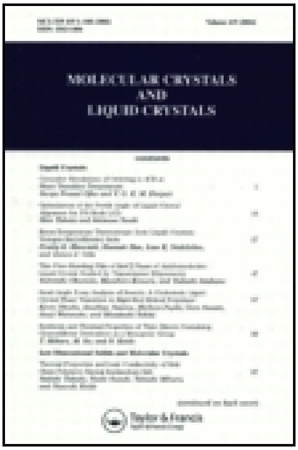

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Molecular Ordering in Liquid Crystals and the Effect of End-Chains on the Even-Odd Effect

T. Kobayashi [a] , H. Yoshida [a] , A. D. L. Chandani [a] , S. Kobinata [a] & S. Maeda [a]

[a] Research Laboratory of Resources Utilization, Tokyo institute of Technology, Midori-ku, Yokohama, 227, Japan

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Molecular Ordering in Liquid Crystals and the Effect of End-Chains on the Even-Odd Effect

T. KOBAYASHI, H. YOSHIDA, A. D. L. CHANDANI, S. KOBINATA and S. MAEDA

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Midori-ku, Yokohama 227, Japan

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The second and fourth orientational order parameters $\overline{P}_2$, $\overline{P}_4$ of the homologous series of 4-*n*-alkyl-4′-cyanobiphenyls (nCB, $n = 5 \sim 8$) in the nematic liquid crystalline state have been determined from the Raman depolarization ratios by the resonance Raman probe method. It was found out that not only $\overline{P}_2$ but also $\overline{P}_4$ exhibits evident even-odd effect when they are compared at the same reduced temperature. For understanding the mechanism of the even-odd effect, a theoretical calculation has been carried out on the basis of the mean field theory of Marcelja, in which the effect of the end alkyl-chain on the liquid crystalline state is taken explicitly into consideration. The observed trend in $\overline{P}_2$, $\overline{P}_4$, nematic-isotropic transition temperature were well reproduced. Detailed inspection of the results shows that the presence of anisotropic molecular field plays an important role in the appearance of the even-odd effect. The anisotropic molecular field produces redistribution of the statistical weight of various conformers in such a way that the end chains of odd-members align better along the direction of the rigid core part than those of even-members.

Keywords: cyanobiphenyl nematics, order parameters, resonance Raman probe method, alkyl chain conformation, even-odd effect.

I. INTRODUCTION

It has been known that some homologous series of nematic liquid crystals show even-odd effect in the nematic-isotropic transition temperature (T_{NI}) and in the second orientational order parameter $\overline{P}_2$ with respect to the number of C—C links in the end alkyl-chain.[1,2] The homologous series 4-*n*-alkyl-4′-cyanobiphenyls (nCB) shows even-odd alternation in T_{NI}.[3] But for this series, the behavior of $\overline{P}_2$ has not been reported so far. We have determined not only $\overline{P}_2$ but also the fourth orientational order parameter $\overline{P}_4$ of nCB (n = 5 ~ 8) by using the resonance Raman probe method. Both $\overline{P}_2$ and $\overline{P}_4$ show remarkable even-odd effect when they are compared at the same reduced temperature $T^* = T/T_{NI}$.

In order to understand the molecular mechanism of such an even-odd effect, it is essential to take into account the effect of the structural behavior of the end alkyl-chain on the liquid crystalline state.[1] In this paper, we investigated the effect by applying the Marcelja's method to nCB molecules.[4,5] The observed trend of T_{NI}, $\overline{P}_2$ and $\overline{P}_4$ were well reproduced by the method. The molecular mechanism of the even-odd effect was studied through detailed inspection of the end-chain conformations in an anisotropic molecular field.

