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Persistence of Directional Correlation between the Terminal Bond Vectors of α,ω-Dihalo-n-alkanes and α,ω-Dihydroperfluoro-n-alkanes†

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ABSTRACT: The dipole moments of α,ω-dihaloalkanes such as $Br(CH_2)_nBr$ and $Cl(CH_2)_nCl$ have been analyzed within the framework of the rotational isomeric state scheme. Similar studies have been extended to include α,ω-dihydroperfluoroalkanes, $H(CF_2)_nH$. Parameters required for the analysis have been mostly taken from the previous studies by Leonard et al. and Bates et al. Spatial orientations of the ω-terminal bond have been elucidated in a Cartesian coordinate system fixed to the α-bond. The angle θ defined by the two terminal bond vectors has been evaluated for each conformation of the backbone chain. Based on the integrated distribution curves of θ thus derived, the characteristic dipole moment ratios $\langle\mu^2\rangle/2m^2 = 1 - \langle\cos\theta\rangle$ (μ is the molecular dipole moment and m represents the dipole moment associated with the terminal bond) and other averages such as $\langle\theta\rangle$ and $\langle\cos^2\theta\rangle$ have been evaluated. It has been concluded that the observed attenuation of the odd–even oscillation in the dipole moment with n is largely due to a proper balance of contributions between highly polar and less polar conformations. The directional correlation between the terminal bond vectors should be far from random in the range $n \leq 10$.

Introduction

Molecular dipole moments of n-alkane chains carrying dipolar substituents at the terminals, $X(CH_2)_nX$, have been known to exhibit an odd–even oscillation when plotted against the number of intervening methylene units.[1,2] Hayman and Eliezer[2] have determined the dipole moments of α,ω-dibromoalkanes ($X = Br$) with $n = 3$–10 in benzene and showed that two curves drawn separately for the n = odd and n = even series merge rapidly with each other, the difference being marginal beyond $n = 8$. Leonard, Jernigan, and Flory[3] carried out the rotational isomeric state analysis on this system by using the neighbor-dependent rotational potentials. Except for lower chain lengths, experimental observations are reasonably well reproduced by the calculation. The odd–even effect observed for the dipole moment is, therefore, a phenomenon associated with the characteristics of the intervening hydrocarbon sequences. Similar studies have been reported on the dielectric properties of α,ω-dichloroalkanes ($X = Cl$, $n = 2$–10) in n-hexane by Dahl and Muller.[4]

Bates and Stockmayer[5] studied the dipole moments of α,ω-dihydroperfluoroalkanes, $H(CF_2)_nH$, with $n = 4$–10 in benzene in an attempt to establish the rotational isomeric state scheme applicable to the perfluoroalkane chains.[6] Theoretical calculations of the dipole moment were carried out by assigning an effective dipole moment to the terminal C–H bonds.[5] An analogy to the aforementioned α,ω-dihaloalkane systems should be apparent.

In all the examples given above, bond dipoles are defined along the direction of the terminal bonds: i.e., the bond dipole may be regarded as an equivalent of the terminal bond vectors. Molecular dipole moments of dialkyl esters of dicarboxylic acids, $ROOC(CH_2)_nCOOR$ (R = methyl or ethyl), are also known to vary sensitively with the parity of n.[1,7,8] According to the assessment of Saiz et al.,[9] the dipole moment associated with the ester group is tilted by ca. 123° with regard to the C(carbonyl)–C bond, thus being situated nearly antiparallel to the carbonyl group. The odd–even oscillation of the dipole moments for these dicarboxylates becomes obscure at somewhat shorter chain lengths.[8] In the present analysis, we especially consider the α,ω-dihaloalkane and α,ω-dihydroperfluoroalkane systems, for which the odd–even alteration of the molecular dipole moment is well ascertained.

Given in Figure 1 is a schematic representation of the molecules under consideration. The angle defined by the two terminal dipoles (or terminal bond vectors), $\mathbf{m}_\alpha$ and $\mathbf{m}_\omega$, is indicated by θ. Thus

$$\mathbf{m}_\alpha \cdot \mathbf{m}_\omega = -m^2 \cos\theta \qquad (1)$$

where m is the magnitude of the bond dipole moment associated with the terminal bond. The average of the square of the molecular dipole moment μ may be given by

$$\langle\mu^2\rangle = 2m^2 + 2\langle\mathbf{m}_\alpha \cdot \mathbf{m}_\omega\rangle = 2m^2(1 - \langle\cos\theta\rangle) \qquad (2)$$

where the angular brackets denote a statistical mechanical average taken over the entire conformational space. The expression may be reduced to a more generalized form:

