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Conformational Energies of *n*-Alkanes and the Random Configuration of Higher Homologs Including Polymethylene

A. Abe, R. L. Jernigan, and P. J. Flory

Contribution from the Department of Chemistry, Stanford University, Stanford, California.

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Abstract: Conformation energies of *n*-butane and *n*-pentane have been calculated as functions of their C–C bond rotation angles using semiempirical expressions for the repulsive and attractive energies between nonbonded atom pairs and an intrinsic threefold torsion potential having a barrier height of 2.8 kcal mole^{-1} for each C–C bond. Parameters for the nonbonded repulsions were adjusted to reproduce the experimental energy difference E_σ of 500 cal mole^{-1} between the *gauche* and the *trans* states. The same parameters yield barrier heights for rotations in propane, *n*-butane, isobutane, and neopentane which agree with experiment. The potential wells about *gauche* and *trans* minima in *n*-butane and *n*-pentane are similar in breadth. The former have been found to occur at *ca.* $\varphi_g = \pm 112.5°$ from *trans*. Neighbor rotations of like sign $g^\pm g^\pm$ in *n*-pentane are essentially unperturbed by one another. The energy of $g^\pm g^\mp$ pairs of opposite sign is prohibitively large. These are superseded by pairs of shallow minima at *ca.* $\pm 115, \mp 80°$, and $\pm 80, \mp 115°$, with energies *ca.* 3.0 to 3.5 kcal mole^{-1} above *tt*. The mean dimensions of polymethylene chains $H(-CH_2)_{n+1}-H$ have been interpreted in light of these features of the conformation energy of first neighbor bonds in lower *n*-alkane homologs. The characteristic ratio $(\langle r^2\rangle_0/nl^2)_\infty$ and its temperature coefficient were computed for various values of the parameters involved. Experimental values of these quantities are well reproduced by taking $E_\sigma = 400 \pm 100$ cal mole^{-1} and by assigning an energy of the order of 3.0 kcal mole^{-1} for the $g^\pm g^\mp$ states cited above, in agreement with the conformation energy calculations.

The random-coil configuration of polymethylene $H(-CH_2)_{n+1}-H$ of high molecular weight has been correlated with known characteristics of the rotational potentials[1-5] of the normal alkanes for which $n + 1 = 4$ to 8 by Hoeve[6] and by Nagai and Ishikawa.[7] They have shown that the experimental values of the characteristic ratio $(\langle r^2\rangle_0/nl^2)_\infty$ for the infinite chain and the temperature coefficient of this ratio can be interpreted in terms of the familiar threefold bond rotational potential having its lowest minimum at the *trans* conformation (t) and two *gauche* minima (g^+ and g^-) situated at rotations $\varphi = \pm 120°$ from the *trans* conformation. Here $\langle r^2\rangle_0$ is the unperturbed mean square of the end-to-end length r of the chain averaged over all of its configurations, and n is the number of bonds of length l in the chain. The configuration was treated in the rotational isomeric state approximation whereby each bond rotation angle is restricted to choice from among several discrete values, these being identified with the minima in the rotational potential. Conformations in which two consecutive skeletal bonds occur in *gauche* "states" of opposite sign, thus forming a g^+g^- or a g^-g^+ pair, were assigned a very low statistical weight or suppressed altogether in recognition of the fact that such conformations precipitate severe steric overlaps between two CH_2 groups separated by four skeletal C–C bonds. Steric interferences of this sort assume foremost importance in accounting for the characteristic dimensions of polymethylene[6,7] and various other chain molecules.[8,9] Neighboring bond rotations are rendered

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(1) G. J. Szasz, N. Sheppard, and D. H. Rank, *J. Chem. Phys.*, **16**, 704 (1948).

(2) N. Sheppard and G. J. Szasz, *ibid.*, **17**, 86 (1949).

(3) S. Mizushima and H. Okazaki, *J. Am. Chem. Soc.*, **71**, 3411 (1949).

(4) K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940).

(5) W. B. Person and G. C. Pimentel, *J. Am. Chem. Soc.*, **75**, 532 (1953).

(6) C. A. J. Hoeve, *J. Chem. Phys.*, **35**, 1266 (1961).

(7) K. Nagai and T. Ishikawa, *ibid.*, **37**, 496 (1962).

interdependent by these interferences. No valid interpretation of the characteristic ratio and its temperature coefficient is possible without due account being taken of the interdependence of bond rotations.

Nagai and Ishikawa[7] suppressed $g^{\pm}g^{\mp}$ pairs by assigning them a statistical weight of zero; *i.e.*, in the notation adopted here they chose to take $\sigma\omega = 0$ (*cf.* below). The experimental temperature coefficient,[10] $d\ln\langle r^2\rangle_0/dT = -1.15\ (\pm 0.1) \times 10^{-3}\ \text{deg}^{-1}$ at 140°, was matched approximately by taking 800 cal mole^{-1} for the energy E_σ of a $tg^{\pm}$ pair relative to tt, the corresponding statistical weight being given by $\sigma = \exp(-E_\sigma/RT)$. This energy difference accords with the value deduced by Szasz, Sheppard, and Rank[1] from the temperature coefficients of Raman intensities for liquid *n*-butane. It exceeds the mean value of 500 cal mole^{-1} found by application of the Raman spectroscopic method to *n*-pentane[2,3] and to *n*-hexane,[2] this value being corroborated by analysis of the entropies of *n*-hexane, *n*-heptane, and *n*-octane according to Person and Pimentel.[5] A corresponding calculation of the characteristic ratio yielded $(\langle r^2\rangle_0/nl^2)_\infty = 8.0$ compared with the experimental value[11] of 6.8.

Hoeve[6] chose $E_\sigma = 500$ cal mole^{-1} in agreement with results cited above[2,3,5] for the C_5 to C_8 *n*-alkanes. (The corresponding free-energy difference for the *gaseous* *n*-alkanes C_4 to C_7 is about 600 cal mole^{-1} according to results of electron diffraction by Kuchitsu[12] and Bartell and Kohl.[13]) The observed values of both the characteristic ratio and its temperature coefficient were reproduced within the experimental error by assigning $g^{\pm}g^{\mp}$ pairs a small statistical weight $0 < \sigma\omega << 1$ corresponding to an energy of about 2500 cal mole^{-1} for such pairs; *i.e.*, $\sigma\omega = \exp(-2500/RT)$.[14] (If the parameter σ is looked upon as the statistical weight for a g^+, or a g^-, following a t bond, then ω is the further factor entering the configuration statistical weight if the preceding bond is in the *gauche* state, g^- or g^+, of opposite sign.)

