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Self-Consistent Field Conformational Energy Calculations for *n*-Alkanes and Characterizations of Polymethylene

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ABSTRACT: Self-consistent field molecular orbital (SCF–MO) methods have been used to determine the energies of *n*-butane and *n*-pentane in various conformations. Complete geometry optimization was employed to obtain the best minimum energy at the trans and various gauche conformations. The values of E_σ and E_ω thus obtained were 1191 and 1930 cal/mol, respectively. The position and magnitude of the rotational potential barrier were found to be $\phi_2 = 60°$ and 3.7 kcal/mol, respectively. The latter is to be compared with the experimental value of 3.3–3.7 kcal/mol. E_σ and E_ω at 140 °C were used in calculating the rotational isomeric state (RIS) statistical parameters $\sigma = 0.23$ and $\omega = 0.095$. The principal advantage of using SCF–MO ab initio methods to calculate the conformational energies is that no arbitrary parameters are required, as are required in semiempirical works.

I. Introduction

For many years, the statistical parameters used for *n*-alkanes and higher homologues have been calculated with semiempirical expressions[1-5] for the energy. In general, the energy has been considered to consist of three parts: (i) intrinsic torsional potentials, (ii) van der Waals repulsions between nonbonded atoms and groups, and (iii) dispersion attractions between nonbonded atoms. The torsional term is considered to be dependent upon the dihedral angles of internal rotation and on the choice of the fixed valence angles and is represented by an expression[4-7] of the form $^1/_2E_0(1 - \cos 3\phi)$, where E_0 is the height of the potential barrier against internal rotation and ϕ is the angle through which a rotation is made about any particular bond. The nonbonded interactions (ii) and (iii) are expressed as a Lennard-Jones 6–12 potential function of the form[3]

$$\sum_{k<l}(a_{kl}/r_{kl}^{12} - c_{kl}/r_{kl}^{6})$$

Flory and others[4,8] have also used a Buckingham potential where the repulsive r^{-12} part is replaced by an exponential term and is expressed as

$$\sum_{k<l}[a_{kl}\exp(-b_{kl}r_{kl}) - c_{kl}/r_{kl}^{6}]$$

In these expressions, r_{kl} is the internuclear distance between atoms k and l for a given conformation and a_{kl}, b_{kl}, and c_{kl} are constants independent of r_{kl}. The van der Waals constant, c_{kl}, can usually be obtained from many theoretical sources very accurately. One source used frequently is values calculated from the Slater–Kirkwood equation.[1] From these, one obtains the expression for the intramolecular energy[2-4,9] associated with a rotation through ϕ_i about the ith bond as

$$E(\phi_i) = \tfrac{1}{2}E_0(1 - \cos 3\phi_i) + \sum_{k<l}(a_{kl}/r_{kl}^{12} - c_{kl}/r_{kl}^{6}) \qquad (1)$$

or in an equivalent form using the Buckingham potential. While using these expressions, one adjusts the parameters a_{kl} and b_{kl} arbitrarily[4] so as to reproduce the observed energy difference between the gauche and trans conformations of the molecule under study. The calculated energies are then used to calculate statistical parameters incorporated into the rotational isomeric state (RIS) theory.[10-13]

Briefly, the rotational isomeric state theory states that the total conformational energy for a chain molecule can

be resolved into a finite number of conformational energy states which depend chiefly upon consecutive pairs of bond rotations. The number of energy states depends on the atoms on either side of the bonds, but for a tetrahedrally bonded carbon, the number of rotational states is three. The energy of the minimum energy state is usually assigned a value of zero and the remaining energy states are calculated relative to this value. These energy values therefore yield a value of 1 for the statistical weight element of the lowest energy state and values less than 1 for higher energy states.[12-14] The statistical weight element is obtained from the well-known expression $\exp(-E/RT)$.

For approximately the past 10 years, quantum mechanical self-consistent field (SCF) ab initio calculations have made great advances. Now computer programs[15,16] are available which can calculate the energy of a molecule in a given conformation with great accuracy in a totally ab initio manner for most reasonably sized molecules.[17,18] Therefore we have been encouraged to recalculate the energies of some *n*-alkanes in various conformations in this manner. Since these programs are based upon Roothaan–Hartree–Fock self-consistent field theory,[19] they do not need any arbitrary parameters and yield ab initio results, the accuracy of which can be made quite high. We have used these energies and RIS theory to recalculate various statistical parameters, characteristic ratio, and temperature coefficient of an infinitely long polymethylene chain. We have then compared these results with experimental values and also with numbers available from calculations performed with energies obtained with the more traditional semiempirical methods already described.