$$\langle\mu^2\rangle/2m^2 = 1 - \langle\cos\theta\rangle \qquad (3)$$

For a freely jointed chain, $\langle\cos\theta\rangle = 0$. For a freely rotating chain with a fixed bond angle $\pi - \tau$, we have $\langle\cos\theta\rangle = \cos^n\tau$. If the bond angle is taken to be tetrahedral, $\cos\tau = {}^1/_3$, and thus

$$\langle\mu^2\rangle/2m^2 = 1 - (1/3)^n \qquad (4)$$

Equation 4 is also applicable to chains with restricted rotations, provided that the rotational potentials are symmetric and neighbor independent.

In Figure 2, experimental values of the characteristic dipole moment ratio $\langle\mu^2\rangle/2m^2$ are plotted as a function of the chain length n for the aforementioned series of molecules,[2,4,5] where values of m were taken from the dipole moments observed for some relevant model compounds such as $Br(CH_2)_3CH_3$ (1.956 D),[2] $Cl(CH_2)_5CH_3$ (1.99 D),[4] and $H(CF_2)_6CF_3$ (1.60 D).[5] Also included in the figure are the limiting values derived above for the simple model chains. As the directional correlation between the two terminal dipoles diminishes, the ratio $\langle\mu^2\rangle/2m^2$ should approach the value of unity as indicated by solid line 1. The results obtained for the two series of α,ω-dihaloalkanes (open circles for X = Br and filled circles for X = Cl) are nearly identical, indicating that the conformational characteristics are similar for these two homologues. The upper and lower solid curves represent the experimental results for the n = odd and n = even series, respectively. These curves reach only 87% of the limiting value at $n \cong 10$,

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† This paper is dedicated, with great appreciation, to Professor Walter H. Stockmayer on his 70th birthday.

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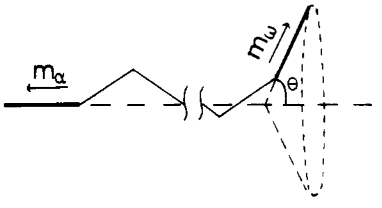


Figure 1.

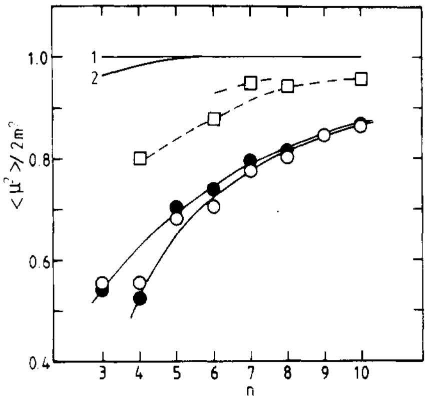


Figure 2. Characteristic dipole moment ratio $\langle\mu^2\rangle/2m^2$ plotted against n. Experimental values are indicated by open circles for $Br(CH_2)_nBr$,[2] by filled circles for $Cl(CH_2)_nCl$,[4] and by open squares for $H(CF_2)_nH$.[5] A pair of solid curves indicate variation of $\langle\mu^2\rangle/2m^2$ for $X(CH_2)_nX$ (X = Br and Cl): the upper curve for n = odd and the lower one for n = even. Dashed curves are used for $H(CF_2)_nH$: the curve drawn for n = odd is tentative. Theoretical curves deduced for some model chains are also included: $\langle\mu^2\rangle/2m^2 = 1$ for the freely jointed chain (line 1) and $\langle\mu^2\rangle/2m^2 = 1 - (1/3)^n$ for the freely rotating chain (curve 2).

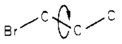
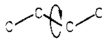
suggesting that the directional correlation between the two terminal dipoles may remain substantial at this chain length. The odd–even oscillation in the molecular dipole moment attenuates more rapidly with n (cf. Figure 2). The characteristic ratios $\langle\mu^2\rangle/2m^2$ for α,ω-dihydroperfluoroalkanes are shown by open squares in Figure 2. Among the five samples studied,[5] $H(CF_2)_7H$ is the only odd member of the series. The dashed curve drawn for n = odd is therefore only tentative. The ratio $\langle\mu^2\rangle/2m^2$ reaches 96% of the limiting value, set for the freely jointed chain, at n = 10. According to the analysis of Bates et al.,[5] however, the gauche–trans energy difference around an internal C–C bond is ca. 1.4 kcal mol^{-1}. In general, the perfluoroalkane chain is considered to be moderately stiff and is incompatible with the free-rotational model.