Examination of models immediately implicates repulsions between CH_2 groups adjoining the C–C bond as being responsible for the higher energy of a *gauche* state of that bond compared with *trans*. The same interaction must also perturb the location of the *gauche* minima, shifting them to angles $|\varphi_g|$ somewhat less than 120° from *trans*, as pointed out by Borisova and Volkenstein.[15,16] This interaction might also be expected to narrow the potential wells for *gauche* states. Finally, the energy to be associated with a g^+g^- or a g^-g^+ pair may conceivably be reduced by a further compromise of the consecutive rotation angles representing such a pair. Critical assessment of these refinements in the representation of the polymethylene chain obviously requires more incisive information on the conformational energy than can be gleaned from visual inspection of models. Ideally, the conformational energy should be computed as a function of pairs of neighboring rotation angles[17] using appropriate analytical expressions for the respective contributions to the total intramolecular energy. At the present time these contributions, comprising intrinsic torsional potentials of the bonds, repulsions between nonbonded atoms, and dispersion attractions, can be given approximate mathematical representation only. In particular, the nonbonded repulsion for a given pair of atoms appears to depend not only on their distance of separation, but also on the nature and directions of the chemical bonds supporting them. Hence, although for reasons of expediency repulsive energies must be represented as functions of distance alone, it is important to choose values for parameters appropriate for the given pair of atoms when in structures closely resembling those of the chain molecules of interest. Experimental results, such as the heights of rotational barriers in analogous small molecules and the energy E_σ for a *gauche* rotation about a skeletal bond of an *n*-alkane, must be relied upon for assigning values to parameters, and extrapolations much beyond the range of experimentally determined data must be viewed with skepticism. Despite their limitations, calculations of conformational energies by semiempirical methods can be helpful in elucidating the pattern of the preferred rotational states in chain molecules, and such information should afford the basis for a more critical treatment of the average properties of these molecules.

In this paper we present calculations of the conformation energies of *n*-butane and *n*-pentane computed as functions of rotations about their C–C bonds The results are directly applicable to higher *n*-alkanes without revision, inasmuch as interactions involving terminal H atoms are of minor importance. The effects of refinements in the representation of rotational isomeric states for *n*-alkanes on the computed characteristic ratios for polymethylene are examined. Recent treatments of the configurational dimensions of a number of polymer chains[6–9] enhance the importance of a critical study of this chain molecule which is structurally one of the simplest of polymers. The results of the present study are especially relevant to the interpretation of vinyl polymers $(\text{-CH}_2\text{CHR})_n\text{-}$ bearing substituents on alternate atoms,[18] which are the subject of the following paper.[19]

The Conformational Energy

Procedures for Estimating the Intramolecular Energy as a Function of Conformation. Energy contributions

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(8) P. J. Flory, V. Crescenzi, and J. E. Mark, *J. Am. Chem. Soc.*, **86**, 146 (1964).

(9) P. J. Flory and J. E. Mark, *Makromol. Chem.*, **75**, 11 (1964); J. E. Mark and P. J. Flory, *J. Am. Chem. Soc.*, **87**, 1415 (1965).

(10) A. Ciferri, C. A. J. Hoeve, and P. J. Flory, *ibid.*, **83**, 1015 (1961); P. J. Flory, A. Ciferri, and R. Chiang, *ibid.*, **83**, 1023 (1961). Further experimental results in support of the value for the temperature coefficient have been obtained recently by A. Nakajima, F. Hamada, and S. Hayashi (in press), and by R. Chiang (private communication).

(11) R. Chiang, *J. Phys. Chem.*, **69**, 1645 (1965). See also Nakajima, *et al.*, cited in ref 10.

(12) K. Kuchitsu, *J. Chem. Soc. Japan*, **32**, 748 (1959).

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

(14) Calculations for polyethylene carried out recently by A. Opschoor, *Makromol. Chem.*, **85**, 249 (1965), using $E_\sigma = 500$ cal mole^{-1} and $\varphi_g = \pm 120°$ yield a temperature coefficient much smaller than that found experimentally by Ciferri, *et al.*[10] His attempt to estimate the effect of an alleged second neighbor interdependence of bond rotational potentials failed to increase the magnitude of the temperature coefficient; at the same time the characteristic ratio was increased well beyond the reliable value established by the work of Chiang[11] and others.

(15) N. P. Borisova and M. V. Volkenstein, *Zh. Strukt. Khim.*, **2**, 346, 437 (1961).

(16) N. P. Borisova, *Vysokomolekul. Soedin.*, **6**, 135 (1964).

(17) Interactions of higher order involving a sequence of more than two rotations are unimportant, as may readily be seen by examination of models (*cf.* below).

(18) P. J. Flory, J. E. Mark, and A. Abe, *J. Polymer Sci.*, **B3**, 973 (1965).

(19) P. J. Flory, J. E. Mark, and A. Abe, *J. Am. Chem. Soc.*, **88**, 639 (1966).

to be considered are those from: (i) intrinsic torsional potentials attributable to the bonds themselves, (ii) van der Waals repulsions between nonbonded atoms and groups, and (iii) dispersion attractions between nonbonded atoms. Attempts to treat the conformational energy without taking i explicitly into account continue to appear in the literature[20] despite the evidence brought together by Wilson[21] and others,[15,22] principally from microwave spectroscopy, showing that even in small molecules this energy cannot be represented as arising solely from nonbonded interactions, *i.e.*, from ii and iii alone. The familiar threefold torsional potential of ethane makes a major contribution to the intramolecular energies of higher paraffinic hydrocarbons, and this contribution eludes expression as a nonbonded repulsion ii, even as an empirical device. The importance of including i explicitly in the estimation of the configurational energy has been stressed by Borisova and Volkenstein.[15]

Following Hendrickson,[23] Borisova, and Volkenstein,[15] Scott and Scheraga,[24] and others,[20] we adopt a function of the form $a_{kl}\exp(-b_{kl}r_{kl}) - c_{kl}/r_{kl}^6$, used previously by Mason and Kreevoy,[25] to represent the nonbonded interactions ii and iii between atoms k and l at a distance of separation r_{kl}, where a_{kl}, b_{kl}, and c_{kl} are constants for the given pair of atoms. Combining expressions of this form for each atom pair with a threefold symmetric torsional potential, in further compliance with (previous procedures cited above[15,23,24] we have for the intramolecular energy associated with rotation φ_i about bond i

$$E(\varphi_i) = (E_0/2)(1 - \cos 3\varphi_i) + \sum_{k<l}[a_{kl}\exp(-b_{kl}r_{kl}) - c_{kl}/r_{kl}^6] \quad (1)$$

where the sum is over all pairs k,l of atoms. The parameters c may be calculated from atomic polarizabilities compiled by Ketelaar[26] using the Slater-Kirkwood equation.[27] The b's governing the steepness of the repulsion at small distances are conveniently obtained from the curve given by Scott and Scheraga[24] for b as a function of atomic number. To each parameter a, these authors assigned the value which would minimize the bracketed term of the summation in eq 1 at the sum of the accepted values for the van der Waals radii of the atoms.[28] Our procedure departs from theirs in that we have assigned arbitrary values to the a's, so chosen as to reproduce, approximately, the observed energy differences between *gauche* and *trans* conformations in the lower n-alkanes.

Values of the various parameters adopted for use in eq 1 are given in Table I. The $r_{\min}$ given in the last column represent the distances at which the energy for the given nonbonded pair is a minimum. They will be seen to be appreciably larger than the sums of van der Waals radii usually accepted for H and C. The larger radii are required to meet the foregoing condition. A value of 2.8 kcal mole^{-1} was assigned to E_0 for each C–C bond. The bond angles θ have been treated as constants of the structure, unaffected by interactions precipitated by bond rotations. Inasmuch as low-energy conformations assume main importance, this procedure seems justified. The carbon–carbon bond angle (∠CCC) was taken to be 112° for the n-alkanes in accordance with observations by electron diffraction,[12,13,29] X-ray diffraction,[30] and microwave spectroscopy.[31] For simplicity, the other bond angles were assumed to be equal to each other; hence, ∠HCH = ∠HCC = 109°. Bond lengths used in the various calculations are C–C = 1.53 Å and C–H = 1.10 Å.