2. EXPERIMENTAL

In previous papers,[6,7] we have reported the determination of order parameters $\overline{P}_2$ and $\overline{P}_4$ by means of the resonance Raman probe method for MBBA and 5CB. By using the same method, we have determined $\overline{P}_2$ and $\overline{P}_4$ of 6CB, 7CB and 8CB.[8]

All-trans β-carotene (0.08 wt%) was used as a resonance Raman probe to reflect the orientational behavior of host liquid crystalline molecules. The Raman measurement was made by a back scattering geometry using 514.5 nm Ar^+ laser radiation. The sample preparation and spectroscopic set-up are essentially unchanged from the previous ones.[6,7] A great merit of resonance Raman probe method resides in that the scattering tensor reduces to a very simple form by virtue of the resonance effect,

$$\alpha_{ZZ}\begin{pmatrix} 0, & 0, & 0 \\ 0, & 0, & 0 \\ 0, & 0, & 1 \end{pmatrix}$$

$\overline{P}_2$ and $\overline{P}_4$ can be determined precisely, without introducing any assumption about the scattering tensor and avoiding serious errors caused by the uncertainty in the scattering tensor, from the two independent depolarization ratios measurement. Depolarization ratios which are extrapolated to zero sample thickness were used in analysis. The results thus obtained are shown in Figure 1. All the $\overline{P}_2$ by resonance Raman probe method coincide well with those obtained from the absorption dichroic ratio measurement, and also with those reported for neat nCB. Details of the results will be published elsewhere.[8]

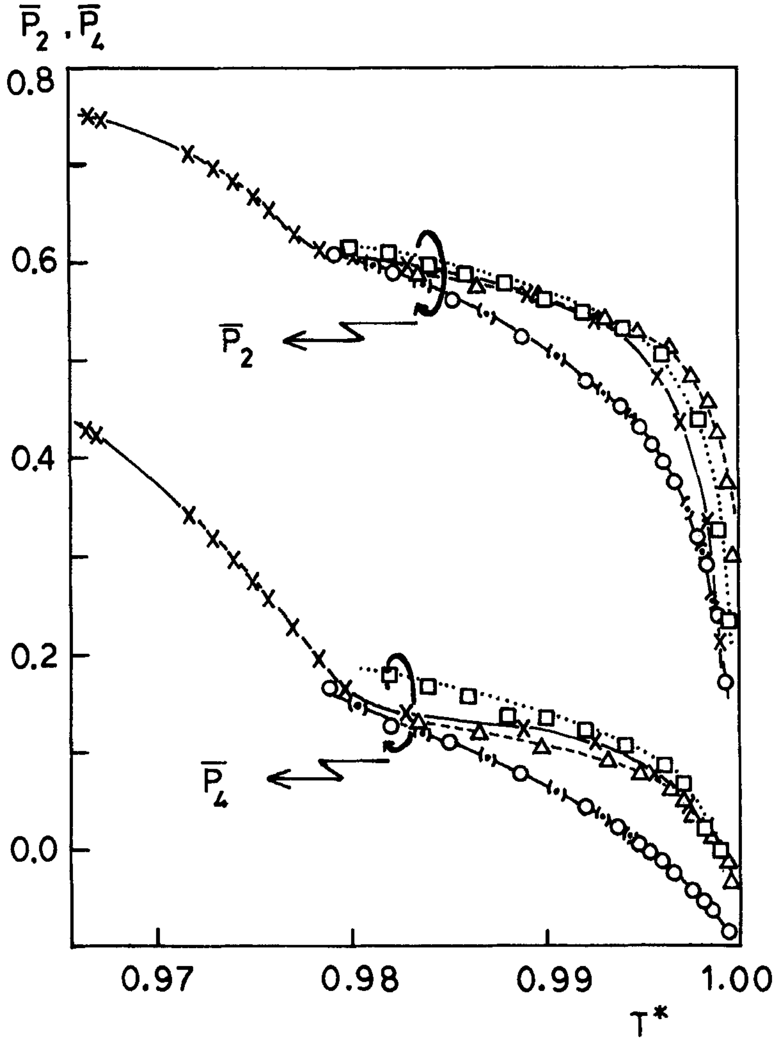

FIGURE 1 Temperature dependence of $\overline{P}_2$ and $\overline{P}_4$ of nCB (n = 5 ~ 8) obtained by resonance Raman probe method.[7,8] T^* indicates reduced temperature $T^* = T/T_{NI}$. --Δ-Δ-Δ-Δ-Δ--, 5CB; —O—O—O—O—, 6CB; ---□--□--□--□--□--, 7CB; —x—x—x—x—, 8CB.