In this study, we have examined the angular correlation between the two terminal bond vectors for the series of chain molecules given above. The rotational isomeric state analyses have been performed by using the parameters established in the previous studies[3,5] on the dipole moment. The odd–even oscillation effect is discussed based on the exact angular distribution curves thus derived.

Procedure of Calculation

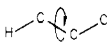
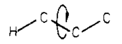
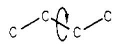
Calculation of the angle θ, defined in Figure 1, for a given conformation of a molecule is straightforward,[10,11] provided that bond angles are all known. Specification of bond lengths is not required. Following Leonard et al.,[3] α,ω-dibromoalkanes were treated in a three-state approximation by using the conventional 3 × 3 statistical weight matrix scheme. Bond angles were fixed at ∠BrCC = ∠CCC = 112°. For simplicity, rotational angles for the trans and gauche± states were taken[10,12] to be $\phi_t = 0$ and $\phi_{g\pm} = \pm 112.5°$ for all rotatable bonds. Statistical weight parameters employed[10] in the calculations are summarized in Table I.

Table I
Statistical Weight Parameters[a] Adopted for α,ω-Dibromoalkanes

bond sequence	rotational state	statistical weight
first-order interaction		
	$g^\pm$	1.0
	$g^\pm$	0.43
second-order interaction[b]		
	$g^\pm g^\mp$	0.034
	$g^\pm g^\mp$	0.034
	$g^\pm g^\mp$	0.034

[a] The weight of unity is assigned to the trans state.
[b] For simplicity, statistical weight parameters for the second-order interactions are taken to be identical.[3]

Table II
Statistical Weight Parameters Adopted for α,ω-Dihydroperfluoroalkanes[a]

bond sequence	rotational state	statistical weight
Four-State Scheme[b]		
	$g^\pm$	2.0
	$t^\pm t^\mp$ $t^\pm g^\pm$ $g^\pm g^\pm$ $t^\pm g^\mp$ $g^\pm g^\mp$	0.16 0.09 0.09 0 0
	$t^\pm t^\mp$ $g^\pm g^\pm$ $g^\pm g^\mp$	0.16 0.09 0.11
	$g^\pm g^\pm$ $g^\pm g^\mp$	2.0 2.33
Three-State Scheme[c]		
first-order interaction		
	$g^\pm$	2.0
	$g^\pm$	0.13
second-order interaction		
	$g^\pm g^\mp$	0
	$g^\pm g^\mp$	0.71

[a] Evaluated from the conformational energies given by Bates et al. (cf. Table III of ref 5). [b] The weight of unity is assigned to the $t^\pm t^\pm$ state. [c] The trans state is taken to be the reference.

For α,ω-dihydroperfluoroalkanes, Bates et al.[5] proposed a four-state model in preference to the conventional three-state scheme. As for the dielectric properties, however, they found a satisfactory agreement with the experimental data for both models. We adopt their prescription. The bond angle used is ∠HCC = ∠CCC = 116°. Locations of the rotational states are assumed to be $\phi_{t\pm} = \pm 15°$ and $\phi_{g\pm} = \pm 120°$ for the four-state model and $\phi_t = 0$ and $\phi_{g\pm} = \pm 115°$ for the three-state model. Statistical weight parameters listed in Table II are those chosen to give a best fit to the observed dipole moments of α,ω-dihydroperfluoroalkanes.[5] Since separation of the statistical weights into the first- and second-order components is

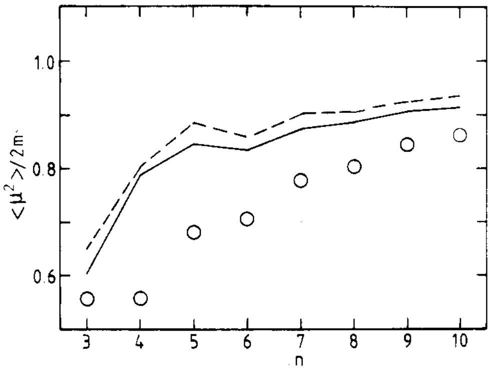


Figure 3. Characteristic dipole moment ratios calculated for $Br(CH_2)_nBr$ (solid line). The results should be equally applicable to $Cl(CH_2)_nCl$. The dashed line corresponds to the original calculation by Leonard et al.[3] The experimental values are shown for comparison by open circles.

