Conformational Energies of Perfluoroalkanes.[1] II. Dipole Moments of $H(CF_2)_nH$

T. W. Bates and W. H. Stockmayer

Department of Chemistry, Dartmouth College,
Hanover, New Hampshire 03755.
Received October 4, 1967

ABSTRACT: Dipole moments in benzene at 25 and 45° have been measured for the compounds $H(CF_2)_nH$ with $n = 4, 6, 7, 8$, and 10 and also for $F(CF_2)_7H$. A rotational-isomeric-state model with two *trans* isomers at ±15° and two *gauche* isomers at ±120° for each bond gives a good fit of the data with the following energy differences: $E(t^{\pm}g^{\pm}) - E(t^{\pm}t^{\pm}) = 1.4 \pm 0.4$ kcal mole^{-1} and $E(t^{+}t^{-}) - E(t^{+}t^{+}) = 1.1 \pm 0.7$ kcal mole^{-1}. These figures are in satisfactory accord with estimates from infrared spectra and from semiempirical energy calculations.

The conformational properties of the perfluoroalkane chain $(-CF_2-)_n$ are of interest because of the simplicity of the chain structure and its simple relation to the paraffins and also because of the practical importance of the polymer. The physical properties of polytetrafluoroethylene (hereafter PTFE) are consistent[2] with the notion that the chains are both rather extended and kinetically sluggish, but quantitative studies are severely restricted by the lack of solvents at temperatures permitting convenient measurements of light scattering, viscosity, or other relevant properties. Some inferences have been drawn from viscoelastic data[3a] or from melting parameters,[3b] but these furnish only an incomplete picture.

We have now obtained somewhat more direct experimental evidence on conformational equilibrium by measuring the dipole moments of five α,ω-dihydroperfluoroalkanes, $H(CF_2)_nH$, in benzene solution. The results are here reported and analyzed with the aid of a theory developed by Leonard, Jernigan, and Flory[4] for dihaloalkanes as appropriately modified in the light of semiempirical calculations[5] of the conformational energies of fluorocarbons. A preliminary account of this work has appeared.[6] In the following paper,[7] the results are used to discuss various properties of PTFE.

Experimental Section

Samples of α,ω-dihydroperfluoroalkanes $H(CF_2)_nH$ with $n = 4, 6, 8$, and 10 were obtained from E. I. du Pont de Nemours and Co. (Organic Chemicals Department, courtesy of Dr. R. D. Richardson). The preparation and properties of these and numerous other α,ω-disubstituted fluoroalkanes have been described by Ward.[8] An odd member of the series, $H(CF_2)_7H$, was prepared in this laboratory by decarboxylating a sample of perfluoroazelaic acid, which was the gift of the Minnesota Mining and Manufacturing Co. through the kindness of Dr. W. S. Friedlander. The sodium salt of the acid was heated with ethylene glycol[9] and the product, after purification in a preparative vapor phase chromatograph (Wilkin Instrument and Research Co., Inc., Model A-90-P2), had a boiling point of 104.2°. Similar technique was used to prepare $H(CF_2)_7F$ (bp 94.5°) from perfluorocaprylic acid (Peninsular ChemResearch, Inc.). The purified compounds all contained less than 0.5% of impurities as estimated from relative peak areas in the chromatograms. This corresponds to an error of less than 0.01 D in the dipole moment.

Dielectric constants were measured at 5×10^3 and 10^4 Hz with a General Radio bridge, Type 1620-A. The sample cell (three terminal, Balsbaugh Laboratories, Type 350M) had an air capacitance of about 33 pF and contained about 40 ml of solution when filled. The capacitance of the cell filled with benzene was reproducible to ±0.001 pF and solution capacitance were reproducible to better than ±0.002 pF. The value obtained for the dielectric constant of benzene (dried over sodium wire and distilled before measurement) was 2.2743 ± 0.0001 at 25°. Measurements were made at both 25 and 45°, the cell temperature being held constant to within ±0.02° by circulating light oil from a thermostated bath through an insulated glass jacket surrounding the cell.

Differences (Δn) in refractive index between the solutions and the pure solvent were measured at 436 and 546 mμ with a Brice-Phoenix differential refractometer.

All solutions were made up by weighing both components and the concentrations were expressed as weight fraction (w_2) of solute. Over the range of about 0.005–0.02 in w_2, it was found that both the dielectric increment ($\Delta\epsilon$) and the refractive index increment (Δn) were accurately proportional to w_2, so that the experimental ratios $\Delta\epsilon/w_2$ and $\Delta n/w_2$ may be taken for the limiting derivatives $(d\epsilon/dw_2)_0$ and $(dn/dw_2)_0$.

The dipole moments were obtained from the measured quantities by means of the Guggenheim–Smith equation[10]

$$\langle\mu^2\rangle = \frac{27kTM_2}{4\pi N_A d_1}\left[\frac{(\Delta\epsilon/w_2)}{(\epsilon_1 + 2)^2} - \frac{2n_1(\Delta n/w_2)}{(n_1^2 + 2)^2}\right] + \frac{9kT}{4\pi N_A}(P_A' - P_A) \quad (1)$$

in which $\langle\mu^2\rangle$ is the mean-square dipole moment, N_A is the Avogadro number, M_2 the molecular weight of the solute, d_1 the density of the solvent, and ϵ_1 and n_1 the low-frequency

---

[1] Supported by the National Science Foundation.

