theta'')}{(1 + \eta^2)(1 - \cos \theta' \cos \theta'') - 2\eta \sin \theta' \sin \theta''}$$
$$(16)$$

where $\eta = \langle \cos \varphi\rangle$. This relationship was first derived by Birshtein, Ptitsyn, and Sokolova.[4] If the potential may be represented by three states consisting of the *trans* with $\varphi = 0$ and two *gauche* states at $\varphi = \pm 2\pi/3$, then

$$\eta = (1 - \sigma)/(1 + 2\sigma) \quad (17)$$

where σ, in accordance with its usage above, is the statistical weight of each *gauche* state relative to a weight of unity for the *trans* state. For free rotation, $\eta = 0$ and eq. 16 reduces to the equation previously given for this case.[26]

Numerical Results

The characteristic ratio $\langle r^2\rangle_0/nl^2$, calculated in the limit of large n according to equations given above,[27] is presented in Fig. 3, 4, and 5 as a function of the statistical weight σ of a *gauche* state (relative to a weight of unity for the *trans*) for various values of other param-

(26) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

(27) We are indebted to the Stanford Computation Center for use of its facilities. The assistance of P. Balestra in programming the calculations is also acknowledged with gratitude.
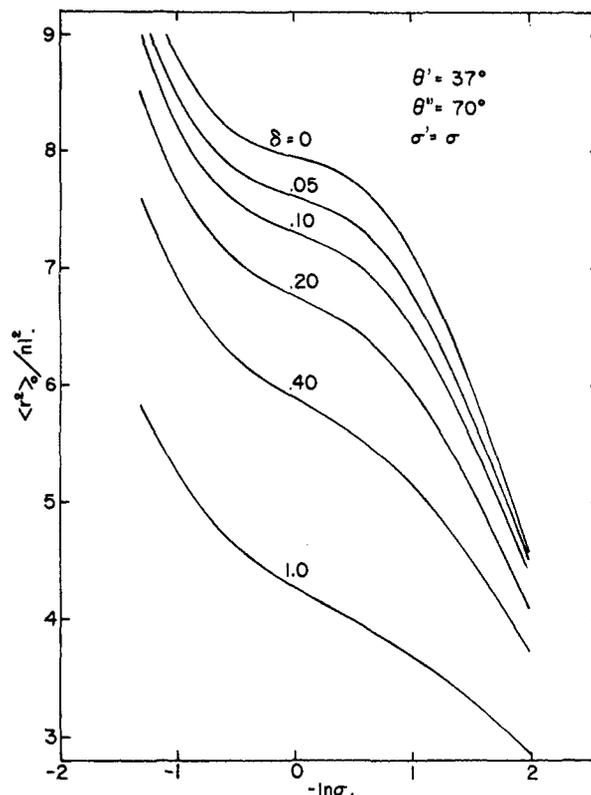
Fig. 4.—The effect of relaxing suppression of $g^{\pm}g^{\mp}$ bond pairs about oxygen, as achieved by rendering $\delta > 0$.

eters. The abscissa of each graph is logarithmic in the reciprocal of σ. A threefold potential with *gauche* states at $\varphi = \pm 2\pi/3$ is assumed throughout. The supplement of the bond angle θ'' at the Si atom has been taken to be 70° in all calculations. Curves for various values of the corresponding angle θ' at the O atoms are shown in Fig. 3. Curves in other graphs explore the effects of variously weighting the interdependence of neighboring *gauche* rotational states in light of structural considerations discussed earlier in this paper.

The simplest case is that of independent bonds, such that a *gauche* state for any given bond is assigned the same weight σ irrespective of the states of its neighbors. Calculations in this approximation, carried out according to eq. 16 and 17 with $\theta' = 37°$, are represented by the dotted curve in Fig. 3. The characteristic ratio increases from 3.32 for $\ln \sigma = 0$, corresponding to free rotation, to a maximum value of 5.28, and then decreases toward zero with further decrease in σ. Calculations not included here show the curve to be fairly insensitive to variations in θ' over the range 35 to 50°.

Even at the maximum in the dotted curve, $\langle r^2\rangle_0/nl^2$ falls below the experimental value[28] of 6.3. This simplest description may therefore be rejected on experimental grounds. It may be rejected with equal cause on the basis of structural-geometric considerations, presented earlier, which disclose the untenability of assuming bond rotations to be independent. Nevertheless, the dotted curve to the right of the maximum reveals the basis for a positive temperature coefficient for $\langle r^2\rangle_0$. This follows at once from the increase in the ratio with σ in this range, together with the virtual certainty that σ, if less than unity, must increase with temperature.