3. RESULTS AND DISCUSSION

In Figure 2, the observed $\overline{P}_2$, $\overline{P}_4$ and T_{NI} of nCB are plotted against the number of carbon atoms in the alkyl chain (n) for several reduced temperatures. The data clearly show the even-odd effect in $\overline{P}_2$, $\overline{P}_4$ and T_{NI}; comparatively high values for odd n and low values for even n. The firstly observed even-odd effect in $\overline{P}_4$ is notable in the point that it has the alternation of the same order of magnitude with that of $\overline{P}_2$, in spite of considerably smaller value of $\overline{P}_4$ compared with $\overline{P}_2$.

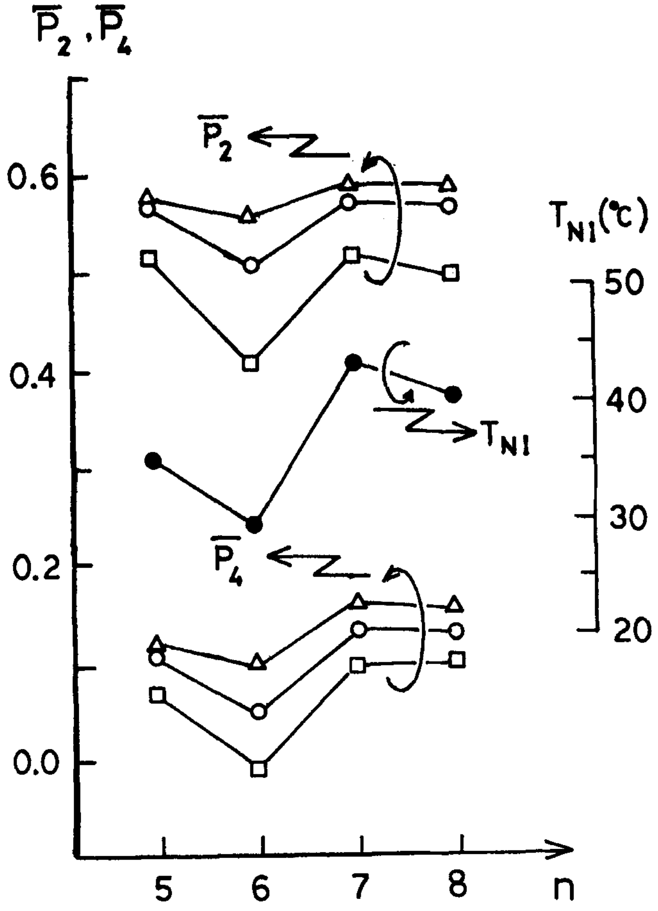

FIGURE 2 Even-odd alternation of T_{NI}, $\overline{P}_2$ and $\overline{P}_4$ of nCB. $\overline{P}_2$ and $\overline{P}_4$ are results of resonance Raman probe method.[7,8]

The even-odd effects indicate most definitely the role of the end-chain in the formation of the liquid crystalline state. If the end-chain is assumed to take all-trans conformation, qualitative explanation of the even-odd effects would be easy. In this case, terminal C—C bond would be parallel to the long axis of the rigid core part for odd n, but protrude from the axis for even n. This would give relatively higher anisotropy of molecular shape for odd n members, accordingly stronger anisotropic orientational molecular field, which results in larger order parameters and T_{NI}.

However, simple consideration on the conformation energy of the end chain reveals that the statistical weight of all-trans conformation is not an overwhelming one, and various gauche conformations may have considerable weight on the whole even for $n = 5$. For accurate and quantitative understanding of the even-odd effect, all the conformations of the end-chain should be taken into consideration. In doing this, we relied on the pioneering work of Marcelja. In the Marcelja's theory, the strength of orientational molecular field acting on flexible end-chain is given by

$$X_c = C_c(n)V_{cc}\overline{P}_2(c) + C_a(n)V_{ca}\overline{P}_2(a) \tag{1}$$

where subscripts a and c stand for aromatic rigid core part and end alkyl chain, respectively. $C_c(n)$ and $C_a(n)$ are the corresponding volume fractions, and V_{cc} and V_{ca} are the coupling constants for c—c and c—a. $\overline{P}_2(a)$ is the second order parameter of core part. $\overline{P}_2(c)$ denotes the second order parameter for the end chain, and was defined as