II. Method of SCF Calculation

In this section we discuss very briefly various aspects of the SCF molecular orbital theory, since more details can be easily found elsewhere.[20]

For a molecule in any particular conformation one writes down the electronic Hamiltonian after the Born–Oppenheimer approximation as

$$\mathcal{H} = \frac{-h^2}{8\pi^2 m}\sum_p \nabla_p^2 - \sum_A\sum_p e^2 Z_A r_{Ap}^{-1} + \sum_{p<q}\sum e^2 r_{pq}^{-1} \quad (2)$$

where h, e, and m have their usual meanings, Z_A is the nuclear charge of atom A, r_{Ap} is the distance of the pth electron from the nucleus of atom A, and r_{pq} is the distance between electrons p and q. The summation A covers all atoms, and p and q go over all electronic indices. The total energy of the system is obtained as a sum of the electronic energy and the nuclear repulsion energy. The electronic energy is the expectation value $\langle\Psi|\mathcal{H}|\Psi\rangle$, where Ψ is the wave function for the system obtained from the solution of the time-independent Schrödinger equation.

For a closed-shell system with $2n$ electrons, one can write Ψ in the form

$$\Psi = N\sum_p (-1)^p P\{\psi_1(1)\alpha(1)\psi_1(2)\ldots\psi_n(2n)\beta(2n)\} \quad (3)$$

where N is the normalizing factor. The ψ_i's are molecular orbitals. The numbers within the parentheses indicate the electron for which the orbital is being assigned. P is a permutation of the electron numbers and $(-1)^p$ is ± 1, depending on even or odd permutations. α and β represent the spin of the electron involved. This compact representation for the total wave function Ψ handles all the physical aspects involved, within the Born–Oppenheimer approximation.

Now the Hamiltonian can be separated into one- and two-electron parts. In terms of atomic units we have

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 \quad (4)$$

where

$$\mathcal{H}_1 = \sum_p H^{\text{core}}(p) \qquad \mathcal{H}_2 = \sum_{p<q}\sum r_{pq}^{-1} \quad (5)$$

with

$$H^{\text{core}}(p) = -\tfrac{1}{2}\nabla_p^2 - \sum_A Z_A r_{pA}^{-1} \quad (6)$$

The quantity H^{core} is the one-electron Hamiltonian corresponding to the motion of an electron in the field of the bare nuclei. Then we get the total electronic energy as

$$\mathcal{E} = 2\sum_i^n H_{ii} + \sum_i^n\sum_j^n (2J_{ij} - K_{ij}) \quad (7)$$

where

$$H_{ii} = \int \psi_i^*(1) H^{\text{core}} \psi_i(1)\, d\tau_1 \quad (8)$$

$$J_{ij} = \int\int \psi_i^*(1)\psi_j^*(2)\frac{1}{r_{12}}\psi_i(1)\psi_j(2)\, d\tau_1\, d\tau_2 \quad (9)$$

$$K_{ij} = \int\int \psi_i^*(1)\psi_j^*(2)\frac{1}{r_{12}}\psi_j(1)\psi_i(2)\, d\tau_1\, d\tau_2 \quad (10)$$

J_{ij} and K_{ij} are known as Coulomb and exchange integrals, respectively. K_{ij} is nonzero only if the electrons i and j have similar spin.

The best value of Ψ is the one that gives the lowest value of $\mathcal{E}$ for that particular configuration of the molecule. Therefore, one can use a variational principle in eq 7 and can adjust the molecular orbitals till $\mathcal{E}$ is minimized. Since Ψ has to be known to get the solution of the Schrödinger equation, which, in turn, yields eigenfunctions leading to Ψ again, one can use this property to get a set of self-consistent, or Hartree–Fock, molecular orbitals.