Table I. Parameters for the Intramolecular Energy Function[a]

Atom pair	$10^{-3}a$	b	c	$r_{\min}$, Å
H···H	9.95	4.54	45.2	2.6
C···H	86.1	4.57	127	3.1
C···C	908.6	4.59	363	3.6

[a] All units are Å and kcal mole^{-1}.

The nonbonded attractions are of minor importance. Hence, errors in the $c_{k,l}$ have little effect on the final results.

That the results are insensitive to the value chosen for b was established by repeating the calculations for n-butane (*cf.* below) with b for all pairs equal to 4.0 instead of *ca.* 4.5 (see Table I), and again with b = 5.0 for all pairs. The values of a were recalculated as required to match the observed energy of the *gauche* form. Rotation angles at the *gauche* minima were altered less than 1° as compared with results presented below and based on the constants of Table I.

As a test of the foregoing procedure, rotational barriers were calculated for simple hydrocarbons using the equations given above and the parameters in Table I. Nonbonded interactions between all atom pairs whose intercenter distances r_{kl} are affected by bond rotations were included in the summation over $k < l$ in eq 1. Inasmuch as symmetry dictates location of the maxima at 60° from *trans* in all cases involving rotation of a methyl group, calculations at this angle only were sufficient for the purpose at hand. For the internal bond of n-butane, calculations carried out over a range of angles near 60° showed the slight displacement of the maximum in the energy from this angle to be inconsequential. Results of these computations are presented in Table II. The barrier heights thus calculated agree remarkably well with experimental values included for comparison. The computation scheme adopted and the parameters chosen to represent the intramolecular energies of paraffin hydrocarbons as functions of their conformations receive substantial support from these comparisons.

Energies of n-butane and of n-pentane were computed at intervals of 5° for each rotation angle; in ranges of special interest the interval was reduced to 2° and in

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(20) V. Magnasco, G. Gay, and C. Nicora, *Nuovo Cimento*, **34**, 1263 (1964); R. L. McCullough and P. E. McMahon, *Trans. Faraday Soc.*, **60**, 2089 (1964); *ibid.*, **61**, 197, 201 (1965); *J. Phys. Chem.*, **69**, 1747 (1965).

(21) E. B. Wilson, Jr., *Advan. Chem. Phys.*, **2**, 367 (1959).

(22) M. Cignitti and T. L. Allen, *J. Phys. Chem.*, **68**, 1292 (1964).

(23) J. B. Hendrickson, *J. Am. Chem Soc.*, **83**, 4537 (1961).

(24) R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, **42**, 2209 (1965).

(25) E. A. Mason and M. M. Kreevoy, *J. Am. Chem. Soc.*, **77**, 5808 (1955).

(26) J. Ketelaar, "Chemical Constitution," Elsevier Publishing Co., New York, N. Y., 1953, p 91.

(27) K. S. Pitzer, *Advan. Chem. Phys.*, **2**, 59 (1959).

(28) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

(29) R. A. Bonham, L. S. Bartell, and D. A. Kohl, *J. Am. Chem. Soc.*, **81**, 4765 (1959).

(30) H. M. M. Shearer and V. Vand, *Acta Cryst.*, **9**, 379 (1956).

(31) D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1514 (1960).

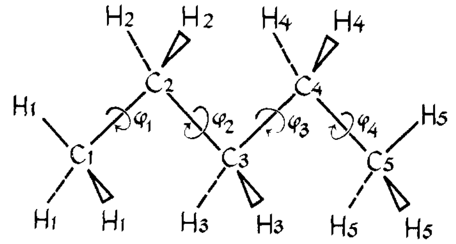

Figure 1.

some cases to 1°. In order to abbreviate the lengthy computations as much as possible, expression of the energies associated with rotation of terminal C–C bonds was simplified by the device of attributing the entire energy for rotation of a terminal methyl group to an adjusted torsion potential intrinsic to the bond itself. Thus, the nonbonded interactions which depend *only* on the angle of rotation about the terminal C_1–C_2 bond in Figure 1 were ignored and in lieu of them the value of E_0 for this bond was raised from 2.8 to 3.6 kcal mole^{-1}; that is, the ethane-like interactions of the three H_1's with the two H_2's and the C_3 were deleted from the sum of terms in eq 1. Interactions of two of the H_1 atoms with other atoms to the right of the H_2 and C_3 in Figure 1 were included in the computations inasmuch as the distances between these atom pairs depend also on other rotation angles. The H_1 atom to the left, *i.e.*, the one nearest the *trans* position relative to C_1, C_2, and C_3, was disregarded altogether inasmuch as its interactions are trivial in all conformations. The terminal group at the other end of the molecule was treated similarly in both the butane and the pentane calculations. Trial calculations show this simplification to have only a trivial effect on positions of the minima (<1°) and on the energies (<3 cal mole^{-1}) at the *gauche* minima of *n*-butane.

Table II. Potential Barriers to Internal Rotation of Some Simple Alkanes

Compound	Barrier height, kcal mole^{-1} Calcd	Barrier height, kcal mole^{-1} Obsd
CH_3–CH_3	3.0	2.9,[f,g] 3.0[h,i]
CH_3–C_2H_5	3.4[a]	3.4[f,g]
CH_3–$CH(CH_3)_2$	3.7[b]	3.6,[f,g] 3.9[i,j]
CH_3–$C(CH_3)_3$	4.3[c]	4.3[f,g]
CH_3CH_2–CH_2CH_3	3.6[d,e]	3.3,[e,g,k] 3.6,[e,g,l] 3.7[e,m]

[a] ∠CCC = 112°. [b] ∠CCC = 111°; see D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1519 (1960). [c] ∠CCC = 109.5°. [d] ∠CCC = 112°. [e] The value given is for the lower potential barriers located on either side of the *trans* state. [f] K. S. Pitzer, *Discussions Faraday Soc.*, **10**, 66 (1951). [g] Estimated from thermodynamic data. [h] D. R. Lide, Jr., *J. Chem. Phys.*, **29**, 1426 (1958). [i] Based on spectroscopic measurements. [j] D. R. Lide, Jr., and D. E. Mann., *J. Chem. Phys.*, **29**, 914 (1958). [k] K. S. Pitzer, *Ind. Eng. Chem.*, **36**, 829 (1944); see also ref 5. [l] K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940); K. S. Pitzer, *J. Am. Chem. Soc.*, **63**, 2413 (1941); B. P. Dailey and W. A. Felsing, *ibid.*, **65**, 44 (1943). [m] Estimated from the heat of formation of cyclopentane by K. Ito, *ibid.*, **75**, 2430 (1953).

The results for propane given in Table II indicate a rotational barrier of 3.4 kcal mole^{-1} for a terminal methyl group. The value 3.6 kcal mole^{-1}, corresponding to the barrier height for the central bond in *n*-butane, was chosen above in order to approximate more closely the characteristics of an internal bond in polymethylene. The effect of this choice on the position of the minima for terminal methyl group rotations is of the order of 0.1°, and therefore is quite negligible.