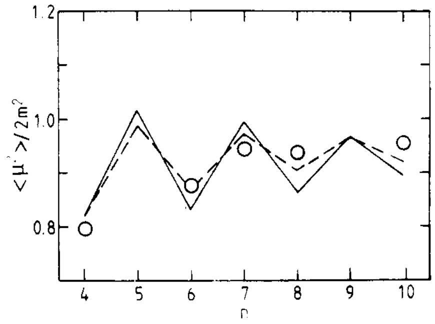


Figure 4. Characteristic dipole moment ratios estimated for $H(CF_2)_nH$. Calculations were performed according to the prescription of Bates et al.[5] Both four-state (solid line) and three-state schemes (dashed line) were examined. The experimental values are indicated by open circles.

difficult in the four-state scheme, both contributions are included in the expression given in Table II.

All possible conformations and orientations of the ω-terminal bond were enumerated in the Cartesian coordinate system fixed to the α-bond.[10,11] For each conformation, the statistical weight was evaluated. The fraction of the ω-bond, $P(\theta_m)$, inclined in the range $0 < \theta \leq \theta_m$ was calculated therefrom for given values of θ_m. The reference angle θ_m was varied from 0 to 180° at 1° intervals. An integrated distribution curve may be easily obtained from a set of $P(\theta_m)$ vs. θ_m data. The same method has been applied to the conformational studies on some polymeric liquid crystals.[11]

Results and Discussion

Odd–Even Oscillation in the Dipole Moment Ratios. For the chosen set of parameters, the average $\langle \cos \theta \rangle$ was computed. The characteristic dipole moment ratios $\langle \mu^2 \rangle / 2m^2 = 1 - \langle \cos \theta \rangle$ calculated in this manner are plotted against n in Figures 3 and 4 for α,ω-dibromoalkanes and α,ω-dihydroperfluoroalkanes, respectively. The values derived from dielectric measurements are also included. As stated earlier, the experimental results for the two series of dihaloalkanes[2,4] are very similar when expressed in terms of the reduced quantity. The calculated results for α,ω-dibromoalkanes may be equally applicable to the corresponding dichlorides. The dashed line shown in Figure 3 was derived by assuming the regular staggering for the gauche forms (i.e., $\phi_{g\pm} = \pm 120°$), with assignment of zero statistical weight to the second-order interaction involving the $g^{\pm}g^{\mp}$ conformation. The agreement with experiments is improved slightly by adoption of more realistic values[10,11] for $\phi_{g\pm}$ (112.5°) and a small, but nonzero statistical weight

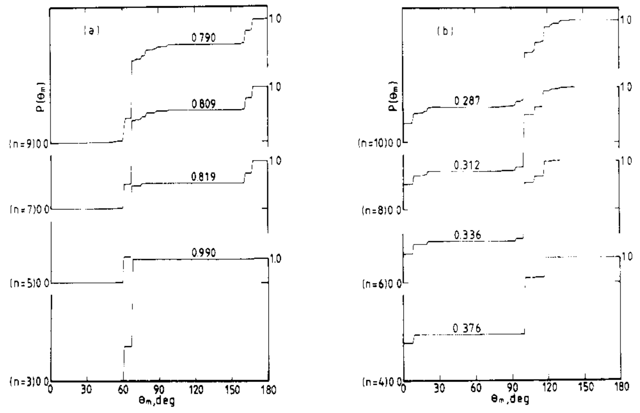


Figure 5. Integrated distribution curves for the angle θ, defined by the two terminal bond vectors, calculated for $Br(CH_2)_nBr$ with (a) n = odd and (b) n = even. The origin of the figure is shown for each curve on the left-hand ordinate. The value $P(\theta_m)$ indicates the fraction of the ω-terminal bond inclined in the range $0 \leq \theta < \theta_m$. Given to each curve is the value of $P(\theta_m)$ for the plateau region.

(0.034) for the $g^{\pm}g^{\mp}$ state as indicated by the solid line (cf. Figure 3). A larger discrepancy between the calculation and experiment for $n = 4$ may be suppressed to some extent by consideration of dipole–dipole interactions.[3] The dipolar induction effect has also been considered in a recent paper by Samulski and Toriumi.[13] Since our major concern lies in the odd–even oscillation of the angular correlation for higher chain lengths, we have not attempted to attain a better agreement for lower members.

Results of calculations for α,ω-dihydroperfluoroalkanes are plotted against n in Figure 4, together with experimental values of $\langle \mu^2 \rangle / 2m^2$. Both three-state and four-state models were examined. The former model seems to give slightly better agreement with experiments. The odd–even alternation in the theoretical values attenuates gradually as n increases but still persists substantially at $n \cong 10$.