In actual practice, one represents a molecular orbital as a linear combination of atomic orbitals (LCAO)

$$\psi_i = \sum_\mu C_{\mu i}\phi_\mu \quad (11)$$

where ϕ_μ, the atomic orbitals, have been obtained by a separate Hartree–Fock procedure. The properties of orthonormality imply that

$$\sum_{\mu\nu} C_{\mu i}^* C_{\nu j} S_{\mu\nu} = \delta_{ij} \quad (12)$$

where

$$S_{\mu\nu} = \int \phi_\mu(1)\phi_\nu(1)\, d\tau_1 \quad (13)$$

The density matrix is defined as

$$P_{\mu\nu} = 2\sum_i^{\text{occ}} C_{\mu i}^* C_{\nu i} \quad (14)$$

where the summation goes over the occupied orbitals of the closed-shell system. Finally, eq 7 reduces to

$$\mathcal{E} = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} + \tfrac{1}{2}\sum_{\mu\nu\lambda\sigma} P_{\mu\nu}P_{\lambda\sigma}[(\mu\nu|\lambda\sigma) - \tfrac{1}{2}(\mu\lambda|\nu\sigma)] \quad (15)$$

where

$$H_{\mu\nu} = \int \phi_\mu^*(1) H^{\text{core}} \phi_\nu(1)\, d\tau_1 \quad (16)$$

Table I
Potential Barriers to Internal Rotations (kcal/mol)

molecule	barrier height		
	semiempirical[a]	present work	observed[b]
n-butane (g^+)	3.6	3.73	3.6 ± 0.2
n-pentane (tg^+)	3.6	3.75	

[a] Reference 4. [b] Reference 20.

and

$$(\mu\nu|\lambda\sigma) = \int\int \phi_\mu^*(1)\phi_\nu^*(1)\frac{1}{r_{12}}\phi_\lambda(2)\phi_\sigma(2)\, d\tau_1\, d\tau_2 \qquad (17)$$

Now the variational principle can be used to minimize the energy; then one ends up with the equations

$$\sum_\nu (F_{\mu\nu} - \epsilon_i S_{\mu\nu})C_{\nu i} = 0 \qquad (18)$$

where

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}[(\mu\nu|\lambda\sigma) - \tfrac{1}{2}(\mu\lambda|\nu\sigma)] \qquad (19)$$

Equation 18 was first set forth by Roothaan[19] and is known as a Roothaan equation. The set of equations (18) for the coefficients $C_{\nu i}$ are to be solved self-consistently to get the final eigenfunctions and the energy.

The SCF procedure involves a choice of atomic orbitals from which the density matrices are calculated by using some arbitrary value of $C_{\nu i}$. Then one solves eq 18 to get the new values of $C_{\nu i}$, which, in turn, are used in (18) again to get further new values of $C_{\nu i}$. This is repeated till the values of $C_{\nu i}$ are self-consistent, i.e., till the final set of $C_{\nu i}$ used as input give the same set of $C_{\nu i}$ (or very close to it) as output. This is known as the Roothaan–Hartree–Fock procedure.

In our work we have used both GAUSSIAN 70 and GAUSSIAN 76 computer programs,[15,16] which go through the above-mentioned procedure self-consistently. Both use a combination of Gaussian functions as the input atomic functions. The only other input is the geometry of the molecule in a particular configuration. The program then finds the best energy for that situation.

Usually there are several choices for the input atomic wave functions. We have used STO-3G type functions for most of our calculations. However, as a test we have also used the split-valence 4-31G and 6-31G wave functions. After a comparison of the results we have chosen the best energies and have presented them in this paper. More discussions on the energy are given in later sections.

As a final step we have also used extra polarization functions (p orbitals with hydrogen atoms and d orbitals with carbon atoms) to ensure further flexibility. This, however, did little to improve the energies.

III. Results

A. Calculation of Statistical Parameters. In the calculation of the statistical mechanical parameters for n-butane and, later, n-pentane, the most important numbers calculated are the relative energies of the various "stable" conformations. There are two drawbacks, however, to the manner in which these energies have been calculated earlier. First, the procedure for partitioning of the total potential energy into a series of components involves necessarily an element of arbitrariness. Second, the fundamental formulas and parameters used to define the various components are chosen in many cases quite arbitrarily and differ appreciably from one author to another.[17] The advantage of calculations carried out with ab initio methods is that it suffers from none of the above-mentioned drawbacks. Once the molecule and its geometry are specified, there are no additional parameters or partitioning necessary.