$$\overline{P}_2(c) = \left\langle \frac{1.88}{n} \sum_i \left(\frac{3}{2} \cos^2\theta_i - \frac{1}{2} \right) \right\rangle \tag{2}$$

where θ_i denotes the angle between the i-th C—C segment and the direction of the molecular field (director). $\overline{P}_2(c)$ depends on both conformation of the end-chain and alignment of the core part to the director. The strength of orientational molecular field acting on the rigid core part is given by

$$X_a = C_a(n)V_{aa}\overline{P}_2(a) + C_c(n)V_{ac}\overline{P}_2(c) \tag{3}$$

The order parameters of the end-chains and core parts were given as the solutions of coupled self-consistent equations,

$$\overline{P}_2(a) = (1/Z_a(X_a))\int_0^1 \left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right) \times \exp\left\{X_a\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right)\Big/kT\right\} d(\cos\theta) \tag{4}$$

$$\overline{P}_2(c) = (1/Z_c(X_c)) \sum_{\substack{\text{all}\\ \text{conf.}}} \sum_{\substack{\text{core}\\ \text{orien.}}} \frac{1.88}{n}\sum_{i=1}^{n}\left(\frac{3}{2}\cos^2\theta_i - \frac{1}{2}\right) \times \exp\left\{\frac{1.88}{n}X_c\sum_{i=1}^{n}\left(\frac{3}{2}\cos^2\theta_i - \frac{1}{2}\right) - E_{\text{int}}\right\}\Big/kT\Big\} \tag{5}$$

where $Z_a(X_a)$ and $Z_c(X_c)$ are the orientational partition functions of core part in the field X_a and that of chain part in the field of X_c. E_{int} is the internal conformation energy of a chain, and was evaluated by summing up conformational energies of a set of neighboring C—C bonds in a chain on the basis of the three rotational isomeric states model of Flory;[9]

$$E_{\text{int}} = \sum_i E(\xi_i, \xi_{i-1}) \tag{6}$$

where i specifies C—C bond number and ξ represents any of the three rotameric states, t(trans), $g^{\pm}$(gauche). Eqs. 4 and 5 have several solutions in some temperature range. Actually realized state was identified by computing the free energy for respective cases. The free energy is given as,

$$\begin{aligned} F = & -\frac{1}{2}C_aV_{aa}\overline{P}_2(a)^2 - \frac{1}{2}C_cV_{ac}\overline{P}_2(a)\overline{P}{}_2^0(c) - \frac{n}{2}C_cV_{cc}\{\overline{P}_2(c)^2 - \overline{P}{}_2^0(c)^2\} \\ & - nC_aV_{ca}\overline{P}_2(a)\{\overline{P}_2(c) - \overline{P}{}_2^0(c)\} + \{C_aV_{aa}\overline{P}_2(a) \\ & + C_cV_{ca}\overline{P}_2(c)\}\overline{P}_2(a) \\ & + n\overline{P}_2(c)\{C_cV_{cc}\overline{P}_2(c) + C_aV_{ca}\overline{P}_2(a)\} - kT\ln Z_a - kT\ln\frac{Z_c(X_c)}{Z_c(0)} \end{aligned} \tag{7}$$

$\overline{P}{}_2^0(c)$ is the value of $\overline{P}_2(c)$ under the condition that $\overline{P}_2(a) \neq 0$ but $X_c = 0$. $Z_c(0)$ is the partition function of the chain in an isotropic liquid state.