Distribution Curves for α,ω-Dibromoalkanes. The spatial orientation of the terminal bonds was studied according to the procedure described in the previous section. Integrated distribution curves, $P(\theta_m)$ vs. θ_m, obtained for α,ω-dibromoalkanes are shown in Figure 5. The results were found to be quite sensitive to the parity, odd or even, of the number n of methylene units. They are therefore plotted in two separate series: parts a and b of Figure 5 correspond to the n = odd and n = even series, respectively. The origin of the figure is indicated for each curve on the left-hand ordinate, together with the n values. Distribution of the angle θ tends to be bimodal as manifested by abrupt transitions in the $P(\theta_m)$ vs. θ_m curves. Lack of smoothness in these curves is due to the artificiality of the rotational isomeric state model.

For chains with n = odd (Figure 5a), the major portion of the calculated angle θ is distributed over the range 60–90° (designated as region O1). To a varying degree (0–20%), orientations are also permitted in the range $160° < \theta < 170°$ (region O2): in this region, the ω-bond is folded back nearly antiparallel to the α-bond. For chains with n = even (Figure 5b), a sizable amount of the ω-bond is found in a rather confined range, 0–20°, of θ (region E1). A larger fraction of the ω-bond is disposed at the inclination of $100° < \theta < 130°$ relative to the α-bond (region E2). Fractions associated with the individual regions can be easily estimated from the height of the plateau (cf. Figure 5). Numerical values of the fractions are summarized in Table III, where the average $\langle \cos \theta \rangle$ is also included for comparison. The $\langle \cos \theta \rangle$–$n$ relation is seemingly irregular for lower values of n (see also Figure 3).[14] Rapid

Table III
Fractions Estimated for the Individual Modes of the Distribution of α,ω-Dibromoalkanes (Figure 5)

	n = odd		n = even		
n	f_{O1} $60° < \theta < 90°$	f_{O2} $160° < \theta < 170°$	f_{E1} $0° < \theta < 20°$	f_{E2} $100° < \theta < 130°$	$\langle \cos \theta \rangle^a$
3	0.990	0.010			0.395
4			0.376	0.624	0.211
5	0.819	0.181			0.155
6			0.336	0.664	0.166
7	0.809	0.191			0.128
8			0.312	0.688	0.118
9	0.790	0.210			0.034
10			0.287	0.713	0.078

[a] Averages taken over all distributions.

Table IV
Fractions Estimated for the Individual Modes of the Distribution of α,ω-Dihydroperfluoroalkanes (Figure 7)

	n = odd		n = even		
n	f_{O1} $60° < \theta < 100°$	f_{O2} $160° < \theta < 162°$	f_{E1} $0° < \theta < 20°$	f_{E2} $100° < \theta < 135°$	$\langle \cos \theta \rangle^a$
4			0.347	0.653	0.175
5	0.707	0.293			0.010
6			0.311	0.689	0.130
7	0.726	0.274			0.027
8			0.295	0.705	0.099
9	0.737	0.263			0.034
10			0.278	0.722	0.078

[a] Averages taken over all distributions.

attenuation of such an odd–even effect in $\langle \cos \theta \rangle$ unnecessarily requires that the parent distribution curves for the n = odd and n = even series are analogous at the same time. The distribution curves transform very slowly with n in each series. The locations of the modes, as indicated by O1 and O2 for the n = odd series and E1 and E2 for the n = even series, are amazingly stable. An increase in one fraction occurs inevitably at the expense of the other: i.e., $f_{O2} = 1 - f_{O1}$ and $f_{E2} = 1 - f_{E1}$. Fluctuations in the rotational angles around the potential energy minima should affect the distribution curves more effectively for higher chain lengths. Calculations carried out tentatively by displacing the rotational minima within ±10° were found to cause only a minor effect in the modes of distribution in the range $n \leq 10$.

Distribution Curves for α,ω-Dihydroperfluoroalkanes. Calculations performed according to the four-state model yielded the integrated distribution curves, $P(\theta_m)$ vs. θ_m, shown in Figure 6. Following the previous treatment, the results for the n = odd and n = even series are plotted in separate parts. Characteristics of the bimodal distribution vanish very rapidly with n. The difference between the n = odd and n = even series seems to be very small beyond n = 6. As demonstrated in Figure 4, however, the odd–even oscillation in the calculated dipole moment ratios remains substantial even around $n \cong 10$. In these respects, the results obtained from the four-state model differ very much from those derived above for α,ω-dibromoalkanes. For larger values of n, the integrated distribution curves given in Figure 6 resemble that for the random orientation, which may be expressed as

$$P(\theta_m) = (1/2)(1 - \cos \theta_m) \qquad (5)$$

Needless to say, this analogy is fortuitous. It does not imply that the perfluoroalkane chains are less rigid than the corresponding n-alkanes. In the four-state model proposed by Bates et al.,[5] the lowest energy conformations involve succession of ...$t^+t^+t^+$... or ...$t^-t^-t^-$... arrangements. A reversal of the sense of helix via t^+t^- or t^-t^+ requires an energy of ca. 1.1 kcal mol^{-1}. The chain is therefore essentially a slowly twisting helix. When this requirement is tentatively relaxed by reducing the energy for $t^\pm t^\mp$ to zero, the distribution curves tend to be bimodal. Thus the distinction between the n = odd and n = even series becomes apparent.