[2] See, for example, F. W. Billmeyer, Jr., "Textbook of Polymer Science," Interscience Publishers, Inc., New York, N. Y., 1962, pp 419–424.

[3] (a) A. Nishioka and M. Watanabe, *J. Polymer Sci.*, **24**, 298 (1957); (b) H. W. Starkweather, Jr., and R. H. Boyd, *J. Phys. Chem.*, **64**, 410 (1960).

[4] W. J. Leonard, R. L. Jernigan, and P. J. Flory, *J. Chem. Phys.*, **43**, 2256 (1965).

[5] T. W. Bates, *Trans. Faraday Soc.*, **63**, 1825 (1967). This is paper I of the present series.

[6] T. W. Bates and W. H. Stockmayer, *J. Chem. Phys.*, **45**, 2321 (1966).

[7] T. W. Bates and W. H. Stockmayer, *Macromolecules*, **1**, 17 (1968).

[8] R. B. Ward, *J. Org. Chem.*, **30**, 3009 (1965).

[9] J. D. LaZerte, L. J. Hals, T. S. Reid, and G. H. Smith, *J. Am. Chem. Soc.*, **75**, 4525 (1953).

[10] J. W. Smith, "Electric Dipole Moments," Butterworth and Co., Ltd., London, 1955.

dielectric constant and visible-light refractive index, respectively, of the solvent. The molar atomic polarization of the solute is represented by P_A, while P_A' is the atomic polarization of the displaced solvent. The latter quantity is given by

$$P_A'/\bar{V}_2 = \frac{\epsilon_1 - 1}{\epsilon_1 + 2} - \frac{n_1^2 - 1}{n_1^2 + 2} \tag{2}$$

where $\bar{V}_2$ is the partial molar volume of the solute. The term involving the atomic polarization difference is especially important here, because of the relatively low vibrational frequencies and high dipole moments of C–F bonds. The values of P_A for the solutes of present interest are estimated by assuming them to be the sums of contributions from individual CF_2 and CF_2H groups. From the available data on perfluoralkanes,[11] we find contributions of 1.5 and 2.4 $cm^3\ mole^{-1}$ to P_A for CF_2 and CF_2H groups, respectively. The importance of the atomic polarization is shown by the fact that the term $P_A - P_A'$ is between 10 and 15% of the total molar polarization for all the solutes involved.

The dipole moments at 25° are shown in Table I, where the uncertainties given are the resultants of the experimental errors and an assigned ±5% uncertainty in P_A. The moments at 45° are the same as at 25° to within the experimental error. This means that the temperature coefficients $|d \ln \langle\mu^2\rangle/dT|$ cannot be greater than $1 \times 10^{-3}\ deg^{-1}$.

TABLE I

DIPOLE MOMENTS IN BENZENE AT 25°

Compound	$\langle\mu^2\rangle^{1/2}$, D
$H(CF_2)_4H$	2.02 ± 0.01
$H(CF_2)_6H$	2.12 ± 0.01
$H(CF_2)_7H$	2.20 ± 0.02
$H(CF_2)_8H$	2.19 ± 0.01
$H(CF_2)_{10}H$	2.21 ± 0.02
$H(CF_2)_7F$	1.60 ± 0.01

Calculations

With Leonard, Jernigan, and Flory,[4] we assume that the only contributions to the molecular dipole moment come from the terminal H–C and C–H bonds 1 and $n + 1$ (see Figure 1). By identification of the effective dipole moment μ_1 of such a terminal bond with the experimental dipole moment of $H(CF_2)_7F$ in benzene (Table I), the errors due to induced moments in neighboring bonds or to any moments associated with the fluorocarbon residue are minimized. The mean-square dipole moment of the molecule is then given by

$$\langle\mu^2\rangle/2\mu_1^2 = 1 - [m]\langle\prod_1^n T_i\rangle\{m\} \tag{3}$$

where $\{m\}^T = [m] = [1, 0, 0]$ and T_i is the familiar transformation matrix rotating the coordinate system based on bond $i + 1$ to that based on bond i

$$T_i = \begin{bmatrix} \cos\theta_i & \sin\theta_i & 0 \\ \sin\theta_i \cos\phi_i & -\cos\theta_i \cos\phi_i & \sin\phi_i \\ \sin\theta_i \sin\phi_i & -\cos\theta_i \sin\phi_i & -\cos\phi_i \end{bmatrix} \tag{4}$$

The average value of the product required in eq 3 can be evaluated[4] in the rotational-isomeric-state approximation. Once the statistical-weight matrix U_i has been constructed for all pairs of chain bonds, the partition function of the molecule is found from

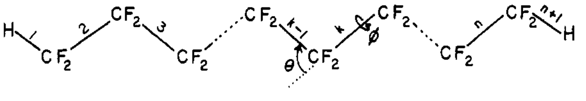

Figure 1. The α,ω-dihydroperfluoroalkane chain $H(CF_2)_nH$.