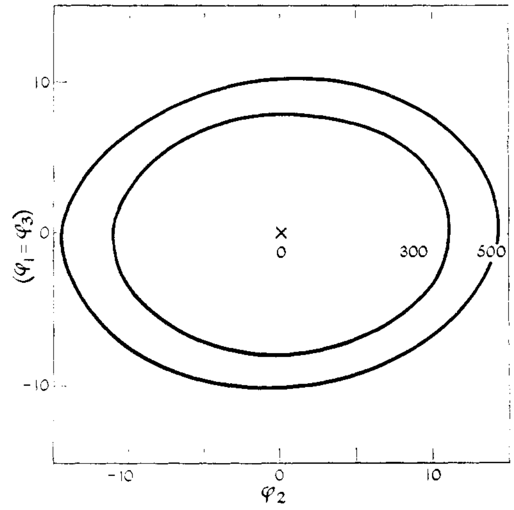

Figure 2. Energy contours in cal mole^{-1} in the neighborhood of the *trans* conformation of *n*-butane. The position of the minimum is marked by ×.

Calculations for *n*-Butane. The energy of *n*-butane in the vicinity of its *trans* minimum, calculated by the procedure described above, is shown in the form of a contour diagram in Figure 2. The angle of rotation φ_2 about the central C–C bond is plotted as abscissa. The rotation angles φ_1 and φ_3 about the terminal C–C bonds are plotted on the ordinate, these angles having been equated for the purpose of the calculation. No significant information is forfeited by this restriction inasmuch as the terminal groups are equivalent. Contour curves are shown for 300 and 500 cal mole^{-1} relative to an energy of zero for the *trans* state $\varphi_2 = 0°$ with staggered terminal methyl groups, *i.e.*, with $\varphi_1 = \varphi_3 = 0°$.

Energy contours similarly calculated at corresponding intervals about the *gauche* state of *n*-butane are shown in Figure 3. The energy at the *gauche* minimum, 530 cal mole^{-1} relative to an energy of zero for the *trans* minimum, approximates the experimental value for the liquid *n*-alkanes beyond butane (see above). This correspondence results from arbitrary choice of values for the *a*'s, as we have taken pains to acknowledge. The *gauche* minimum, located at $\varphi_2 = 112.5°$, $\varphi_1 = \varphi_3 = 4°$, is displaced from the symmetrical $\varphi_2 = 120°$ position as expected.[15] Kuchitsu[12] and Bonham and Bartell[32] found $\varphi_2 = 112.5 \pm 1.1$ and $117 \pm 8°$, respectively, from electron diffraction by gaseous *n*-butane; Bartell and Kohl[13] have reported $\varphi_2 = 119 \pm 3°$ for higher *n*-alkanes. The 4° value for φ_1 and φ_3 is suggestive of a comparable displacement of the *trans* bond adjacent to a *gauche* bond in a higher hydrocarbon. Bartell and Kohl[13] did in fact find evidence for a small displacement of 7 ± 4° in the electron diffraction spectra of the gaseous C_5, C_6, and C_7 *n*-alkanes. Recently, Scott and Scheraga[33] have calculated a somewhat larger displacement of 11 to 12° for a *trans* bond adjoining one in the *gauche* conformation. In their

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(32) R. A. Bonham and L. S. Bartell, *J. Am. Chem. Soc.*, **81**, 3491 (1959).

(33) R. A. Scott and H. A. Scheraga, *Biopolymers*, in press.

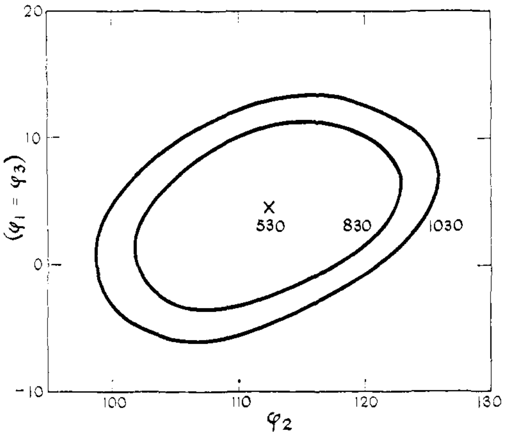

Figure 3. Energy contours for the *gauche* conformation of *n*-butane ($\varphi_1 = \varphi_3$ *vs.* φ_2). Numerical values are in cal mole^{-1} relative to the *trans* state.

treatment, however, the "6-exp" potential functions for nonbonded interactions which they previously[24] used were replaced by Lennard-Jones "6–12" potentials.

The breadth of the *gauche* potential well differs little from that for the *trans* state. Expression of the relative statistical weight σ for the *gauche* state (*cf.* below) as a simple Boltzmann factor of the energy difference is therefore justified.

These calculations suggest that the *gauche* states should be located at angles $\varphi_g = 112.5 \pm 3°$. The intimated small displacement of the neighboring *trans* state is more difficult to incorporate in the rotational isomeric state scheme because of the fact that the revision applies only to *trans* bonds adjoining *gauche* and not to those adjoined by bonds which are also *trans*. Incorporation of the small displacement in the rotational isomeric scheme would require a plurality of *trans* states, and this would complicate the analysis considerably. The effect on the $\langle r^2 \rangle_0$ and related quantities can amount to no more than would result from slight over-weighting of *gauche* states. We shall therefore ignore the indicated small distortion of these *trans* states and take $\varphi = 0°$ for all of them.

Calculations for *n*-Pentane. An approximate energy contour diagram calculated for *n*-pentane is sketched in Figure 4 with rotation angles φ_2 and φ_3 as independent variables. The calculations yielding this diagram were carried out with the terminal rotations φ_1 and φ_4 fixed at zero (staggered bonds). Energies indicated in kcal mole^{-1} with each curve are taken relative to the *tt* state for which $\varphi_2 = \varphi_3 = 0°$. The balance of the diagram covering the range $\varphi_2 = 0$ to $-180°$ is generated by inversion through the origin.

The $tg^{\pm}$ and $g^{\pm}t$ minima are equivalent to the $g^{\pm}$ minima for *n*-butane, and hence do not require separate consideration. The next higher minima are the g^+g^+ at $\varphi_2 = \varphi_3 \cong 110°$ and its analog g^-g^- occurring in the part of the diagram omitted from Figure 4. The energy calculated for the region corresponding to g^+g^-, *i.e.*, at $\varphi_2 = -\varphi_3 \cong 110$ to $120°$, is in excess of 6 kcal mole^{-1}, which is so high as to warrant disregard of this region. Nearby, however, a pair of associated minima occur at $\varphi_2 = 115°$, $\varphi_3 = -77°$ and at $\varphi_2 = 77°$, $\varphi_3 = -115°$. These may be looked upon as modified g^+g^- which might be labeled $g^+g_*^-$ and $g_*^+g^-$, respectively. Similar minima have been found independently by Scott and Scheraga.[33] No other energy minima are present.

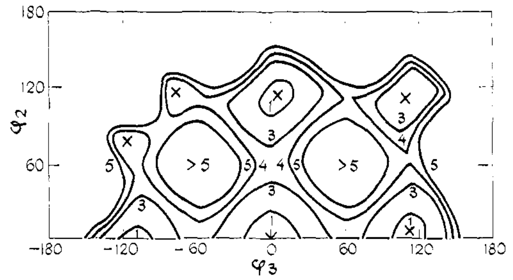

Figure 4. Energy map for the internal rotations of *n*-pentane. The terminal C–C bonds are fixed in *trans* states ($\varphi_1 = \varphi_4 = 0°$). Energy contours are given at intervals of 1 kcal mole^{-1} relative to the *tt* state ($\varphi_2 = \varphi_3 = 0°$). Positions of minima are marked by X.