The case considered above corresponds to

$$U' = U'' = \begin{bmatrix}1 & \sigma & \sigma\\1 & \sigma & \sigma\\1 & \sigma & \sigma\end{bmatrix}$$

(28) V. Crescenzi and P. J. Flory, J. Am. Chem. Soc., **86**, 141 (1964).

Choice of $\sigma' = \sigma$ in eq. 1 for U' and of $\delta = 0$ in eq. 2 for U'' results in identical statistical weight matrices U' and U'' which differ from that above by replacement of the 2,3 and 3,2 elements by zeros, thus eliminating g^+g^- and g^-g^+ pairs about both O and Si. Calculations carried out on this basis are shown in Fig. 3 for various angles θ'. Over the range of small $-\ln \sigma$, the curves are raised markedly by presence of zero elements in the U matrices. As $-\ln \sigma$ increases, however, $\langle r^2 \rangle_0/nl^2$ converges with results calculated for independent rotations, as is illustrated by the $\theta' = 37°$ curve. This is an obvious consequence of the low incidence of *gauche* states when $-\ln \sigma$ is large; pairs of *gauche* neighbors then seldom occur irrespective of the statistical weights assigned to pair sequences.

Trends of the curves with θ' are interesting, but scarcely significant within the allowable range of θ' for the siloxane chain. A minimum and a maximum appear for $\theta' > ca. 40°$, and these become more pronounced as θ' increases. For all $\theta' \neq \theta''$ the curves converge to zero for large $-\ln \sigma$, as required by the considerations presented in the Introduction. For $\theta' = \theta'' = 70°$, however, the ratio diverges with $-\ln \sigma$, as obviously it must.

The curve for $\theta' = 37°$ in Fig. 3 approximates the experimental $\langle r^2 \rangle_0/nl^2$ in the vicinity of $-\ln \sigma = 1$. The downward slope with $-\ln \sigma$ denotes a strong positive temperature coefficient for $\langle r^2 \rangle_0$, in accordance with experimental observations.[2,29] This assertion depends however on the sign of $-\ln \sigma$. For $-\ln \sigma < 0$, the slope of the $\theta' = 37°$ curve remains negative, but σ, being greater than unity, should then decrease with temperature. Hence, if σ exceeded unity, i.e., if the *gauche* states were favored, then the curve in question would lead one to predict a negative temperature coefficient for $\langle r^2 \rangle_0$, contrary to experiment.[2,29] Thus, the sign observed for the temperature coefficient provides compelling evidence that the *trans* state is favored over the *gauche*, i.e., that $\sigma < 1$. This assertion is not contingent on the value assigned to θ', as examination of curves in Fig. 3 for other angles shows.

The effect of relaxing the exclusion of $g^{\pm}g^{\mp}$ pairs about the O atom (but not about the Si atom) is examined in Fig. 4 where calculations are shown for $\delta > 0$, the conditions $\sigma' = \sigma$ and $\theta' = 37°$ being retained. A pronounced decrease in $\langle r^2 \rangle_0/nl^2$ with increase in δ is evident, even for small values of δ. This result accords with expectation inasmuch as an increase in δ corresponds to revision in the direction of the *trans-gauche* model with independent bond rotations (dotted curve in Fig. 3).

The effect of suppressing g^+g^+ and g^-g^- pairs about Si, accomplished by making $\sigma' < \sigma$, is shown in Fig. 5. In the region of interest, i.e., for $-\ln \sigma > 0$, the displacement of the curves is quite small.[30] This being the case, we may without hazarding serious error take $\sigma' = \sigma$ for the following analysis of the temperature coefficient.

Let us assume that σ and δ can be expressed simply by

$$\sigma = \exp(-\Delta\epsilon_\sigma/kT) \qquad (18)$$

$$\delta = \exp(-\Delta\epsilon_\delta/kT) \qquad (18')$$

(29) A. Ciferri, *Trans. Faraday Soc.*, **57**, 846, 853 (1961).

(30) The insensitivity of $\langle r^2 \rangle_0/nl^2$ to σ'/σ may be rationalized as follows. First, we note that whereas the characteristic ratio is decreased by diminishing the proportion of *gauche* states through reduction of σ, it is increased by suppressing $g^{\pm}g^{\mp}$ pairs. Such pairs represent compact conformations, as inspection of models shows; hence, the net effect of their elimination is an increase in $\langle r^2 \rangle_0/nl^2$. The g^+g^+ and g^-g^- pairs, on the other hand, appear to be less compact; hence the effect of enhancement of the *trans* population accompanying their suppression prevails by a small margin.