$$Z = J^T(\prod_2^n U_i)J \tag{5}$$

and the required average is[4] then

$$\langle\prod_1^n T_i\rangle = Z^{-1}(J^T \times E_3)\mathfrak{T}[\prod_2^n (U_i \times E_3)\mathfrak{T}](J \times E_3) \tag{6}$$

If each bond is taken to have r rotational-isomeric states, the matrix U_i is of order $r \times r$ and J is a column vector of r elements each equal to unity. In the above equation, the symbol × denotes the direct product, E_3 is the identity matrix of rank 3, and $\mathfrak{T}$ is a pseudo-diagonal matrix of order $3r \times 3r$ whose elements are the transformation matrices $T(\alpha)$ for the various rotational isomeric states.

$$\mathfrak{T} = \begin{bmatrix} T(1) & & & & & \\ & \cdot & & & & \\ & & \cdot & & & \\ & & & T(\alpha) & & \\ & & & & \cdot & \\ & & & & & \cdot \\ & & & & & & T(r) \end{bmatrix} \tag{7}$$

Here the matrices T and $\mathfrak{T}$ have been written without any bond-denoting subscript, since they are the same for all the bonds of the $H(CF_2)_nH$ chain.

The above plan of calculation is based on the supposition that direct correlations exist only between the states of neighboring bonds and it therefore neglects the direct electrostatic interaction between the permanent dipoles of the two terminal bonds. The existence of this interaction was taken into account by Leonard, Jernigan, and Flory,[4] who found it not altogether negligible for the first few α,ω-dibromoalkanes. Trial calculations for $H(CF_2)_4H$ show that its effect can be neglected in the present case, doubtless because the dipole moments are smaller and because of the somewhat greater preeminence of *trans* states.

Now the perfluoroalkane chain is structurally analogous to that of polyethylene, whose conformational characteristics[4,12–14] are well represented by an isomeric state model with rotation angles restricted to one *trans* ($\phi = 0°$) and two *gauche* ($\phi \cong \pm 120°$) conformations. However, X-ray measurements[15,16] on crystalline PTFE show that the most stable conformation of a perfluoroalkane chain in the crystal at room tem-

---

[11] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 421.

[12] C. A. J. Hoeve, *J. Chem. Phys.*, **32**, 888 (1960).

[13] P. J. Flory and R. L. Jernigan, *ibid.*, **42**, 3509 (1965).

[14] A. Abe, R. L. Jernigan, and P. J. Flory, *J. Am. Chem. Soc.*, **88**, 631 (1966).

[15] C. W. Bunn and E. R. Howells, *Nature*, **174**, 549 (1954).

[16] E. S. Clark and L. T. Muus, *Z. Krist.*, **117**, 119 (1960).

perature is a slowly twisting helix in which each C–C bond is rotated in the same sense through about 17° from the planar *trans* position. As emphasized by Bunn and Holmes,[17] this deviation from the planar form is almost certainly to be attributed to intramolecular rather than intermolecular interactions, and this conclusion has been rationalized by various semiempirical calculations of conformational energies,[5,18–20] according to which a helical conformation with $\phi = 17 \pm 2°$ is more stable than the planar *trans* form by an energy of 0.2–0.9 kcal/mole of $-CF_2-$ units. There are several contributions to this energy difference, but the essential reasons for the nonplanarity are the relatively large van der Waals radius of the F atom and the polarity of the C–F bonds. In view of these considerations, a realistic treatment of the perfluoroalkane chain requires the use of a bond rotation potential energy with two equivalent *trans* minima in addition to the two *gauche* states. The reality of still other minima which have appeared in certain semiempirical calculations[14,19–21] need not be argued here, as their inclusion for polyethylene appears[14] not to produce much change in calculated conformational properties. We therefore adopt a four-state model for $(-CF_2-)_n$, with states t^+ and t^- at $\phi \cong \pm 15°$ and g^+ and g^- at $\phi \cong \pm 120°$.