In the actual calculation, volume fractions C_a and C_s were determined by the following equations,

$$C_a = 323.9/\{323.9 + 28.3(n - 2)\}, \quad C_a + C_c = 1 \qquad (8)$$

The denominator denotes the volume of nCB molecule (A^3) derived from the molar volume of nCB.[10] The first two segments of the end-chain are included in the rigid part. The coupling constants V_{aa} and V_{cc} were determined following Marcelja as $V_{aa} = 2664$ cal/mol and $V_{cc} = 680$ cal/mol. The values of V_{ac} and V_{ca} were determined so as to reproduce the experimental values of T_{NI} under the restriction of $C_cV_{ac} = nC_aV_{ca}$, as $V_{ac} = 5016$ cal/mol and $V_{ca} = 440$ cal/mol. As to conformation energy in Eq. 6, following values were used; $E(t, t) = 0$, $E(g^{\pm}, g^{\pm}) = E(t, g^{\pm}) = 400$ cal/mol, $E(g^{\pm}, g) = 2200$ cal/mol.[9]

Figure 3 shows the calculated results of T_{NI} and order parameters $\overline{P}_2(a)$, $\overline{P}_2(c)$ and $\overline{P}_4(a)$ at the reduced temperature $T^* = 0.995$. It is seen that Marcelja's method reproduces fairly well the observed trend of even-odd effects of these quantities, especially T_{NI}. The order parameter of the end-chain $\overline{P}_2(c)$ is evaluated to be distinctly smaller than that of the core $\overline{P}_2(a)$. The experimentally observed $\overline{P}_2$ would be the result of cooperative action of order parameters of core and chain parts. These agreements as a whole would guarantee the essential pertinence of the theory in describing the influence of alkyl chains in the nematic phase, in spite of several drastic approximations included in the theory.[4,5]

To get more detailed information about the mechanism of the even-odd effect, we calculated the strength of the anisotropic molecular field X_a and X_c of Eqs. (1) and (3) at the transition point T_{NI}. Figure 4 indicates that the strength of the molecular field itself shows remarkable even-odd alternation. As expected, X_a is much larger than X_c. X_c is about one third of kT_{NI} in magnitude and about a half of the energy of gauche conformation. This causes redistribution of the statistical weight of various chain conformers in a considerable degree compared with that in the isotropic phase. The statistical weight of various conformers of 5CB in nematic and isotropic phases is shown, as an example, in Table 1, together with that obtained by Emseley et. al.[11] The two results show a slight quantitative difference which arises probably from the difference in the values of X_a, X_c and $E(tg^{\pm})$. Our values are somewhat smaller than those of Emseley et. al.[11] In general, the statistical weight of all-trans conformer increases considerably in the nematic phase compared with that in the isotropic