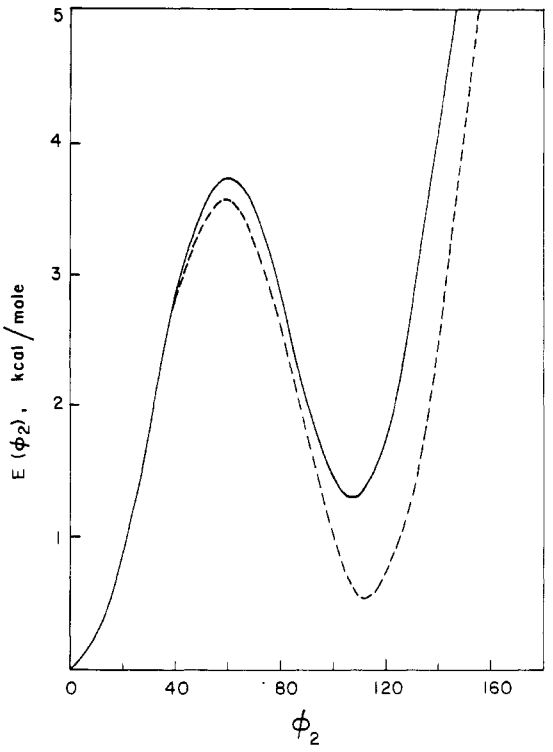

Figure 1. Plot of conformational energy of butane vs. the angle of rotation ϕ_2. The solid line is from present work. The dashed curve represents results from semiempirical calculations.[4,13]

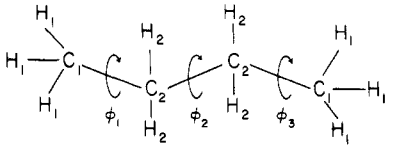

Figure 2. Representative structure of butane molecule labeled in accordance with Table II.

The strengths of various features of our calculations can best be seen by referring to Table I and Figure 1, where the energies obtained from our ab initio work have been compared with those from semiempirical works. The representative structure for a butane molecule is given in Figure 2. The possible internal rotations about the three C–C bonds are represented by angles ϕ_1, ϕ_2, and ϕ_3. For n-butane the trans state (t) is when $\phi_1 = \phi_2 = \phi_3 = 0$. For gauche states g^+ or g^-, the angle ϕ_2 is increased in a positive or negative direction, respectively, until a potential minimum is obtained. As observed in Figure 1, our calculation automatically produces a threefold rotational potential for rotations through ϕ_2. This matches almost exactly with the semiempirical work, where the threefold rotational potential was assumed and then introduced into the calculations. In our case, no such assumption was made. The positions of the barrier maximum, the $g^\pm$ minima, and the value of the barrier height have also been approximately reproduced by our calculations.

Further strength of our calculation lies in our choice of the model for the molecule. In calculations using semiempirical methods[3,4,13] the atoms of the molecule are

Table II
Geometrical Parameters for *n*-Butane and *n*-Pentane[a]

	bond lengths, A				bond angles, deg					
					n-butane[b]			*n*-pentane[c]		
conformation	H_1-C_1	C_1-C_2	C_2-C_2	C_2-H_2	H_1-C_1-C_2	C_1-C_2-C_2	H_2-C_2-C_2	H_1-C_1-C_2	C_1-C_2-C_2	H_2-C_2-C_2
trans	1.096	1.537	1.537	1.073	109.9514	111.8228	109.6536	109.9464	111.7910	109.7571
gauche ($\phi_2 = \pm 107.6°$) ($\phi_3 = \pm 107.6°$)[c]	1.096	1.537	1.537	1.073	109.8616	112.0150	109.6749	109.8155	112.6231	109.6517

[a] Bond angles and lengths[20] used in the present calculations for butane and pentane. The bond angles and gauche rotational angles were determined by complete SCF optimization procedure. [b] Refer to Figure 2 for geometry of butane. [c] Refer to Figure 3 for geometry of pentane.

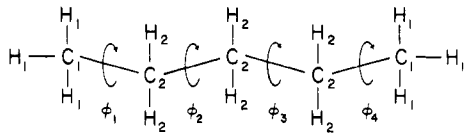

Figure 3. Representative structure of pentane molecule labeled in accordance with Table II.

chosen as hard spheres with a radius equal to their van der Waals radii plus 0.1 Å.[8] The bonds are fixed at a given bond angle and are maintained at that angle for all conformations. In our case the geometry of the molecule has been optimized at each conformation. We have chosen the best bond lengths[21] available from experiment and then allowed the bond angles to "flex" to get the best energy. The resultant geometry is represented in Table II. It is easily noticed that the C–C–C angles have changed appreciably from the rigid tetrahedral values. The necessity of such flexibility to ensure the best energies has been pointed out before by Pople[18] and others.[17]

Another interesting feature of our ab initio calculation is the position of the $g^{\pm}$ minimum. In the semiempirical work the value of $\phi_2 = 112.5°$ has been used. To minimize the $g^{\pm}$ energy further, the value of $\phi_1 = \phi_3 = 4°$ has been used as an afterthought.[4] In our work no necessity for the rotation of the end methyl groups was observed. On the contrary, introduction of such rotation actually increased the energy. We believe that since, in our case, the bonds have been allowed to flex freely, no additional rotations are required to reduce the energy. It is interesting to note that our value for $\phi_2 = 107.6°$ differs from the semiempirical value[4] of 112.5° by an amount which was introduced in their case later as end rotation.