Fig. 5.—The effect of suppressing g^+g^+ and g^-g^- bond pairs about silicon through choice of $\sigma' < \sigma$.

where $\Delta\epsilon_\sigma$ is the energy of a *gauche* state relative to a *trans*, and $\Delta\epsilon_\delta$ is the energy associated with a g^+g^- pair about 0. It follows that

d ln $\langle r^2 \rangle_0$/d$T = -(1/T)[\ln \sigma(\partial \ln \langle r^2 \rangle_0/\partial \ln \sigma) +$

ln δ ($\partial \ln \langle r^2 \rangle_0/\partial \ln \delta$)]   (19)

Temperature coefficients may be estimated using this equation, from the calculated curves presented in Fig. 4. For this purpose, we adopt the experimental value 6.3 for $\langle r^2 \rangle_0/nl^2$ in methyl ethyl ketone and other Θ-solvents having a cohesive energy density greater than that of the polymer,[28] and the required derivatives are determined for this value of the ordinate in Fig. 4. Results thus obtained for several values of δ are summarized in Table I. The values of σ required for $\langle r^2 \rangle_0/nl^2 = 6.3$ according to the curves in Fig. 4 are given in the second column. The third column of figures has been calculated from the slopes of these curves at the specified points. The fourth column has been calculated for different δ at the specified σ. The temperature coefficient calculated for $\delta = 0$ is twice that observed. Agreement with experiment may be achieved, however, by assigning δ a small, nonzero value. By interpolations of results in Table I, the best fit is secured for $\sigma = 0.286$ and $\delta = 0.06$. Corresponding conformational energies are $\Delta\epsilon_\sigma = 850$ cal. mole^{-1} and $\Delta\epsilon_\delta = 1900$ cal. mole^{-1}.

TABLE I

CALCULATIONS OF THE TEMPERATURE COEFFICIENT OF $\langle r^2 \rangle_0$

$\theta' = 37°$, $T = 343°K.$, $\sigma' = \sigma$, $\langle r^2 \rangle_0/nl^2 = 6.3$

δ	σ	$\partial \ln \langle r^2 \rangle_0/\partial \ln \sigma$	$\partial \ln \langle r^2 \rangle_0/\partial \ln \delta$	d ln$\langle r^2 \rangle_0$/dT × 10^3, deg.$^{-1}$
0.00	0.249	0.391	0	1.58
.05	.281	.333	−0.0397	0.88
.07[a]	.295	.310	− .0556	.67
.10	.320	.270	− .0952	.26
			Observed[2]	.75

[a] Curve not included in Fig. 4.

The substantially larger value of 7.7 found in the preceding paper[28] for $\langle r^2 \rangle_0/nl^2$ in the fluorinated solvent mixture of low cohesive energy density requires an even smaller δ ($\cong 0$) and a larger $\sigma \cong 0.5$ to 0.6, according to the curves shown in Fig. 4. The temperature coefficient of $\langle r^2 \rangle_0$ being unknown for this medium, unique assignment of parameters is impossible.

Discussion

The model and approximations are obviously too crude to lend significance to exact values of parameters deduced above and to support quantitative interpretations of the interactions they represent. Several important conclusions of a qualitative nature find solid basis nevertheless in the comparison of calculations with experiment.

The inadequacy of the independent bond approximation has been demonstrated through its failure to account for values for $\langle r^2 \rangle_0/nl^2$ as large as observed. Exclusion of $g^{\pm}g^{\mp}$ neighbor pairs about both Si and O raises this ratio into the range of the experimental results. The positive temperature coefficient admits of explanation only by assignment of $\sigma < 1$. Complete exclusion of all $g^{\pm}g^{\mp}$ sequences tends to over-estimate either the temperature coefficient or the magnitude $\langle r^2 \rangle_0/nl^2$. Guided by structural considerations, we achieve a more refined agreement with experiment by relaxing the exclusion of such sequences about O (but not about Si), adopting $\delta \cong 0.06$ to this end.

The main conclusions, namely, that $g^{\pm}g^{\mp}$ sequences are largely suppressed and that the *trans* state is preferred over the *gauche* ($\sigma < 1$), are firmly established by the foregoing analysis. The calculations in support of these conclusions are insensitive to minor changes in θ' or other structural parameters. The idealization implicit in the model whereby discrete rotational states are substituted for averages over ranges of angle may distort the calculations in detail, but could scarcely affect our principal conclusions to a significant degree. The former of these conclusions finds independent basis in the structure. The latter confirms that nonbonded methyl groups attract at a distance of about 3.8 Å.; no other grounds for the preference of the *trans* state over the *gauche* is apparent.