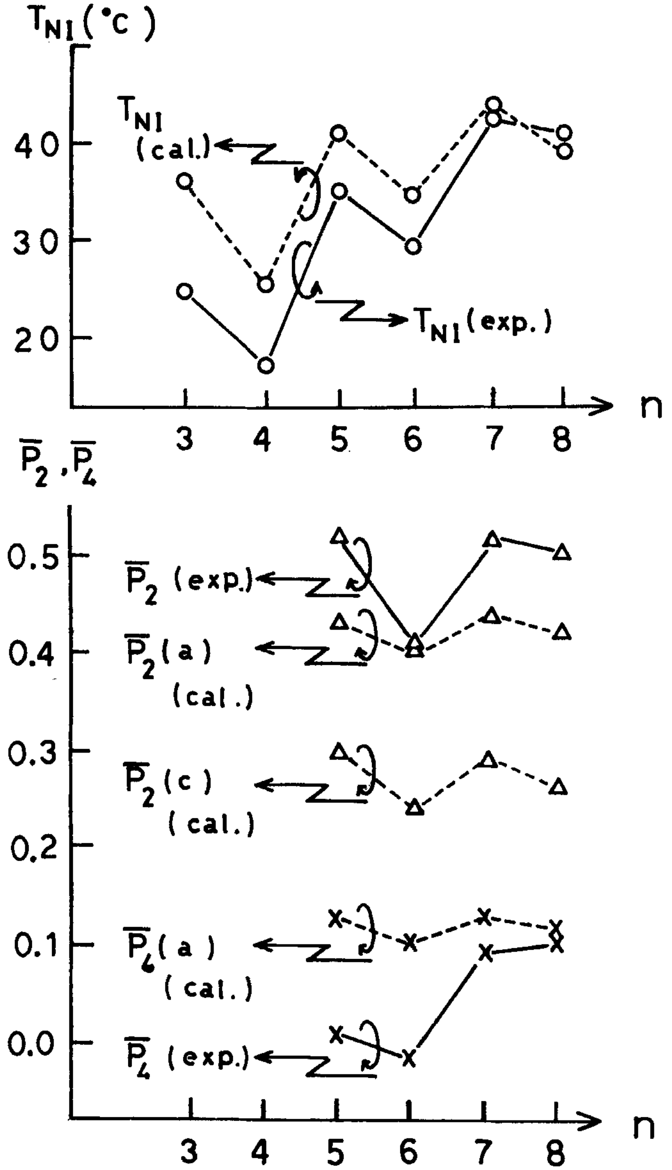

FIGURE 3 Comparison of calculated and observed results of T_{NI}, and $\overline{P}_2$, $\overline{P}_4$ at the reduced temperature $T^* = 0.995$. Real lines are used to connect the observed values, and dotted lines are used to connect the calculated values. △, $\overline{P}_2(a)$ and $\overline{P}_2(c)$; ○, T_{NI}; ×, $\overline{P}_4$.

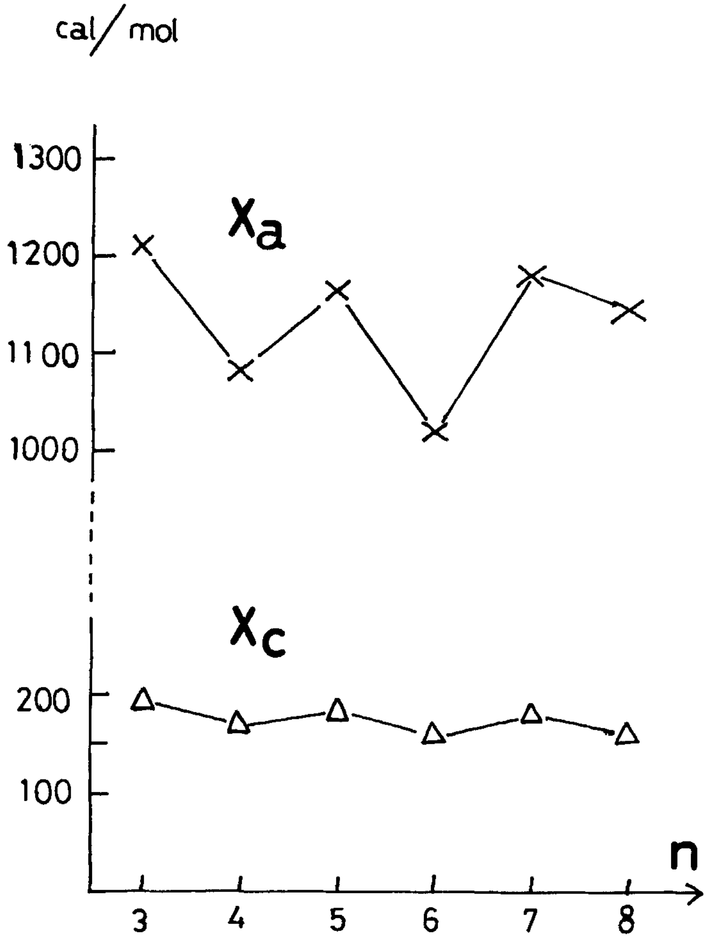

FIGURE 4 X_a and X_c evaluated at phase transition temperatures of nCB. —×—×—, X_a; —△—△—△—, X_c.

phase. Furthermore, conformers which have an extended form along core axis increase their weight in nematic state, for example ($tg^{\pm}t$) conformers in 5CB as can be seen in Table 1, and kink conformers (. . . $g^{+}tg^{-}$ . . .) and (. . . $g^{-}tg^{+}$ . . .) in 6CB ~ 8CB.[12] But, X_c is not so large as to reject other various conformers.[11,12] On the other hand, conformers which have a bulky shape decrease their weight in the nematic phase. These conclusions are qualitatively in good accord with those of Emseley et. al.[11]

It should be noted that the even-odd alternation of the strength of anisotropic field for the chain X_c is not essential for the appearance

TABLE 1

Statistical weights (%) of 5CB conformers in nematic and isotropic phases. Values in the parenthesis are from ref. 11.