The energy of a given rotational-isomeric state of bond i may depend on the rotational states of its neighboring bonds. Only first-neighbor dependence need concern us here. It is taken into account by assigning a statistical weight parameter $u_i\,(\alpha,\beta)$ to the rotational state β of bond i when the preceding bond $i - 1$ is in a rotational state α; $\alpha, \beta = 1, 2, \ldots r$. For the purpose of constructing the statistical-weight matrices U_i, we assign an arbitrary statistical weight of unity to the helical conformation, $t^+t^+t^+$ or $t^-t^-t^-$. Considering first the internal bonds k ($4 \leqslant k \leqslant n - 1$) to the $H(CF_2)_nH$ chain (see Figure 1), we assign a statistical weight σ to a *gauche* rotational state of bond k when bond $k - 1$ is *trans* of the same sign; *i.e.*, $\sigma = u_k(t^+g^+) = u_k(t^-g^-)$. The parameter σ represents interactions between CF_2 groups separated by three bonds (see Table II). *gauche* rotations of opposite sign, $g_{k-1}{}^+g_k{}^-$ and $g_{k-1}{}^-g_k{}^+$, about successive bonds result in very severe steric interactions between CF_2 groups separated by four bonds. These "pentane" interferences are considerably greater for the fluorocarbon chain than for the hydrocarbon chain (for which $E(g^+g^-) \cong 3$ kcal mole^{-1})[14] because of the larger size of the CF_2 group; consequently, $g_{k-1}{}^{\pm}g_k{}^{\mp}$ pairs may be excluded. A *gauche* state preceded by a *trans* state of opposite sign (*i.e.*, $t_{k-1}{}^+g_k{}^-$ and $t_{k-1}{}^-g_k{}^+$) also results in severe steric interactions between CF_2 groups separated by three C–C bonds. The semiempirical energy calculations of paper I[5] for n-C_4H_{10} indicate that such conformations are about 4 kcal mole^{-1} higher in energy than the helical form. A zero statistical weight may thus also be assigned to $t_{k-1}{}^{\pm}g_k{}^{\mp}$. Sequences $t_{k-1}{}^+t_k{}^-$ and $t_{k-1}{}^-t_k{}^+$, which result in a reversal in the pitch of the helix, are assigned a statistical weight ω in recognition of the repulsive interactions precipitated by such conformations. Finally, a study of models shows that $g_{k-1}{}^{\pm}g_k{}^{\pm}$ sequences produce essentially the same interactions as those involved in $t_{k-1}{}^+g_k{}^+$ sequences. The appropriate statistical weight is therefore again σ. The matrix U_k for the internal bonds is then given by

$$U_k = \begin{array}{c} \begin{array}{cccc} (t^+) & (g^+) & (g^-) & (t^-) \end{array} \\ \begin{bmatrix} 1 & \sigma & 0 & \omega \\ 1 & \sigma & 0 & 0 \\ 0 & 0 & \sigma & 1 \\ \omega & 0 & \sigma & 1 \end{bmatrix} \end{array} ;\ 4 \leqslant k \leqslant n - 1 \qquad (8)$$

where bonds $k - 1$ and k are indexed in the order t^+, g^+, g^-, t^- on the rows and columns.

TABLE II

STATISTICAL-WEIGHT PARAMETERS FOR A FOUR-STATE MODEL OF $H(CF_2)_nH$

Bond type	Conformation	Interacting atoms	No. of bonds apart	Statistical weight
Internal	$t^{\pm}$			1
	$t_{k-1}{}^{\pm}t_k{}^{\mp}$	F···F	4	ω
	$t_{k-1}{}^{\pm}g_k{}^{\pm}$, $g_{k-1}{}^{\pm}g_k{}^{\pm}$	F···F	5	σ
	$t_{k-1}{}^{\pm}g_k{}^{\mp}$	F···F	5	0
	$g_{k-1}{}^{\pm}g_k{}^{\mp}$	F···F	6	0
Terminal	$g_2{}^{\pm}$	H···F	4	σ'
	$t_2{}^{\pm}t_3{}^{\mp}$	F···F	4	ω
	$g_2{}^{\pm}g_3{}^{\pm}$	F···F	5	σ
	$g_2{}^{\pm}g_3{}^{\mp}$	H···F	5	$\sigma\beta$

If entropy differences between the rotational isomers are neglected, the parameters σ and ω are related to the corresponding molar energies E_σ and E_ω by

$$\sigma = \exp(-E_\sigma/RT);\ \omega = \exp(-E_\omega/RT) \qquad (9)$$

The energy E_σ is the energy difference between t^+ and g^+ states of bond k when all the neighboring bonds are t^+; *i.e.*, $E_\sigma = E(t_{k-1}{}^+g_k{}^+) = E(t_{k-1}{}^-g_k{}^-)$. Similarly, $E_\omega = E(t_{k-1}{}^+t_k{}^-) = E(t_{k-1}{}^-t_k{}^+)$.

For the terminal bond 2, a semiempirical calculation similar to those described elsewhere,[5] reinforced by contemplation of models, indicates that there is very little hindrance to rotation about this bond. The conformations $g_2{}^+$ and $g_2{}^-$ may, therefore, be assigned a weight σ', where we expect $\sigma' \cong 1$. The matrix U_2 is then given by

$$U_2 = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & \sigma' & 0 & 0 \\ 0 & 0 & \sigma' & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \qquad (10)$$

the diagonal form being dictated by the absence of a bond rotation preceding bond 2. The matrix U_3 for bond 3 is strongly affected by the small size of the H atom.

---

(17) C. W. Bunn and D. R. Holmes, *Discussions Faraday Soc.*, **25**, 95 (1958).

(18) M. Iwasaki, *J. Polymer Sci.*, **A1**, 1099 (1963).

(19) P. deSantis, E. Giglio, A. M. Liquori, and A. Ripamonti, *ibid.*, **A1**, 1383 (1963).

(20) P. E. McMahon and R. L. McCullough, *Trans. Faraday Soc.*, **61**, 197, 201 (1965).

(21) R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, **44**, 3054 (1966).