A value of $\Delta\epsilon_\sigma$ in the range 500 to 1000 cal. mole^{-1} accords with structural considerations presented earlier. According to the numerical calculations (Table I), $\Delta\epsilon_\delta \cong 2000$ cal. mole^{-1}, which is twice the estimate for this quantity on the basis of coulombic repulsion between oxygen atoms. The sensitivity of numerical calculations (Fig. 4) to the value of δ suggests that this parameter (and therefore $\Delta\epsilon_\delta$ also) is subject to greater error than is σ from idealizations underlying the calculations. The discrepancy is well within the limits of error in either the model or in the experimental results.

If the suppression of $g^{\pm}g^{\mp}$ sequences about O is indeed to be accounted for by coulombic repulsions, a decrease in the polarity of the medium should further diminish δ. To the extent that σ also is influenced by electrostatic effects associated with the slightly closer proximity of the pairs of atoms, Si and O, separated by three bonds in the chain (see above), it should increase with decrease in polarity of the medium. Both changes should increase $\langle r^2 \rangle_0/nl^2$. Results for the fluorocarbon mixture,[28] in which $\langle r^2 \rangle_0/nl^2$ was found to be 7.7, are qualitatively in accord with this deduction.

A satisfactory account of the spatial configurations of the siloxane chain in terms of structural considerations appears to have been achieved.

Microwave Absorption and Molecular Structure in Liquids. LIII. Hydrogen Bonding and Dielectric Properties in Chloroform Mixtures[1,2]

BY ARTHUR A. ANTONY[3] AND CHARLES P. SMYTH

Dielectric constant and loss measurements are reported on mixtures of chloroform with cyclohexane, dioxane, and diazabicyclo[2.2.2]octane, and of trichlorofluoromethane with dioxane. The data are used to calculate relaxation times and distribution functions. Dipole moments are calculated for chloroform–dioxane mixtures. Viscosities, densities, and refractive indices of the four series of mixtures are also reported. The relaxation times are compared with those previously obtained in other solvents and interpreted in terms of hydrogen bonds between chloroform and the various proton acceptors. Trichlorofluoromethane is discussed because of its similarity to chloroform in size and shape and its inability to hydrogen bond. Two relaxation times are obtained for the chloroform–diazabicyclo[2.2.2]octane mixtures, one of which is attributed to chloroform rotation, the other to rotation of the complex formed between chloroform and the amine.

This work was undertaken in order to study the effect of hydrogen bonding on dielectric relaxation processes in simple systems. Chloroform was selected because it was expected to behave as a rigid, nearly spherical molecule with a dipole moment of 1.1 D. in solution.[4] The dielectric relaxation of trichlorofluoromethane was also studied because this is a compound similar to chloroform in its molecular shape, but incapable of forming hydrogen bonds by proton donation.

Experimental Methods

Purification of Materials.—The chloroform used was washed with concentrated sulfuric acid, then with distilled water, and then was distilled from phosphorus pentoxide. Trichlorofluoromethane obtained from Matheson Coleman and Bell was fractionally distilled. The dioxane was distilled from sodium, and its purity verified by measuring the static dielectric constant at 25°. Cyclohexane purchased from Matheson Coleman and Bell was used without further purification. Diazabicyclo[2.2.2]octane obtained from Aldrich Chemical Co. was recrystallized from ether; m.p. 157–158°.

Apparatus.—Dielectric constants and losses were measured by methods previously described.[5-9] Viscosity measurements were made with an Ostwald viscometer, calibrated with distilled water and benzene.

Experimental Results

Calculations of the dielectric constants and losses for the high-loss solutions were made with the aid of an

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(2) This paper represents part of the work submitted by A. A. Antony to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Allied Chemical Fellow, 1961–1962; Woodrow Wilson Fellow 1959–1960.

(4) A. N. Campbell, E. M. Kartzmark, and H. Triesen, *Can. J. Chem.*, **39**, 735 (1961).

(5) H. L. Laquer and C. P. Smyth, *J. Am. Chem. Soc.*, **70**, 4097 (1948).

(6) L. M. Kushner and C. P. Smyth, *ibid.*, **71**, 1401 (1949).

(7) W. M. Heston, Jr., A. D. Franklin, E. J. Hennelly, and C. P. Smyth, *ibid.*, **72**, 3443 (1950).

(8) F. H. Branin and C. P. Smyth, *J. Chem. Phys.*, **20**, 1121 (1952).

(9) W. M. Heston, Jr., E. J. Hennelly, and C. P. Smyth, *J. Am. Chem. Soc.*, **70**, 4093 (1948).