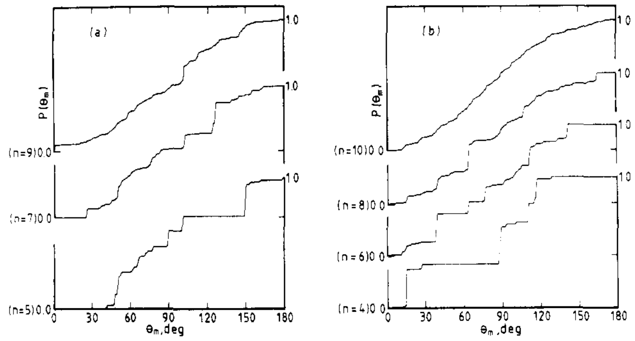


Figure 6. Integrated distribution curves for the angle θ, calculated for $H(CF_2)_nH$ by using the four-state model: (a) n = odd; (b) n = even. Since none of the curves exhibit any well-defined plateau, numerical values of $P(\theta_m)$ are not given in the intermediate region. (See legend to Figure 5.)

Shown in Figure 7 are the integrated distribution curves obtained for the three-state scheme. In this model, the trans state occurs at $\phi_t = 0$. The most stable conformation is a planar-zigzag form. Accordingly, the distributions of θ are bimodal in all the cases examined. As may be expected, the $P(\theta_m)$ vs. θ_m curves calculated resemble those derived for α,ω-dibromoalkanes. The results are plotted in two separate parts, one for the n = odd members (Figure 7a) and the other for the n = even members (Figure 7b). The fractions of θ estimated for each of the characteristic regions are listed in Table IV. In contrast to the trend observed for α,ω-dibromoalkanes (cf. Table III), fraction f_{O1} increases as n varies in the order 5, 7, and 9. Such an increase in f_{O1}, and thus a decrease in f_{O2} (=1 − f_{O1}), is responsible for the upward tendency in the calculated values of $\langle \cos \theta \rangle$ for the n = odd series. These considerations offer an explanation for the decreasing trend in the

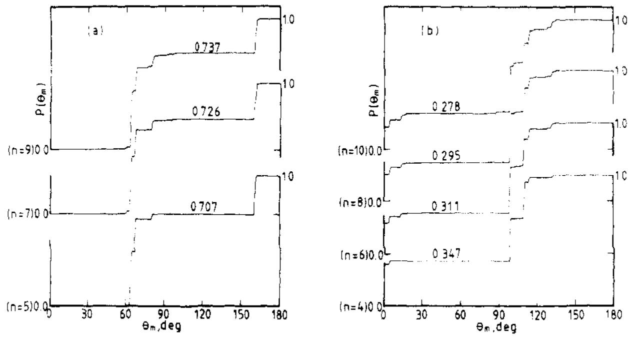


Figure 7. Integrated distribution curves for the angle θ, calculated for $H(CF_2)_nH$ according to the three-state model: (a) n = odd; (b) n = even. (See legend to Figure 5.)

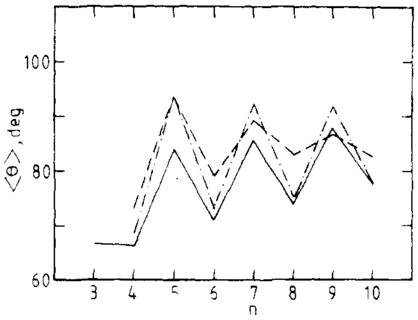


Figure 8. Odd–even effect in the averaged angle $\langle\theta\rangle$. The solid line is that calculated for $Br(CH_2)_nBr$. The dashed and chained lines represent the results for $H(CF_2)_nH$ calculated by using the four-state and three-state schemes, respectively.

plot of the calculated dipole moment ratio $\langle\mu^2\rangle/2m^2 = 1 - \langle\cos\theta\rangle$ for n = odd (cf. Figure 4). As can be shown by simple calculations, the slope of the theoretical curve for n = odd may be positive or negative, depending on the choice of the statistical weight for the terminal H–C–C–C bond.