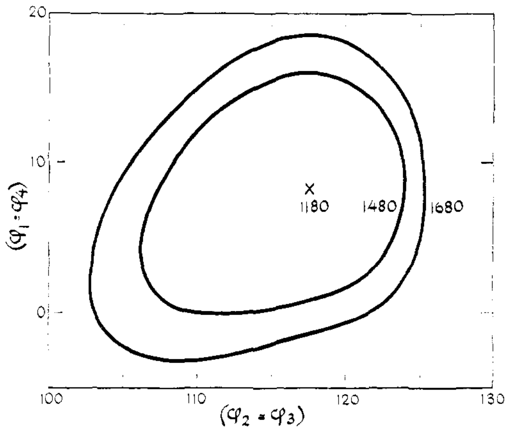

Figure 5. Energies in the vicinity of the ($g^{\pm}g^{\pm}$) conformation of *n*-pentane with $\varphi_1 = \varphi_4$; contours are labeled in cal mole^{-1} relative to the *tt* state ($\varphi_1 = \varphi_2 = \varphi_3 = \varphi_4 = 0°$).

The energy in the vicinity of the g^+g^+ (or g^-g^-) state is shown more precisely in Figure 5. Here the energy along a line corresponding to $\varphi_2 = \varphi_3$ in Figure 4 is expressed as a function of these angles and of $\varphi_1 = \varphi_4$. Relaxation of the condition $\varphi_1 = \varphi_4 = 0°$ causes Figure 5 to depart somewhat from Figure 4 in this region. Contours are shown in Figure 5 at 300 and at 500 cal mole^{-1} above the minimum, which occurs at $\varphi_2 = \varphi_3 = 117.5°$ with $\varphi_1 = \varphi_4 = 8°$. In the g^+t state of *n*-pentane, and likewise in the g^+ state of *n*-butane, repulsion between a pair of hydrogens, H_1 and H_4 in Figure 1, is largely responsible for displacing φ_g from 120 to *ca.* 112.5°, If bond 3 of *n*-pentane is also g^+ as in the g^+g^+ state, then an H_2, H_5 interaction opposes the decrease of φ_{g^+} for bond 2. This will be readily apparent from inspection of a suitable model. It is on this account that the computations place the g^+g^+ minimum at $\varphi_2 = \varphi_3 = 117.5°$ instead of at the same location, 112.5°, as for a single *gauche* state. The same interactions are responsible for the enhanced rotations of 8° for the terminal methyl groups at their minima, as compared with 4° for the CH_3 groups in the g^+ state of *n*-butane and likewise in the tg^+ state of *n*-pentane. The energy of the g^+g^+ state is increased by these interactions to a value, 1180 cal mole^{-1}, only a little above $2E_\sigma = 1060$ cal mole^{-1}, the energy for two separated *gauche* conformations. Finally,

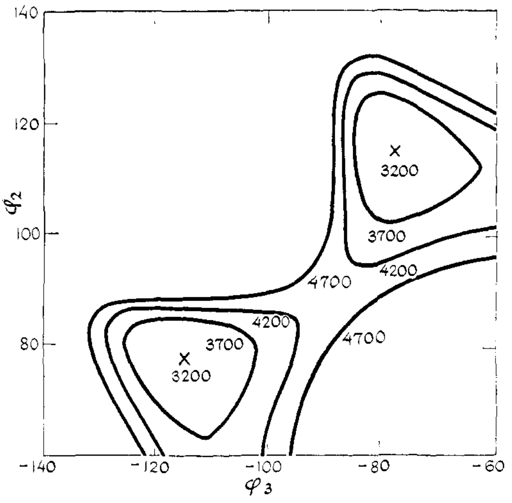

Figure 6. Conformation energy of n-pentane in the region of the $g^{\pm}g^{\mp}$ conformation, the adjoining bonds being fixed in *trans* states (*i.e.*, $\varphi_1 = \varphi_4 = 0°$). Energies indicated in cal mole^{-1} are relative to the *tt* state.

the breadth of the g^+g^+ energy well is comparable to that for a single *gauche* conformation.

None of the alterations discussed above is of sufficient importance to warrant separate characterization of either the energy or the location of a *gauche* state when it occurs next to a *gauche* bond of like sign. Insofar as the g^+g^+ and g^-g^- states are concerned, the condition of invariance in the location of the rotational state required for the rotational isomeric state treatment is satisfactorily met.

The portion of Figure 4 in the neighborhood of the modified g^+g^- "doublet" is plotted in greater detail in Figure 6. Here the condition $\varphi_1 = \varphi_4 = 0°$ has been retained and φ_2 and φ_3 are the independent variables, exactly as in Figure 4. The energy of each minimum is 3200 cal mole^{-1}, or about 2000 cal mole^{-1} above g^+g^+. The saddle point between them occurs at about 4400 cal mole^{-1}. Computations employing $\varphi_2 = -\varphi_3$ and $\varphi_1 = -\varphi_4$ as the pair of independent variables slightly reduce this saddle-point energy to 4100 cal mole^{-1}; the saddle point then occurs at $\varphi_2 = -\varphi_3 = 95°$ and $\varphi_1 = -\varphi_4 = 11°$. The saddle separating these minima from a *tg* or a *gt* state is somewhat lower (see Figure 4). Thus, none of the minima in Figure 4 is isolated from the others by a high-energy barrier. Adjustment of φ_1 and φ_4 about these minima did not lower the energy appreciably (*ca.* 100 cal mole^{-1}), nor did it alter the locations of the minima significantly ($<5°$).

Relaxation of the condition of constancy of bond angles θ might alter the form of Figure 6 somewhat because of the comparatively large repulsive and torsional energies involved. The energy probably would be lowered slightly by such a revision. However, accurate representation of this portion of the energy diagram is neither possible by the approximate equations used nor is it required for subsequent purposes inasmuch as conformations in the region of $g^{\pm}g^{\mp}$ assume only marginal importance in the configurations of long chains.

All of the energies calculated for the various minima should be viewed as approximate in recognition of the limitations of the potential functions used. The general features of the energy diagram are believed to be fairly well represented, however.

The Configuration of Infinite Polymethylene Chains

Statistical Weights for Long Chains. As examination of models shows, the interactions arising from rotation of a given bond to the *gauche* conformation are virtually unaffected by more remote parts of the molecule provided that neighbor bonds are *trans*. It follows that the energy calculated for $g^{\pm}$ in n-butane or for $tg^{\pm}$ in n-pentane can be taken to be representative of bonds in chains of greater length. The associated statistical weight will be designated $\sigma = \exp(-E_\sigma/RT)$, the entropy factor being set equal to unity in light of the close similarity in the breadths of the *gauche* and *trans* minima.

The calculations for g^+g^+ or g^-g^- in n-pentane can likewise be accepted as representative for such pairs in longer chains, provided that the pair does *not* adjoin a *gauche* bond of opposite sign. As noted above, the energy and location of the minimum for such a pair approximate those for two separate $g^{\pm}$ bonds adjoined by bonds in *trans* states. It is a legitimate approximation therefore to adopt the same "state" to represent $g^{\pm}$ preceded by $g^{\pm}$ of the same sign as for $g^{\pm}$ preceded by t, and to assign it the same statistical weight σ.