(a) *gauche* sequences of opposite sign, $g_2^{\pm}g_3^{\mp}$, can have a nonzero statistical weight (in contrast to the situation for the internal bonds k). This is because $g_2^{\pm}g_3^{\mp}$ conformations result in H···CF$_2$ nonbonded interactions which are much less repulsive than the corresponding CF$_2$···CF$_2$ interactions for $g_{k-1}^{\pm}g_k^{\mp}$ pairs. A statistical weight $\sigma\beta$ is, therefore, assigned to $g_2^{\pm}g_3^{\mp}$ sequences; *i.e.*, $\sigma\beta = u_3(g^{\pm}g^{\mp})$. Because of the way in which the statistical weight matrices are constructed, the energy $E(g_2^+g_3^-)$ is equal to $E_\sigma + E_{\sigma'} + E_\beta$. Thus E_β may be regarded as the energy of a $g_2^+g_3^-$ pair after subtraction of the energies $E_{\sigma'}$ (of an isolated g_2 conformation) and E_σ (of an isolated g_3 conformation).

(b) *gauche–trans* sequences of opposite sign, $g_2^{\pm}t_3^{\mp}$, demand a similar statistical weight to *gauche–trans* sequences of the same sign, $g_2^{\pm}t_3^{\pm}$, since a study of models shows that the interactions for both sequences are similar.

The number of parameters may be kept within reasonable bounds by assuming that $u_3(g^+t^-) = u_3(g^+t)^+ = \sigma'$. These assumptions should introduce no significant error. The matrix U_3 is then given by

$$U_3 = \begin{bmatrix} 1 & \sigma & 0 & \omega \\ 1 & \sigma & \sigma\beta & 1 \\ 1 & \sigma\beta & \sigma & 1 \\ \omega & 0 & \sigma & 1 \end{bmatrix} \qquad (11)$$

and, for consistency, U_n must be written as

$$U_n = \begin{bmatrix} 1 & \sigma' & \sigma' & \omega \\ 1 & \sigma' & \sigma'\beta & 0 \\ 0 & \sigma'\beta & \sigma' & 1 \\ \omega & \sigma & \sigma' & 1 \end{bmatrix} \qquad (12)$$

The above considerations are summarized in Table II.

The foregoing eq 8 and 10–12 for the U_i, when used in eq 3–7, allow the mean-square dipole moment of H(CF$_2$)$_n$H to be computed as a function of the statistical weight parameters σ, σ', β, and ω. These parameters may then be evaluated by comparing calculated and experimental moments. For the principal calculations μ_1 was taken as 1.60 D, which is the dipole moment of H(CF$_2$)$_7$F in benzene at 25°; the valence angles were assumed to be the same for all bonds and were taken as 116°, which is the value obtained by Bunn and Howells[15] from X-ray measurements on PTFE; and the rotational angles $\phi(t^{\pm})$ and $\phi(g^{\pm})$ were taken as ± 15 and $\pm 120°$, respectively. Calculations of $\langle\mu^2\rangle$ were carried out systematically on a digital computer (Dartmouth Computation Center, GE-265) for values of σ between 0 and 0.5, σ' between 0.1 and 3.0, and ω between 0.01 and 0.5. The parameter β was chosen so that $\sigma\sigma'\beta$ was always between 0.5 and 0.1, as suggested by semiempirical calculations[22] for H(CF$_2$)$_4$H. Some of the results are shown graphically in Figure 2.

Because of uncertainties in the experimental dipole moments and in the various approximations of the model, calculated moments $\langle\mu^2\rangle^{1/2}$ which were within ± 0.05 D of the experimental values were considered acceptable. The parameters σ, σ', and ω thus determined have the following ranges: $0.06 \leqslant \sigma \leqslant 0.5$, $1.5 \leqslant \sigma' \leqslant 2.5$ and $0.05 \leqslant \omega \leqslant 0.5$. The corresponding energies, calculated at 25° from the Boltzmann expressions in eq 9, are $0.4 \leqslant E_\sigma \leqslant 1.7$, $E_\omega = 1.1 \pm 0.7$, $-E_{\sigma'} = 0.40 \pm 0.13$, and $E(g_2^+g_3^-) = E(g_{n-1}^+g_n^-) = E_\sigma + E_{\sigma'} + E_\beta = 0.9 \pm 0.5$ kcal mole^{-1}. The calculated moments are fairly insensitive to the magnitude of ω. For example, when $\sigma = 0.1$ and $\sigma' = 2.0$, $\langle\mu^2\rangle^{1/2}$ changes by less than 0.05 D for all homologs on increasing ω from 0.05 to 0.2.