The value for E_σ, the energy of the $g^{\pm}$ conformation relative to the trans conformation, was obtained by Flory et al.[4] as 530 cal/mol. In our case, when we kept the geometry of the molecule rigidly fixed, we obtained for E_σ a value of 1400 cal/mol. However, after introducing the flexibility through the optimization of geometry and after using a good 4-31G set of basis functions, we obtained E_σ as 1191 cal/mol. There are two experimental numbers for E_σ that have been widely quoted; 500 (±70) and 800 (±100) cal/mol. The former value was found as the mean value obtained by application of Raman spectroscopy on *n*-pentane[22,23] and *n*-hexane.[22] The second value was found from the temperature coefficients of Raman intensities for liquid *n*-butane.[24] More recent work[25] has obtained a value of 966 ± 54 cal/mol for gaseous *n*-butane. A quick comparison of the theoretical values with the experimental value of 800 ± 100 cal/mol shows that both the semiempirical value of 530 cal/mol and the ab initio value of 1191 cal/mol are off by a similar percentage. However, the ab initio value is on the higher side and, therefore, will approach the experimental value when correlation corrections are incorporated. On the other hand, correlation will decrease the semiempirical value of E_σ and will increase the error as a consequence. Further comments regarding these points will be discussed later.

Table III
Energies for Different Conformations of Pentane (cal/mol)[a]

	i		
$i-1$	t	g^+	g^-
t	(0, 0) 0	(0, 107.6) 1191	(0, −107.6) 1191
g^+	(107.6, 0) 1191	(107.6, 107.6) 2443	(113, −73) 4312
g^-	(−107.6, 0) 1191	(73, −113) 4312	(−107.6, −107.6) 2443

[a] The numbers within the parentheses indicate the values (deg) of the angles ϕ_2 and ϕ_3, respectively. The energies have been given relative to the $\phi_2 = \phi_3 = 0.0°$ conformation. i and $i-1$ refer to rotations ϕ_3 and ϕ_2, respectively.

Calculations similar to those performed on *n*-butane were also performed on *n*-pentane. In this case, Figure 3 shows the representative model of the molecule. There are two C–C bonds now connecting the end methyl groups. Therefore, there exists the possibility that simultaneous rotation of ϕ_2 and ϕ_3 creates many more "stable" states than those present in the case of *n*-butane. For nomenclature, the rotations about the $(i-1)$th and ith bond are given as ϕ_2 and ϕ_3, respectively. Table III summarizes the results of our SCF calculations, giving the possible minima for different combinations of ϕ_2 and ϕ_3. As usual, the energies are given with respect to the tt state ($\phi_2 = 0$, $\phi_3 = 0$). It has been observed in the case of the semiempirical calculations that the tg^+ and tg^- states and their equivalent g^+t and g^-t conformations are the same as the $g^{\pm}$ of *n*-butane. Hence, this case will not be discussed further.

The next higher minima occur at the conformations g^+g^+ and its analogue g^-g^-. These conformations occur at $\phi_2 = 107.6°$ and $\phi_3 = 107.6°$ for the conformation g^+g^+ and conversely for g^-g^-. The energy is calculated to be 2443 cal/mol. Semiempirical calculations yield $\phi_2 = \phi_3 = 110°$ and an energy of 1180 cal/mol. It should be noted that both energies are approximately $2E_\sigma$, where E_σ for the ab initio calculations is 1191 cal/mol and E_σ from semiempirical calculations is 530 cal/mol.

As with semiempirical calculations, SCF ab initio calculations give two additional minima at the conformations $g^{\pm}g^{\mp}$. From semiempirical calculations, their minima occur at $\phi_2 = 115°$ and $\phi_3 = -77°$ and at $\phi_2 = 77°$ and $\phi_3 = -115°$ for g^+g^- and g^-g^+, respectively.[4] The energy is calculated to be 3200 cal/mol. Ab initio calculations yield values for g^+g^- of $\phi_2 = 72.8°$ and $\phi_3 = -113.3°$ and conversely for g^-g^+. The ab initio energy is found to be 4312 cal/mol. These