The angular distribution curves calculated based on the three-state model (Figure 7) are very much different from those shown in Figure 6 for the four-state model. Nevertheless, as reported by Bates et al.,[5] both models adequately reproduce the experimental results on the dipole moment. Preference of the four-state scheme has been concluded[5] from other evidence such as the crystal structure of poly(tetrafluoroethylene)[15] and semiempirical energy calculations.[16]

Estimation of $\langle\theta\rangle$ and $\langle\cos^2\theta\rangle$ from the Distribution. In Figure 8, the averages $\langle\theta\rangle$, computed for the distributions shown in Figures 5–7, are plotted against n. Except in the case of $Br(CH_2)_3Br$, the odd–even oscillation in $\langle\theta\rangle$ is quite regular. Attenuation of the oscillation is somewhat more rapid for the four-state model of α,ω-dihydroperfluoroalkanes.

The order parameters S defined conventionally by

$$S = (1/2)(3\langle\cos^2\theta\rangle - 1) \qquad (6)$$

were calculated from the averages $\langle\cos^2\theta\rangle$ and are plotted as a function of n in Figure 9. The calculated values of S are generally small. The odd–even oscillation is evident only for the α,ω-dibromoalkane chains, for which the sign of S changes with the parity of n. For α,ω-dihydroperfluoroalkanes, neither model exhibits a distinct odd–even alternation. Values of S are positive throughout and tend to decrease gradually with n.

Concluding Remarks

As shown in Figure 5, the integrated distribution curves derived for α,ω-dibromoalkanes exhibit a sharp contrast in their appearance between the n = odd and n = even members. The distinction between these two series is unambiguous up to the highest member investigated (i.e., n = 10). Recently, similar results have been obtained in the analysis of polyesters comprising rigid (aromatic) cores interconnected by flexible $(CH_2)_n$ spacers.[11] In these studies, the odd–even oscillation observed in the isotropization entropies of the liquid crystalline phase has been interpreted based on the distribution curves derived for the spatial orientation of the neighboring cores.

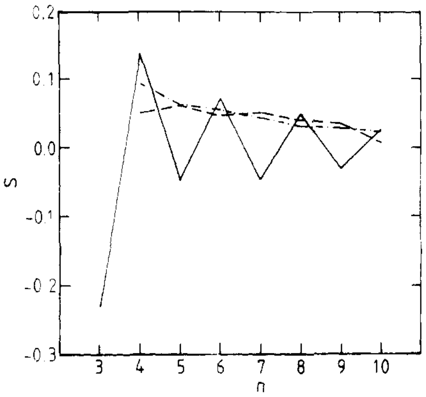


Figure 9. Variation of the order parameter S with n. (See legend to Figure 8.)

The distribution curves for α,ω-dihydroperfluoroalkanes are shown in Figures 6 and 7. The odd–even oscillation is distinct only when the trans–gauche three-state model is employed. Both three-state and four-state models have been elucidated from the analysis of the dipole moment data,[5] and therefore they exhibit a similar trend in the $\langle\cos\theta\rangle$–n relation (cf. Figure 4). It is interesting to note that the averages $\langle\theta\rangle$ and $\langle\cos^2\theta\rangle$ vary with n more or less in the same manner for both models.

Finally, the present results indicate that the directional correlation between the terminal bond vectors is far from random for $n \leq 10$ for the chain molecules investigated. Attenuation of the odd–even oscillation in the dipole moments at an early stage is due to a proper balance of contributions between highly polar and less polar conformations.

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Ring-Closure Probabilities for Twisted Wormlike Chains. Application to DNA[†]

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ABSTRACT: The ring-closure probability with the end orientations specified, or the corresponding *J* factor, as defined as the ratio of equilibrium constants for cyclization and bimolecular association, is evaluated for a twisted wormlike chain, i.e., a special case of the helical wormlike chain. For large length *L* of the chain contour, evaluation is carried out by the use of the Daniels approximation and the weighting function method previously developed. For small *L*, the continuous chain is replaced by an equivalent discrete chain in order to treat directly the configuration integral, taking proper account of fluctuations in the configuration of the closed ring around its most probable one, the continuous limit being taken at the final stage of calculation. This is a refinement of the previous approach of Yamakawa and Stockmayer. The evaluation for small *L* is carried out through (topological) linking-number-dependent *J* factors, the sum of which is equal to the desired *J*. It is predicted that the *J* factor as a function of *L* stays at zero for very small *L*, then increases oscillating, and finally decreases monotonically. The derived equations are applied to an analysis of experimental data obtained by Shore et al. for DNA to determine its bending and torsional elastic constants, or its persistence length and Poisson ratio, and also the helix repeat.