If for the moment we ignore the implications of Figure 6 to the effect that rotations of opposite sign lead to displaced minima, and assume instead that the pair g^+g^- can be represented as occurring at normal *gauche* angles, then the molecular configuration can be described in terms of three rotational isomeric states: t at $\varphi = 0°$, and $g^{\pm}$ at $\pm\varphi = 112.5 \pm 3°$. The statistical weight matrix for the ith bond of the chain where $2 < i < n$ would then assume the form[6]

$$U = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \tag{2}$$

with rows and columns indexed in the order t, g^+, g^-. Since, for the second bond of the chain, no preceding bond rotation angle is specified, the second statistical weight matrix consequently may be expressed in diagonal form

$$U_2 = D(1,\sigma,\sigma) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \sigma & 0 \\ 0 & 0 & \sigma \end{bmatrix} \tag{2'}$$

For later convenience, we define U_1 as the identity E_3 of order three, or in general as the identity E_s of order s equal to the number of rotational states. Then, according to the method of Kramers and Wannier[34] with minor modifications, the sum of the products of the statistical weight factors, one for each total configuration of the chain, is given exactly by

$$Z = J^T \left[\prod_{i=1}^{n-1} U_i \right] J \tag{3}$$

where J is the $s \times 1$ column, each element of which is unity, and J^T is the transpose of J, *i.e.*, the corresponding row. The partition function Z in the present case of a

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[34] 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).

chain of identical repeating units can be written

$$Z = J^T U_1 U_2 U^{n-3} J \tag{3'}$$

The energy of the g^+g^- (or the g^-g^+) pair as represented in diagrams above corresponds to $-RT \ln (\sigma^2\omega)$; that is, $-RT \ln \omega$ is the energy attributed to g^+g^- after subtraction of the energy (*ca.* 1000 cal mole^{-1}) for two isolated *gauche* bonds. The preceding calculations indicate, however, that the energy of a $g^\pm g^\mp$ pair thus represented is so great as to obviate its consideration. Instead of these states, four minima appear at the approximate angles $\varphi_i \cong \pm 80°$, $\varphi_{i+1} \cong \mp 115°$ and $\varphi_i \cong \pm 115°$, $\varphi_{i+1} \cong \mp 80°$. These minima can be incorporated in a five-state scheme comprising rotational states t, $g_*{}^+$, g^+, g^-, and $g_*{}^-$ at angles $\varphi_i = 0$, 80, 115, -115, and $-80°$, respectively. The corresponding statistical weight matrix for bonds i in the range $2 < i < n$ assumes the form

$$U = \begin{array}{c} \begin{array}{ccccc} (t) & (g_*{}^+) & (g^+) & (g^-) & (g_*{}^-) \end{array} \\ \begin{bmatrix} 1 & \sigma^* & \sigma & \sigma & 0 \\ 1 & \sigma^* & \sigma & \sigma\omega^* & \sigma^* \\ 1 & \sigma^* & \sigma & 0 & \sigma^*\omega^* \\ 1 & \sigma^*\omega^* & 0 & \sigma & \sigma^* \\ 1 & 0 & \sigma\omega^* & \sigma & \sigma^* \end{bmatrix} \end{array} \tag{4}$$

For $i = 2$

$$U_2 = D(1,\sigma^*,\sigma,\sigma,\sigma^*) \tag{4'}$$

and U_1 is the identity of order five. The partition function is given by eq 3 or 3′. Here σ assumes its previous definition, σ^* is the statistical weight for rotation to the 80° state, when unaffected by rotation of the neighboring bond, and ω^* is the factor, analogous to ω above, for placement of a g_* next to a g state of opposite sign. Thus the statistical weight for the sequence $tg^+g_*{}^-t$ is $\sigma\sigma^*\omega^*$. The $g^\pm g^\mp$ pairs, and likewise $g_*{}^\pm g_*{}^\mp$ pairs, are suppressed by assigning weights of zero to the appropriate elements of U in consideration of the excessive energies of these conformations.

In terms of energies, $-RT \ln \sigma^*$ is the energy for a g_* rotation free of complications from the rotational states of its neighbors. Taking $\varphi_g{}^* = 80°$, this energy is about 2100 cal mole^{-1}. According to calculations above, $-RT \ln (\sigma\sigma^*\omega^*) \cong 3100$ cal mole^{-1}, from which it follows that $-RT \ln \omega^* \cong 500$ cal mole^{-1}. These energies are not of course to be taken literally in view of the approximate character of the calculations from which they are deduced.

Interactions dependent upon a sequence of more than two successive rotation angles may legitimately be ignored. Conformations in which groups separated by five or six C–C bonds are brought into steric conflict require at least one $g^\pm g^\mp$ or $g^\pm g_*{}^\mp$ pair for intervening bonds, and these are of such rare occurrence as to render interactions of higher order quite negligible. The effects of interactions of much longer range are suppressed by correcting measured values of $\langle r^2 \rangle$ to the condition of null covolume, as signified by the subscript on $\langle r^2 \rangle_0$.

Procedures for Computing the Characteristic Ratio. The calculation of this quantity involves the appropriate statistical weight matrices U and the orthogonal axis transformation matrices T which serve to transcribe the representation of a vector in the coordinate system of bond $i + 1$ into that of bond i. With the customary definition of these coordinate systems (x-axis along bond i, y-axis in the plane of bonds i and $i - 1$ and in the direction making a positive projection on bond $i - 1$, and z-axis in the direction for a right-handed Cartesian reference frame), we have

$$T(\theta, \varphi) = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ \sin\theta\cos\varphi & -\cos\theta\cos\varphi & \sin\varphi \\ \sin\theta\sin\varphi & -\cos\theta\sin\varphi & -\cos\varphi \end{bmatrix} \tag{5}$$

where θ is the supplement of the bond angle. For the chains of interest here and in the following paper,[19] all bond pairs may be assigned the same angle $\theta = 68°$ (see above). Hence, serial indexes are not required for the T's. They depend through φ on the rotational state of the particular bond.

As shown previously,[35] the characteristic ratio is given by

$$\langle r^2 \rangle_0 / nl^2 = 1 + (2/Znl^2)[J^T 0 \ldots 0]\left[\prod_{i=1}^{n-1} \mathcal{G}_i\right]\begin{bmatrix} 0 \\ \vdots \\ J \times \mathbf{l} \\ J \end{bmatrix} \tag{6}$$

where $J \times \mathbf{l}$ is the direct product of J with the column vector l,0,0; *i.e.*, for the threefold potential the elements of $J \times \mathbf{l}$ are l,0,0,l,0,0,l,0,0, in column form, and the $\mathcal{G}_i$'s are defined by

$$\mathcal{G}_i = \begin{bmatrix} U & (E_s \times \mathbf{l}^T)(U \times E_3)\|T\| & 0 \\ 0 & (U \times E_3)\|T\| & (E_s \times \mathbf{l})U \\ 0 & 0 & U \end{bmatrix} \tag{7}$$

Here and elsewhere × denotes the direct product, and

$$\|T\| = \begin{bmatrix} T^{(1)} & & & & \\ & T^{(2)} & & & \\ & & \cdot & & \\ & & & \cdot & \\ & & & & T^{(s)} \end{bmatrix} \tag{8}$$

is the pseudo-diagonal matrix formed from the transformation matrices $T^{(1)}, \ldots, T^{(s)}$ for the various rotational states.