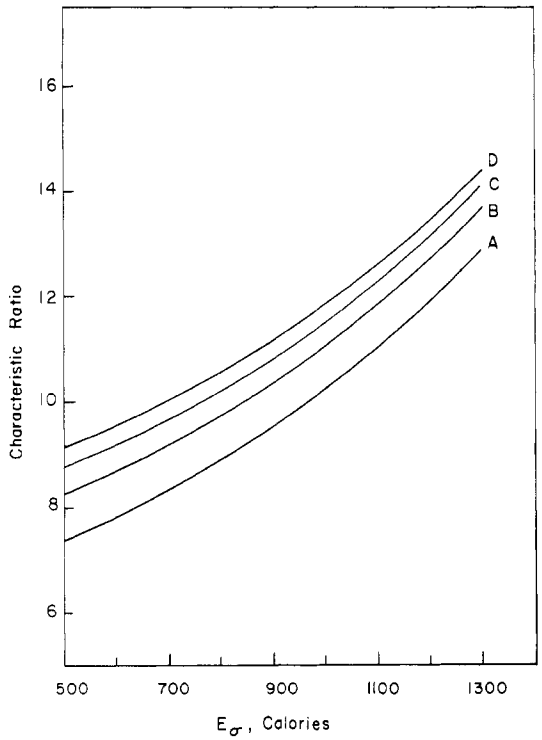

Figure 4. Dependence of characteristic ratio $(\langle r^2\rangle_0/nl^2)_\infty$ upon E_σ and E_ω. Curves A–D represent values of E_ω = 1000, 1500, 1930, and 2500 cal/mol, respectively. The results presented are for T = 140 °C.

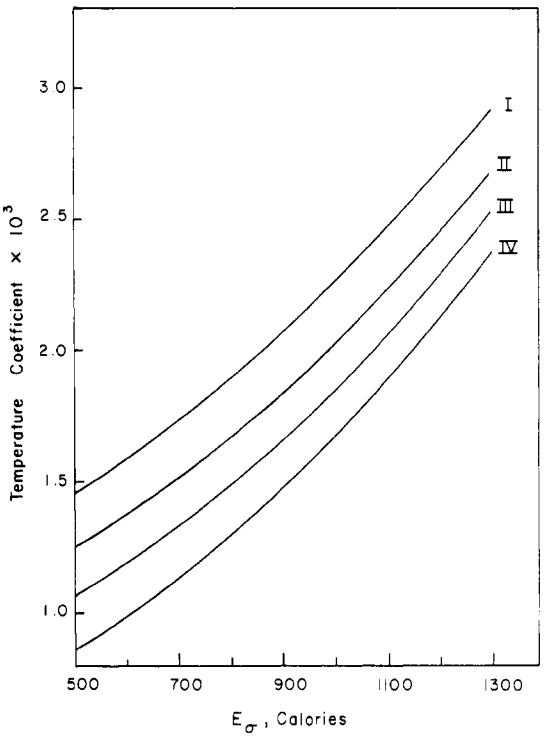

Figure 5. Dependence of the temperature coefficient $-10^3(\mathrm{d}\ \ln \langle r^2\rangle_0/\mathrm{d}T)$ upon E_σ and E_ω. Curves I–IV are for values of E_ω = 1000, 1500, 1930, and 2500 cal/mol, respectively.

two energies yield a value for E_ω of 2140 and 1930 cal/mol from semiempirical and ab initio methods, respectively, where $E_\omega = E_{g^+g^-} - 2E_\sigma$. The ab initio value of E_σ = 1191 cal/mol is the best value calculated with the 4-31G basis set, as explained in the SCF calculation section of this paper. It should be noted that for all practical purposes, the two numbers for E_ω are the same. A summary of numerical results can be found in Table III.

Finally, it should be noted that both methods obtain saddle points in the conformational energy map. Semiempirical methods give their positions at $\phi_2 = -\phi_3 = 95°$; $\phi_1 = -\phi_4 = 11°$. Ab initio methods yield the values of $\phi_2 = 95°$; $\phi_3 = -95°$; $\phi_1 = \phi_4 = 0°$. Semiempirical and ab initio methods yield energies of 4100 and 5500 cal/mol, respectively. At these very high values, these energies play virtually no role in calculations of mean statistical properties.