I. Introduction

For DNA fragments having cohesive ends, Shore et al.[1] have recently measured the ring-closure probability, or the Jacobson–Stockmayer (*J*) factor,[2] as defined as the ratio of equilibrium constants for cyclization and bimolecular association. The results are in semiquantitative agreement with the theoretical prediction for the angle-independent ring-closure probability derived by Yamakawa and Stockmayer[3] on the basis of the Kratky-Porod (KP) wormlike chain.[4] Strictly, however, the *J* factor for DNA is not a smooth function of chain length but seems to exhibit oscillations for fragments below 500 base pairs. This may be regarded as arising from the fact that if the number of base pairs in the DNA fragment is not an integral multiple of the number of base pairs per helix turn, i.e., the helix repeat, then the need to twist the DNA helix in order to make strand ends meet decreases the *J* factor significantly for sizes less than 500 base pairs.[1] Thus we must consider a more general ring-closure probability with the end orientations specified. The object of the present paper is to evaluate it by modeling DNA as a special case of our helical wormlike (HW) model,[5-7] i.e., a twisted wormlike chain.

The HW chain is defined as an elastic wire model with both bending and torsional energies such that at the minimum of its total configurational (elastic) energy, its contour (as a space curve) becomes a regular helix specified by the constant curvature κ_0 and torsion τ_0. We can then affix a localized Cartesian coordinate system $[\mathbf{e}_\xi(s), \mathbf{e}_\eta(s), \mathbf{e}_\zeta(s)]$ to the chain at the contour point *s*, with $\mathbf{e}_\zeta$ being identical with the unit tangent vector $\mathbf{u}(s)$ and with $\mathbf{e}_\xi$ and $\mathbf{e}_\eta$ being in the directions of the principal axes of inertia of its cross section at *s*. For the present purpose, we may represent DNA by a special case of the HW chain with $\kappa_0 = 0$ and $\tau_0 \neq 0$, i.e., the KP1 chain,[8] affixing properly a localized coordinate system to each base pair.[7,9] Then, at the minimum of energy, the regular helix above reduces to a straight line; as the contour distance *s* is changed, the localized coordinate system at *s* moves, rotating about its ζ axis (contour), the locus of the end of the ξ or η axis being a regular helix of pitch $2\pi/\tau_0$ (see Figure 2 of SMHWC-IX[8]) and this helix corresponding to one of the sugar–phosphate backbones. (It is right-handed for $\tau_0 > 0$ and left-handed for $\tau_0 < 0$.) In order to completely define the model, we need two other parameters, i.e., the bending and torsional force constants, but it is convenient to use, instead of them, the stiffness parameter λ^{-1} and Poisson's ratio σ (see the next section). In the present case ($\kappa_0 = 0$), λ^{-1} is equal to the Kuhn segment length and twice the persistence length.[5] We note that similar elastic models have been adopted by Fuller,[10] Benham,[11] and Le Bret[12] in the study of the supercoiling of DNA and by Barkley and Zimm[13] in the study of its dynamics.

Now let $\mathbf{r}(s)$ be the radius vector of the contour point *s* ($0 \leq s \leq L$) of the chain of total contour length *L* and let $\Omega(s) = [\theta(s), \phi(s), \psi(s)]$ ($0 \leq \theta \leq \pi, 0 \leq \phi \leq 2\pi, 0 \leq \psi \leq 2\pi$) be the Euler angles defining the orientation of the localized coordinate system at *s* with respect to an external coordinate system. We can define the conditional distribution function, i.e., the Green's function $G(\mathbf{R},\Omega|\Omega_0;L)$ of $\mathbf{r}(L) = \mathbf{R}$ and $\Omega(L) = \Omega$ when $\mathbf{r}(0) = 0$ and $\Omega(0) = \Omega_0$, $\mathbf{R}$ being the end-to-end distance. Following the Jacobson–Stockmayer theory[2] and its extension,[14,15] the desired *J* factor (in molecules per unit volume) may be related to the ring-closure probability $G(0,\Omega_0|\Omega_0;L)$ as

$$J = 8\pi^2 G(0,\Omega_0|\Omega_0;L) \qquad (1)$$

It is, however, important to recall that the reaction product is not a homogeneous species but rather a mixture of closed circular DNA with different topological linking numbers.[10,16,17] The linking number, which is an integer

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[†] This paper is dedicated to Professor Walter H. Stockmayer on his 70th birthday.

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