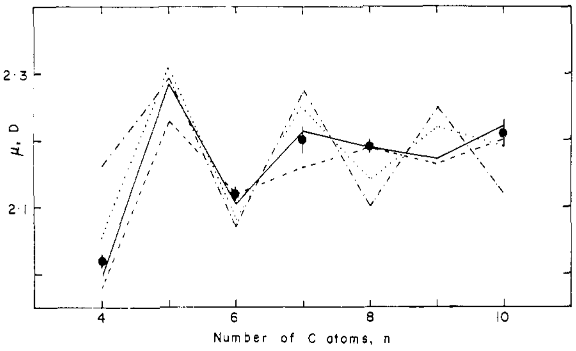

Figure 2. Dipole moments for H(CF$_2$)$_n$H at 25° in benzene. Experimental values are indicated by filled circles. The lines connect points calculated for the four-state model with $\theta = 64°$, $\phi(t^{\pm}) = \pm 15°$, $\phi(g^{\pm}) = \pm 120°$, $\mu_1 = 1.60$ D, $\sigma' = 2.0$, $\sigma\sigma'\beta = 0.20$, and with various values of the statistical weights σ and ω as follows: - - - -, $\sigma = 0.50$, $\omega = 0.20$; ———, $\sigma = 0.20$, $\omega = 0.05$; · · · ·, $\sigma = 0.05$, $\omega = 0.05$; -·-·-·, $\sigma = 0.01$, $\omega = 0.20$.

In view of previous suggestions that perfluoroalkanes are highly extended,[3] *i.e.*, $\sigma \cong 0$, several calculations were carried out for very small values of σ. A limiting case of the four-state model was investigated by putting $\sigma = 10^{-5}$, thereby effectively excluding all *gauche* states for the internal bonds k. This is equivalent to treating the internal bonds in terms of a two-state model since only $t_{k-1}^{\pm}t_k^{\pm}$ and $t_{k-1}^{\pm}t_k^{\mp}$ sequences are then allowed. *gauche* states are permitted about bonds 2 and n. Because values of $\sigma\sigma'\beta$ close to zero are physically unrealistic, β must be given a very large value. Bonds 3 and $n - 1$ can therefore adopt *gauche* states, but only if bonds 2 and n respectively are *gauche* of opposite sign. Agreement between calculated and observed moments was unattainable for this model for any values of σ', β, and ω. A purely *trans*-perfluoroalkane chain is therefore inconsistent with the observed dipole moments. Indeed, σ must be greater than 0.05, as is clearly shown by the calculated $\langle\mu^2\rangle^{1/2}$ values shown in Figure 2.

The sensitivity of the calculated dipole moments to variations in the rotational angles $\phi(t^{\pm})$ and $\phi(g^{\pm})$ and in the moment μ_1 was also investigated. Although identification of μ_1 with the dipole moment of H(CF$_2$)$_7$F in benzene is reasonable, it may not be exactly equal to 1.60 D. However, one might reasonably expect μ_1 to lie between 1.55 and 1.65 D. Changing μ_1 from 1.65 to 1.55 D lowers the calculated moments by about 0.10 D, but σ must still exceed 0.05. There appears to be no direct experimental evidence on the value of $\phi(g)$ in perfluoroalkanes. A value between 114.5 and 123° is predicted (paper I) for n-C$_4$F$_{10}$, which is to be

---

(22) T. W. Bates, unpublished results.

Table III

Conformation Energies (Kilocalories per Mole) Calculated from the Dipole Moments of $H(CF_2)_nH$ at 25°

Bond type	Four-state model	Three-state model
Internal	$E(t^\pm t^\pm) = 0$ $E(t^\pm g^\pm) = E_\sigma = 1.4 \pm 0.4$ $E(t^\pm g^\mp) \gg 0$ $E(t^\pm t^\mp) = E_\omega = 1.1 \pm 0.7$ $E(g^\pm g^\pm) = 2E_\sigma = 2.8 \pm 0.8$ $E(g^\pm g^\mp) \gg 0$	$E(tt) = 0$ $E(tg^\pm) = E_\sigma = 1.2 \pm 0.2$ $E(g^\pm g^\pm) = 2E_\sigma = 2.4 \pm 0.4$ $E(g^\pm g^\mp) \gg 0$
Terminal	$\left.\begin{matrix} E(g_2^\pm t_3^\pm) \\ E(g_2^\pm t_3^\mp) \end{matrix}\right\} = E_{\sigma'} = -(0.4 \pm 0.1)$ $E(g_2^\pm g_3^\pm) = E_\sigma + E_{\sigma'} =$ 1.0 ± 0.5 $E(g_2^\pm g_3^\mp) = E_\sigma + E_{\sigma'} +$ $E_\beta = 0.9 \pm 0.5$	$E(g_2^\pm t_3^\pm) = E_\sigma =$ $-(0.41 \pm 0.03)$ $E(g_2^\pm g_3^\pm) = E_\sigma + E_{\sigma'} =$ 0.8 ± 0.2 $E(g_2^\pm g_3^\mp) = E_\sigma + E_{\sigma'} +$ $E_\beta = 1.0 \pm 0.3$

compared with the experimental value of 119 ± 3° for $\phi(g)$ for the lower n-alkanes.[23] We might reasonably expect the *gauche* rotational angle to lie between 115 and 125°. The dipole moment calculations are not significantly altered by increasing $\phi(g)$ from 115 to 125°, $\langle \mu^2 \rangle^{1/2}$ being increased by less than 0.04 D for all homologs. The calculated moment is also fairly insensitive to variations in $\phi(t^\mp)$ in the range 15–20°.

The dipole moments were also analyzed with the three-state model which has been used for polyethylene.[4,12-14] It seemed worthwhile to investigate the influence of the choice of model (*i.e.*, three-state or four-state) on the calculated dipole moments; moreover, we cannot[5] rule out completely the possibility that the most stable configuration of an *isolated* PTFE chain is the planar *trans* form.