The value of the characteristic ratio in the limit $n = \infty$ is easily approached by successively squaring[35,36] the matrix for $i > 2$ dominating the products in eq 6. Some of the calculations reported here were carried out in this manner. For others, the method of Hoeve[37] explicitly derived for infinite chains was used. The essential equation is

$$(\langle r^2 \rangle_0 / nl^2)_\infty = 1 + \{2(X^* \times E_3)\|\mathrm{T}\|[E_{3s} - (U \times E_3)\lambda^{-1}\|T\|]^{-1}(X \times E_3)\}_{11} \tag{9}$$

where X^* is the eigenrow corresponding to the maximum eigenvalue λ of U, and X is the eigencolumn of U for the same eigenvalue. The subscript 11 specifies the 11 element of the matrix within the braces. The two methods, of course, yield identical results, the choice being dictated by convenience. Only the former method is applicable to the finite chains of random sequence treated in the following paper, however.

(35) P. J. Flory and R. L. Jernigan, *J. Chem. Phys.*, **42**, 3509 (1965).
(36) P. J. Flory, *Proc. Natl. Acad. Sci. U. S.*, **51**, 1060 (1964).
(37) C. A. J. Hoeve, *J. Chem. Phys.*, **32**, 888 (1960).

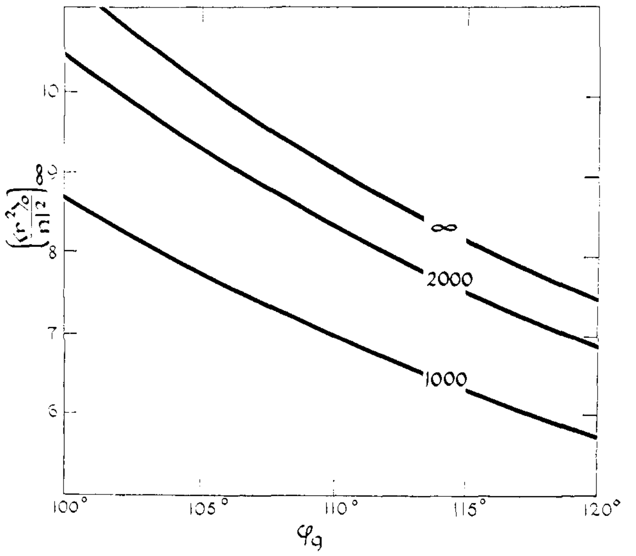


Figure 7. Dependence of the characteristic ratio on the angle $\pm\varphi_g$ for *gauche* rotational states. All calculations were carried out for E_σ = 500 cal mole^{-1}. The value of E_ω in cal mole^{-1} is indicated with each curve.

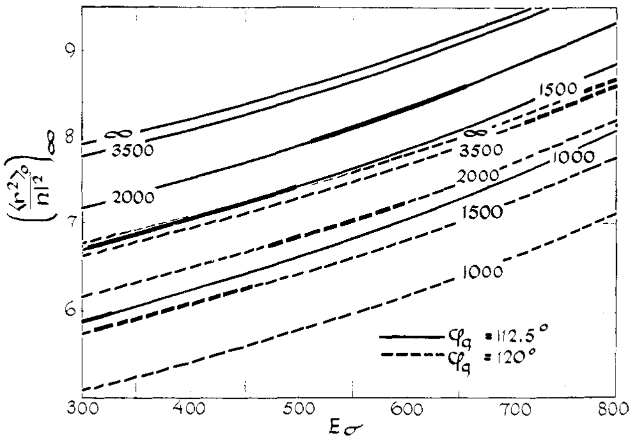


Figure 8. Influence of conformation energies E_σ and E_ω on the characteristic ratio. Values of E_ω are indicated with each curve. Heavy-line portions represent range of E_σ within which d ln $\langle r^2\rangle_0$/dT = -1.15 ($\pm$0.1) $\times$ 10^{-3} in agreement with experiment.

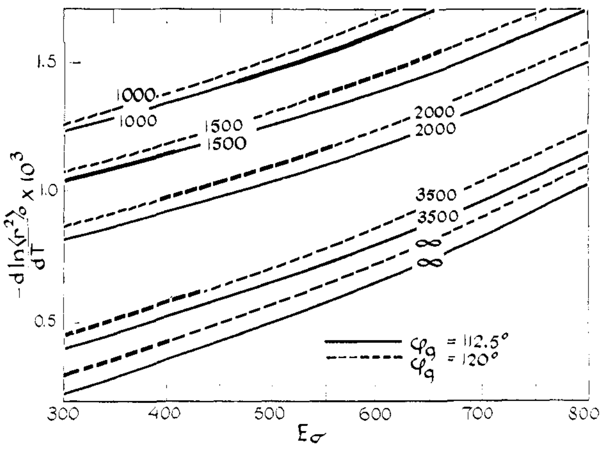


Figure 9. Influence of conformation energies E_σ and E_ω on the temperature coefficient of $\langle r^2\rangle_0$. Values of E_ω are indicated with each curve. Heavy-line portions represent ranges of E_σ within which $(\langle r^2\rangle_0/nl^2)_\infty$ = 6.8 $\pm$ 0.3 in agreement with experiment.

Temperature coefficients of $\langle r^2\rangle_0$ were obtained by varying σ and ω over small ranges about their specified values to ascertain the coefficients ∂ ln $\langle r^2\rangle_0/\partial$ ln σ and ∂ ln $\langle r^2\rangle_0/\partial$ ln ω. On the assumption that σ and ω can be equated to Boltzmann factors for the corresponding energies, the temperature coefficient was calculated from

$$\frac{\mathrm{d}\ln\langle r^2\rangle_0}{\mathrm{d}T} \cong -\frac{1}{T}\left[\ln\sigma\left(\frac{\mathrm{d}\ln\langle r^2\rangle_0}{\mathrm{d}\ln\sigma}\right)_\omega + \ln\omega\left(\frac{\mathrm{d}\ln\langle r^2\rangle_0}{\mathrm{d}\ln\omega}\right)_\sigma\right] \quad (10)$$

Numerical Results. Calculations carried out according to the five-rotational-state scheme yielded values of the characteristic ratio only a little smaller than were obtained using three rotational states with comparable values of the parameters. For example, taking E_σ = 500 cal mole^{-1}, E_{σ^*} = 2000 cal mole^{-1}, and $E_{g^+g_*^-} = E_\sigma + E_{\sigma^*} + E_{\omega^*}$ = 3000 cal mole^{-1}, we have at 140°, σ = 0.54, σ^* = 0.048, and $\sigma\sigma^*\omega^*$ = 0.026, or ω^* = 0.54. These in conjunction with φ_g = 115° and φ_{g^*} = 80° yield $(\langle r^2\rangle_0/nl^2)_\infty$ = 7.4 according to the five-state scheme. Assignment of a corresponding energy, 3000 cal mole^{-1}, to $E_{g^+g^-} = 2E_\sigma + E_\omega$ yields E_ω = 2000 cal mole^{-1} in the three-state scheme. Retaining the same values of φ_g and σ (and hence of E_σ), we find $(\langle r^2\rangle_0/nl^2)_\infty$ = 7.6 at 140°.