B. Calculation of the Characteristic Ratio and Temperature Coefficient for an Infinite Polymethylene Chain. As derived by Hoeve[26] and modified by Flory[13] the equation to calculate the characteristic ratio of an infinitely long molecule is

$$(\langle r^2\rangle_0/nl^2)_\infty = [(\mathbf{B}_1^* \otimes \mathbf{E}_3)(\mathbf{E}_{3\nu} + \mathbf{S})(\mathbf{E}_{3\nu} - \mathbf{S})^{-1} \times (\mathbf{A}_1 \otimes \mathbf{E}_3)]_{11} \quad (20)$$

where $\langle r^2\rangle_0$ is the mean-square end-to-end distance of an unperturbed chain, l is the bond length, and n is the number of bonds; $\mathbf{B}_1^*$ and $\mathbf{A}_1$ are the mutually normalized eigenrow and eigencolumn of $\mathbf{U}$ (see ref 12, p 109), $\mathbf{E}_3$ and $\mathbf{E}_{3\nu}$ are identity matrices of 3 and 3ν dimensions, respectively, and $\mathbf{S}$ is defined as

$$\mathbf{S} = (\mathbf{U} \otimes \mathbf{E}_3)||\mathbf{T}||/\lambda_1 \quad (21)$$

where $||\mathbf{T}||$ is a pseudodiagonal matrix of order $3\nu \times 3\nu$ obtained by placing the $\mathbf{T}$ matrix for various rotational states of bond i in diagonal array. The $\mathbf{T}$ matrix is defined as the orthogonal transformation matrix given by the expression

$$\mathbf{T} = \begin{bmatrix} \cos\theta_i & \sin\theta_i & 0 \\ \sin\theta_i\cos\phi_i & -\cos\theta_i\cos\phi_i & \sin\phi_i \\ \sin\theta_i\sin\phi_i & -\cos\theta_i\sin\phi_i & -\cos\phi_i \end{bmatrix} \quad (22)$$

where θ_i and ϕ_i are the bond angle and dihedral angle, respectively. The subscript 11 specifies the 1,1 element of the matrix within the brackets.

Results of the calculations for an infinitely long polymethylene chain are presented in Figures 4 and 5. The characteristic ratio is calculated as a function of E_σ for values of E_ω equal to 1000, 1500, 1930, and 2500 cal/mol, respectively. The ranges of values for E_σ and E_ω are chosen to overlap the most frequently used values for E_σ and E_ω obtained by semiempirical methods and to overlap the values obtained by this work.

The experimental numbers most quoted for the characteristic ratio of polymethylene are 6.7, 6.8, and 6.6.[27] As can be seen from Figure 4, the value of E_σ which gives the closest value to the average experimental number of 6.7 is E_σ = 500 cal/mol. However, this is with a value of E_ω = 1000 cal/mol, which yields a value of $E_{g^+g^-}$ = 2000 cal/mol. This is very much lower than the numbers $E_{g^+g^-}$ = 3200 and $E_{g^+g^-}$ = 4312 cal/mol calculated by semiempirical and ab initio methods, respectively. If the best E_σ and E_ω as calculated from semiempirical methods are used, the characteristic ratio is calculated to be about 8.6. If the best values of E_σ and E_ω from this work are used, the characteristic ratio is calculated to be approximately 12.4. It should be pointed out that our optimized geometry was used in all calculations.

The values of E_σ and E_ω which give the correct value[28] of -1.15×10^{-3} deg^{-1} for the temperature coefficient are

$E_\sigma \cong 600$–720 and $E_\omega \cong 2100$–2500 cal/mol. The values for E_ω calculated by both methods are close to this range. The values for E_σ, however, are both out of the range given but the number calculated by semiempirical methods seems to give closer agreement.

IV. Summary and Discussion

The main thrust of this paper was to demonstrate the feasibility of calculating the conformational energies of molecules by quantum mechanical ab initio methods for use in parameterization of quantities used in rotational isomeric state theory. To this end, we believe this goal has been achieved.

First, it should be noted that the SCF ab initio calculations successfully reproduced the number and position of all energy maxima and minima as calculated by semiempirical methods. For example, both methods predicted an absolute energy minimum at the all-trans configuration, i.e., all $\phi_i = 0°$. Both methods predicted an energy barrier at $\phi_2 \cong 60°$ and the magnitude of this barrier was predicted to be 3.6 and 3.7 kcal/mol for semiempirical vs. ab initio methods, respectively. Both methods calculated a second energy minimum located at $\phi_2 = 112.5°$ and $\phi_2 = 107.6°$ for semiempirical vs. ab initio methods, respectively. An explanation for the small discrepancy was discussed in section IIIA.