Conformation	Statistical weights	
	Nematic	Isotropic
ttt	23.4 (33.2)	14.8 (22.7)
$tg^{+}t$	10.27 (11.59)	7.78 (8.35)
$tg^{-}t$	10.27 (11.59)	7.78 (8.35)
ttg^{+}	7.69 (7.17)	7.78 (8.35)
ttg^{-}	7.69 (7.17)	7.78 (8.35)
$g^{+}tt$	5.14 (4.85)	7.78 (8.35)
$g^{-}tt$	5.14 (4.87)	7.78 (8.35)
$g^{+}tg^{-}$	4.05 (2.64)	4.10 (3.07)
$g^{-}tg^{+}$	4.05 (2.64)	4.10 (3.07)
$tg^{+}g^{+}$	3.39 (2.48)	4.10 (3.07)
$tg^{-}g^{-}$	3.39 (2.48)	4.10 (3.07)
$g^{+}tg^{+}$	3.06 (1.82)	4.10 (3.07)
$g^{-}tg^{-}$	3.06 (1.82)	4.10 (3.07)
$g^{+}g^{+}t$	2.29 (1.74)	4.10 (3.07)
$g^{-}g^{-}t$	2.29 (1.74)	4.10 (3.07)
$g^{+}g^{+}g^{+}$	1.81 (0.95)	2.16 (1.13)
$g^{-}g^{-}g^{-}$	1.81 (0.95)	2.16 (1.13)
$tg^{+}g^{-}$	0.22 (0.05)	0.23 (0.06)
$tg^{-}g^{+}$	0.22 (0.05)	0.23 (0.06)
$g^{+}g^{-}t$	0.18 (0.04)	0.23 (0.06)
$g^{-}g^{+}t$	0.18 (0.04)	0.30 (0.06)
$g^{+}g^{-}g^{-}$	0.11 (0.02)	0.12 (0.02)
$g^{-}g^{+}g^{+}$	0.11 (0.02)	0.12 (0.02)
$g^{+}g^{+}g^{-}$	0.08 (0.01)	0.12 (0.02)
$g^{-}g^{-}g^{+}$	0.08 (1.74)	0.12 (3.07)
$g^{+}g^{-}g^{+}$	0.01 (0.00)	0.01 (0.00)
$g^{-}g^{+}g^{-}$	0.01 (0.00)	0.01 (0.00)

of the even-odd alternation in the order parameters of the chain. As can be seen in Figure 5, $\overline{P}_2(c)$ evaluated under constant X_c shows remarkable even-odd effect. This suggests that the origin of the even-odd effect is of intramolecular nature or it is caused by the difference in response of alkyl chains to the anisotropic field. To clarify this point, we have evaluated the statistical average of several quantities of alkyl chains, such as the distance between the terminal and the first C atom. We found that the direction cosine between core axis and the terminal C—C bond $\langle \mathbf{l}_1 \cdot \mathbf{l}_n \rangle$, where $\mathbf{l}_1$ and $\mathbf{l}_n$ are the unit vectors along the first and terminal C—C bonds, is a quite sensitive measure of alkyl chain ordering. The results of $\langle \mathbf{l}_1 \cdot \mathbf{l}_n \rangle$ calculation are shown in Figure 6, for nematic state just below T_{NI} (solid line) and for isotropic state just above T_{NI} (broken line). In the nematic phase, even-odd alternation of $\langle \mathbf{l}_1 \cdot \mathbf{l}_n \rangle$ is remarkable, indicating that the ter-