This similarity of results was not unanticipated in light of experience gained from computations on other chains. It admits of rationalization as follows. The three-state scheme offers only two $g^\pm g^\mp$ pairs in place of the four pairs $g^\pm g_*^\mp$ and $g_*^\pm g^\mp$ in the more realistic five-state model. On the other hand, the calculated characteristic ratio sustains a greater reduction from g^+g^- pairs at 115, -115° than from $g^+g_*^-$ pairs at 115, -80°, owing to the greater departure of the former from the more extended *tt* and $tg^\pm$ conformations.

The inaccessibility of the $g^\pm g^\mp$ states shown by the energy calculations notwithstanding, use of the simpler three-state scheme as a computational device is fully justified by calculations by the two methods. The value adopted for the energy E_ω may be considered to approximate the difference by which the energy of a $g^+g_*^-$ pair exceeds the energy of two isolated *gauche* bonds (*i.e.*, $2E_\sigma$). As the foregoing comparison indicates, it should be somewhat less than this difference for the reason mentioned, but the discrepancy may amount to only several hundreds of calories per mole, *i.e.*, less than the uncertainty in the energy calculations set forth above. Use of the three-state model was therefore adopted for all succeeding calculations, E_ω being treated as an empirical parameter.

The effect of *gauche* rotation angle φ_g on the characteristic ratio is shown in Figure 7. The dependence is fairly large; the relationship is only slightly curved, and its form is about the same for the different values chosen for the $g^\pm g^\mp$ interaction energy E_ω, given with each curve in Figure 7. The same *gauche* energy, $E_\sigma = -RT\ln\sigma$ = 500 cal mole^{-1}, was used throughout. The temperature chosen for these and the further calculations presented below was 140°, which falls within the range of experimental measurements on polymethylene.[11]

The effects of E_σ on the characteristic ratio and on its temperature coefficient are shown in Figures 8 and 9, respectively. Dashed lines have been calculated for $\varphi_g = \pm 120°$, and solid lines for $\pm 112.5°$, the value indicated by the energy calculations. Values of E_ω are shown with each curve. Heavy-line portions of the curves in Figure 8 represent ranges of E_σ within which $-(\mathrm{d} \ln \langle r^2\rangle_0/\mathrm{d}T) \times 10^3 = 1.15 \pm 0.1$, in agreement with experiment.[10] Similarly, the heavy-line sections of curves in Figure 9 denote ranges over which the characteristic ratio matches the experimental value, 6.8 ± 0.3.[10,11]

Comparison of Figures 8 and 9 shows the temperature coefficient of $\langle r^2\rangle_0$ to be more sensitive than the magnitude of the characteristic ratio to both E_σ and E_ω (and therefore to both σ and ω). Changes in the rotation angle φ_g have a relatively small effect on the temperature coefficient (Figure 9).

Ranges of the conformational energies E_σ and E_ω affording agreement with experimental values for the characteristic ratio and its temperature coefficient are presented in Table III. The results for $\varphi_g = \pm 120°$ agree with the previous calculations of Hoeve.[6] The more realistic choice of $\pm 112.5°$ for φ_g suggests a value of E_σ less than 500 cal mole^{-1} and probably about 400 cal mole^{-1}. The uncertainty in φ_g, about $\pm 3°$, is alone sufficient to displace the value of E_σ required to match the experimental results for polymethylene by as much as 100 cal mole^{-1}. The experimental value of 500 cal mole^{-1} found for the lower n-alkanes is subject to an error of similar magnitude. The intimation in Table III of a discrepancy with this latter figure is not therefore significant.

Table III. Conformation Energies Consistent with Experimental Value for the Characteristic Ratio for Polymethylene at 140° and with Its Temperature Coefficient

φ_g, deg	Energies, cal mole^{-1} E_σ	E_ω	$E_{g^+g^-} = 2E_\sigma + E_\omega$
120	430–590	1700–1900	2560–3080
112.5	260–450	1300–1600	1820–2500

The range of energy for $E_{g^+g^-}$ found with $\varphi_g = \pm 112.5°$ is 1800 to 2500 cal mole^{-1}. This result compares favorably with the figure of 3100 cal mole^{-1} calculated for the *perturbed* $g^+g_*^-$ minima in Figure 6. The agreement is improved if allowance is made for the adjustment of the energy required to compensate the artificial assignment of this paired state to the unperturbed locations for g^+g^-, *i.e.*, to φ_g, $-\varphi_g$.

Acknowledgment. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Contract No. AF49(638)-1341.

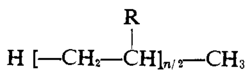
Random-Coil Configurations of Vinyl Polymer Chains. The Influence of Stereoregularity on the Average Dimensions

P. J. Flory, J. E. Mark, and A. Abe

Contribution from the Department of Chemistry, Stanford University, Stanford, California. *Received October 8, 1965*

Abstract: The random-coil configurations of α-olefin polymers $(\text{–CH}_2\text{CHR–})_{n/2}$, where $\mathrm{R = CH_3}$ or $\mathrm{CH_2CH_3}$, etc., are treated in terms of three rotational states for each skeletal bond, the states being weighted as dictated by interactions between CH, $\mathrm{CH_2}$, and R groups separated by three and by four C–C bonds. Interactions between these groups produce systematic displacements of the rotational states from symmetrical positions of 0 and ±120° for *trans* and *gauche* conformations, respectively. The treatment is applied to isotactic, syndiotactic, and atactic chains, with proper account of the configurations of the asymmetric CHR centers in each instance. Characteristic ratios $\langle r^2\rangle_0/nl^2$ calculated for a perfect isotactic chain are much greater than observed by experiment (*ca.* 9 to 10). Also, a large negative temperature coefficient is predicted, contrary to observations. These large discrepancies are not diminished by adoption of a more realistic array of four rotational states for each bond, or by incorporation of refinements suggested by detailed calculations of the conformational energy of 2,4-dimethylpentane as a function of its internal rotation angles. Agreement can be achieved, however, by postulating the presence of *ca.* 5 to 10% of syndiotactic units in isotactic polymers of n-butene-1 and n-pentene-1. The high degrees of crystallinity and narrow melting ranges found for typical isotactic polymers can be reconciled with so large a proportion of heterotactic units only if these units are incorporated in the crystalline phase as imperfections. Effects on the crystalline structure are discussed. Positive temperature coefficients found for the corresponding atactic polymers are attributable to steric interactions of the β-$\mathrm{CH_2}$ of R when the adjoining skeletal bonds of the chain are both *trans*.

In this paper we treat the random-coil configurations of vinyl polymers with emphasis on isotactic chains



$$\mathrm{H\,[-CH_2-\overset{\displaystyle R}{\overset{|}{C}}H]_{n/2}-CH_3}$$

in which all, or most, of the asymmetric -CHR- groups have the same configuration as their immediate neighbors in the chain.[1] The presence on alternate skeletal carbon atoms of the substituent R (where for example $\mathrm{R = CH_3}$ or $\mathrm{C_2H_5}$) proliferates steric inter-

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[1] See P. J. Flory, J. E. Mark, and A. Abe, *J. Polymer Sci.*, B3, 973 (1965), for a preliminary report.