The statistical weights are again defined relative to an arbitrary weight of unity for the planar *trans* form *ttt*. For the internal bonds k, the weight for $t_{k-1}g_k^+$ and $t_{k-1}g_k^-$ conformations is σ. Successive *gauche* states of opposite sign $g_{k-1}^\pm g_k^\mp$ receive zero weight. The matrix U_k is then given by

$$U_k = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & 0 \\ 1 & 0 & \sigma \end{bmatrix}; \quad 4 \leqslant k \leqslant n - 1 \qquad (13)$$

where the states of bonds $k - 1$ and j are indexed in the order t, g^+, g^-. As for the four-state model, U_2 is diagonal

$$U_2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \sigma' & 0 \\ 0 & 0 & \sigma' \end{bmatrix} \qquad (14)$$

where $\sigma' = u_2(g_2^\pm)$. *gauche* rotations of opposite sign about the bond pair 2, 3 are assigned a statistical weight $\sigma\beta$ in view of the relatively weak H · · · CF_2 repulsions precipitated by such $g_2^+g_3^-$ and $g_2^-g_3^+$ sequences. Then

$$U_3 = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\beta \\ 1 & \sigma\beta & \sigma \end{bmatrix}; \quad U_n = \begin{bmatrix} 1 & \sigma' & \sigma \\ 1 & \sigma' & \sigma'\beta \\ 1 & \sigma'\beta & \sigma \end{bmatrix} \qquad (15)$$

Calculations of $\langle \mu^2 \rangle$ for the three-state model were carried out systematically for values of σ between 0 and 0.1, σ' between 0.1 and 2.5, and β between 0.25 and 1000. The principal calculations were carried out with $\theta = 64°$, $\phi(g^\pm) = \pm 115°$, and $\mu_1 = 1.60$ D. The results of some of these calculations were reported previously.[6] The only acceptable values of the parameters σ, σ', and β are as follows: $0.1 \leqslant \sigma \leqslant 0.3$, $\sigma' = 2.0 \pm 0.1$, $0.1 \leqslant \sigma\sigma'/\beta \leqslant 0.3$. The corresponding energies, calculated at 25° from the Boltzmann expressions, are $0.7 \leqslant E_\sigma \leqslant 1.4$, $-E_{\sigma'} = 0.41 \pm 0.003$, $E(g_2^+g_3^-) = (E_\sigma + E_{\sigma'} + E_\beta) = 1.0 \pm 0.3$ kcal mole^{-1}. The results are not substantially altered by small variations in μ_1 (between 1.55 and 1.65 D) and $\phi(g)$ (between 115 and 120°).

Temperature coefficients for the dipole moments were computed with the assumption of eq 9, and were very small for the ranges of parameters shown in Tables II and III. For example, with $\sigma = 0.2$, $\sigma' = 2.0$, $\beta = 0.5$, and $\omega = 0.2$ in the four-state model, $|\mathrm{d}\ln\langle \mu^2 \rangle/\mathrm{d}T| < 4 \times 10^{-4}$ deg^{-1} for all homologs. Agreement with the experimental results is therefore satisfactory for both four- and three-state models.

Discussion

Although the four-state model is favored by both the crystal structure of PTFE and several semiempirical energy calculations, the present dipole moment results can be adequately reproduced by either three- or four-state models. Fortunately this ambiguity does not seriously jeopardize the assessment of the *gauche–trans* energy difference. Thus, the preferred four-state model gives $E_\sigma = E(t^+g^+) - E(t^+t^+) = 1.1 \pm 0.7$ kcal mole^{-1} for the perfluoroalkane chain, while the corresponding energy difference in the less realistic three-state model is $E_\sigma = E(tg) - E(tt) = 1.05 \pm 0.35$ kcal mole^{-1}. The lower limits may be raised somewhat by comparison with the well-established results for polyethylene,[14,21] for which $E_\sigma = 0.45 \pm 0.15$ kcal mole^{-1}. The barrier to internal rotation in C_2F_6 is[24] about 4 kcal mole^{-1} as compared to about 3 kcal mole^{-1} for ethane[25] and this difference may reasonably be ascribed to the greater van der Waals radius of fluorine and the greater polarity of the C–F bond. For the same reasons, E_σ for fluorocarbons must surely be appreciably larger than for paraffins. It therefore seems reasonable

---

(23) L. S. Bartell and D. A. Kohl, *J. Chem. Phys.*, **39**, 3097 (1963).

(24) D. A. Swick and I. L. Karle, *ibid.*, **23**, 1499 (1955).

(25) D. R. Lide, Jr., *ibid.*, **29**, 1426 (1958).

to assign a lower limit of about 1.0 kcal mole^{-1} to E_σ for the perfluoroalkane chain. Final conformational energy values incorporating this restriction are summarized in Table III.