In regards to calculations on pentane, both methods yielded additional energy minima at the conformations g^+g^+ and g^-g^-. Again there are discrepancies in the positions of these minima but they are relatively small. RIS theory predicts that the energy calculated for these two conformations should be approximately $2E_\sigma$. When the appropriate E_σ is introduced (see Table III), both methods approximately give this result.

A third set of minima was calculated at the conformations $g^\pm g^\mp$. Again small deviations are present in the position of the minima but are quite small. There is also a difference calculated in the relative magnitude of the energy by the two methods. However, when the appropriate E_σ was used along with the formula for E_ω, $E_\omega = E_{g^+g^-} - (2E_\sigma)$, both methods yielded virtually identical numbers.

The major difference between the two methods was in the values of E_σ. Semiempirical methods gave a value of approximately 500 cal/mol; ab initio calculations yielded $E_\sigma = 1191$ cal/mol. One of the experimental numbers quoted for E_σ is 500 (±70) cal/mol. If this number is correct, then semiempirical calculations yield the correct value quite nicely. It should, however, be pointed out that the parameters used in semiempirical calculations are adjusted so as to reproduce approximately the observed energy differences between gauche and trans conformations for the lower n-alkanes.[4] When this value for E_σ is used to calculate the characteristic ratio $(\langle r^2\rangle_0/nl^2)_\infty$ and temperature coefficient $d \ln \langle r^2\rangle_0/dT$, with the value of $E_\omega = 2140$ cal/mol, semiempirical calculations yield values of about 7.8 and -0.85×10^{-3} deg^{-1}, respectively,[28] which do not match too well with experimental values.

A second much-quoted experimental number for E_σ is ~800 (±100) cal/mol. It was determined by Abe, Jernigan, and Flory[4] that the experimental temperature coefficient equal to -1.15 (±0.1) $\times 10^{-3}$ deg^{-1} was matched approximately by taking 800 cal/mol for E_σ. However, the characteristic ratio was calculated to be about 9.2 as compared to the experimental value 6.8 ± 0.3 at 140 °C.[26,29]

The experimental number, however, which is probably the most appropriate to compare with is the value 966 ± 54 cal/mol found by Verma et al.[25] for gaseous n-butane. In most calculations using semiempirical methods, both long-range interactions and intermolecular interactions are considered null, or at least constant.[12] When measurements are made on random coil polymers, they are normally conducted in Θ solvents under Θ conditions, or at least corrections are made to the Θ point,[14,26,27] where it is assumed that long-range effects vanish. In some very recent work,[31,32,33] however, there was shown to be some possible solvent dependence of ΔE_{tg^+} for n-butane. The values obtained range from ~440 to ~540 cal/mol for butane in different solvents. A third number of 550 cal/mol was quoted for pure liquid n-butane. It therefore appears that when a comparison is made between these latter numbers and the value obtained for gaseous n-butane, intermolecular interactions can be considered a probable contributing factor to the value of ΔE. Since both calculation methods restrict themselves to only intramolecular energy interactions, it would appear that the experimental value obtained for n-butane gas, where intermolecular interactions would be at a minimum, is more appropriate for comparison purposes.

If the latter experimental number of 966 cal/mol is found to be appropriate for the energy, the SCF ab initio number for $E_\sigma = 1191$ cal/mol is approximately 200 cal/mol in excess. Since it was previously stated that this energy was the lowest value obtainable, after total optimization, one may inquire whether further minimization of this energy is possible. It has been determined that relative energies calculated by the Hartree–Fock method could be too high by several percent. In Hartree–Fock SCF wave functions, interactions between electrons are only considered in an average way. However, the effect of electron correlation, that is, the instantaneous interactions between electrons, should also be considered. Current ab initio programs (GAUSSIAN 70 and GAUSSIAN 76) do not take this correlation energy into account. There are, however, techniques available to incorporate correlation effects into the ab initio programs, which, if successful, could lead to further reduction of the energy. Such attempts are currently being pursued by us, and results will be published in the future.

Finally, it should be pointed out that even when the best energies calculated by either semiempirical or ab initio methods are used, the values obtained for the temperature coefficient, and especially the characteristic ratio, leave much to be desired. Flory[29] has calculated, for example, that in order to obtain good agreement between calculated and experimental numbers for the characteristic ratio, E_σ must be in the range 260–450 cal/mol and $E_\omega = 1300$–1600 cal/mol. These numbers are much lower than either method of calculation obtains. There are reasons to believe that modifications in the manner in which the statistical weight elements are calculated may produce closer agreement. Such methods are under investigation and future publications will deal with them.

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