The *gauche–trans* energy difference E_σ is thus found to be 1.4 ± 0.4 and 1.2 ± 0.2 kcal mole^{-1} for the four-state and three-state models, respectively. It is gratifying that these figures fall within the range of 1.1–2.3 kcal mole^{-1} predicted.[5] An earlier estimate of 4.3 kcal mole^{-1} by Starkweather and Boyd was based on the temperature coefficient of the recoverable elastic modulus in molten uncross-linked PTFE,[3a] as interpreted with a three-state model; but this result rests on the doubtful assumption that the number of "effective" cross-links does not vary with temperature and cannot be given great weight.

In the four-state model, $E_\omega = E(t^+t^-) - E(t^+t^+) =$ 1.1 ± 0.7 kcal mole^{-1}. This figure is in reasonable accord with paper I, where about 0.7 kcal mole^{-1} was found for the energy difference between $t^+t^-t^-$ and $t^+t^+t^+$ conformations in n-C_4F_{10}. It also overlaps energy differences of about 0.5 ± 0.2 kcal mole^{-1}, between unspecified rotational isomers, found from the ir spectra of simple liquid fluorocarbons by Szasz.[26] Finally, it is also consistent with the interpretation given by Brown[27] of the ir spectrum of PTFE. From the temperature dependence of the absorption in the region 600–650 cm^{-1}, he found an energy of 1.2 kcal mole^{-1} for a structural defect which he believed to be reversal of the helix and this was reinforced by his own semiempirical energy calculations.

The possibility cannot be ignored that the conformational energies of the fluorocarbon chain depend measurably on the solvent. Rather large effects have been observed[28–30] with other polymers bearing strongly polar bonds attached directly to the chain backbone. It would obviously be desirable to repeat the dipole moment measurements in some solvent other than benzene and it is hoped to do this in the near future. It is also planned to study some other homologous series $X(CF_2)_nX$, preferably with much bulkier substituents X than hydrogen, in order to reduce the sensitivity of the results to the effects of the end groups. In the meantime, the generally good agreement between the present results and the semiempirical calculations of conformational energies gives us some confidence that the solvent and end-group effects are not large.

Acknowledgments. We thank Drs. R. G. Richardson and W. S. Friedlander for gifts of compounds and our colleagues, Drs. J. F. Hornig and D. M. Lemal, for loan of apparatus.

---

(26) G. J. Szasz, *J. Chem. Phys.*, **18**, 1417 (1950).

(27) R. G. Brown, *ibid.*, **40**, 2900 (1964).

(28) K. J. Ivin, H. A. Ende, and G. Meyerhoff, *Polymer*, **3**, 129 (1962).

(29) T. W. Bates and K. J. Ivin, *ibid.*, **8**, 263 (1967).

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

Conformational Energies of Perfluoroalkanes.[1] III. Properties of Polytetrafluoroethylene

T. W. Bates and W. H. Stockmayer

Department of Chemistry, Dartmouth College,
Hanover, New Hampshire 03755.
Received October 4, 1967

ABSTRACT: Properties of polytetrafluoroethylene which depend on the configurational statistics of the chain are discussed in terms of the four-state rotational-isomeric model used in the preceding paper to correlate the dipole moments of $H(CF_2)_nH$. Solution and melt viscosities are calculated from the predicted characteristic ratio, $\langle r^2\rangle_0/nl^2 = 30 \pm 15$ at 600°K, and are in satisfactory agreement with experimental data. The temperature coefficient $d \ln \langle r^2\rangle_0/dT$ is predicted to be $-(0.9 \pm 0.5) \times 10^{-3}$ deg^{-1}. The thermodynamics of both the solid–solid and solid–liquid phase transitions of the polymer are consistent with the four-state model. The calculated conformational entropy change on melting is 0.8 ± 0.1 cal deg^{-1} mole^{-1}, in good agreement with the experimental constant volume entropy of melting of 0.76 cal deg^{-1} mole^{-1}.

In the preceding paper[2] (hereafter II), it was found that a four-state rotational-isomeric model gave a good account of the observed dipole moments of the compounds $H(CF_2)_nH$. The rotational isomers consist of two *trans* states, $t^{\pm}$, at about ±15° from the planar zigzag conformation and two *gauche* states, $g^{\pm}$, at about ±120°; the potential energy differences $E_\sigma = 1.4 \pm 0.4$ kcal mole^{-1} and $E_\omega = 1.1 \pm 0.7$ kcal mole^{-1} determine the probabilities (relative to the most stable $t^{\pm}t^{\pm}$ helical conformation) of the bond sequences $t^{\pm}g^{\pm}$ and $t^{\pm}t^{\mp}$, respectively. A less convincing three-state model also can fit the dipole moments, but it does not account for the helical conformation of the chains in crystalline polytetrafluoroethylene.

In the present paper the rotational-isomeric model developed in II is used to discuss some of the properties of polytetrafluoroethylene (PTFE) which are related to chain conformation. These include chain dimensions, solution and melt viscosities, and phase transitions.

Temperature Dependence of Statistical Weights

Before attempting to discuss the properties of PTFE at temperatures exceeding 300°, it is prudent to inquire

---

(1) Supported by the National Science Foundation.

(2) T. W. Bates and W. H. Stockmayer, *Macromolecules*, **1**, 12 (1968).