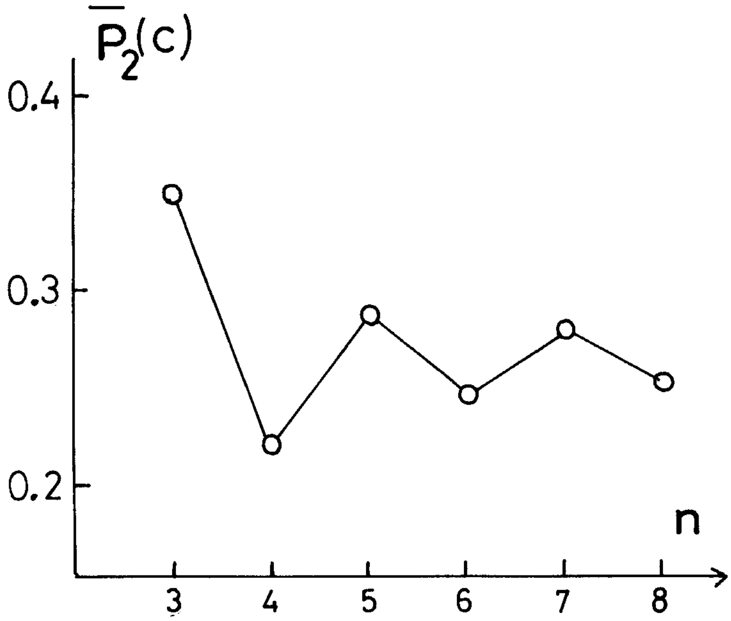

FIGURE 5 Calculated chain order $\overline{P}_2(c)$ under the constant X_c and T. X_c = 187.5 cal/mol, $1/kT$ = 0.00160 (cal/mol)$^{-1}$.

minal C—C bond of odd members are comparatively better oriented along the direction of the rigid part compared with those of even members. Whereas in the isotropic phase ($X_c = 0$), $\langle \mathbf{l}_1 \cdot \mathbf{l}_n \rangle$ decreases rather monotonously with increase of the chain length n without showing appreciable even-odd alternation. Adoption of a larger value for $E(tg^{\pm})$ than 400 cal/mol, for example 800 cal/mol, results in somewhat increased even-odd alternation of $\langle \mathbf{l}_1 \cdot \mathbf{l}_n \rangle$ in the isotropic phase. But even in that case, the extent of alternation is by far smaller than that in the nematic phase. This result clearly shows, together with the previous observation that even a constant X_c produces even-odd alternation in the chain order $\overline{P}_2(c)$, that the presence of anisotropic orientational field is of essential importance for the appearance of even-odd effect. The response of alkyl chains to the anisotropic field is different between even n and odd n species i.e. the response of odd members is more sensitive than that of even members. It can be said that the anisotropic field amplifies greatly and essentially the small even-odd alternation of intramolecular origin. This mechanism will explain why even-odd effects are remarkable in the nematic-isotropic phase transition across which anisotropic field changes remarkably.

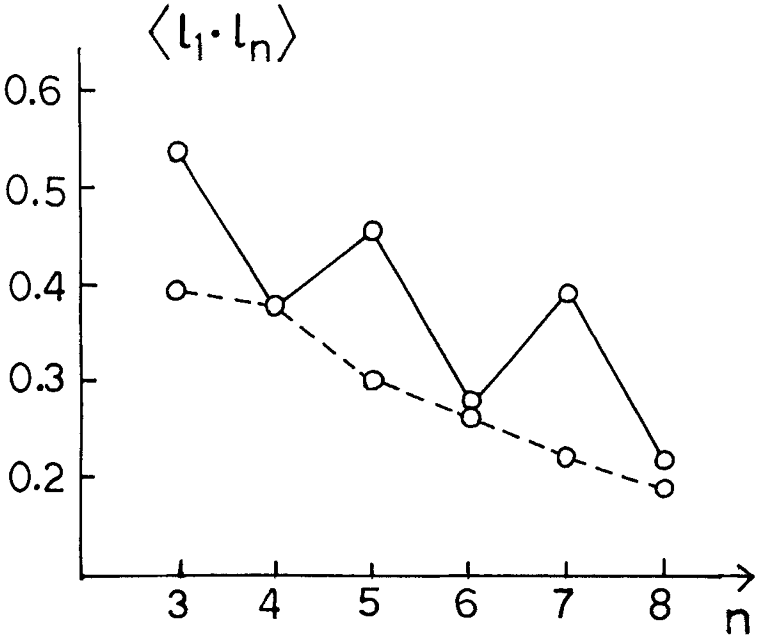

FIGURE 6 Statistical average of the direction cosine between the first and terminal C—C bonds, $\langle \mathbf{l}_1 \cdot \mathbf{l}_n \rangle$. —O——O—, in the isotropic phase just above T_{NI}, --O---O--, in the nematic phase just below T_{NI}.

As to $\overline{P}_4$ of chain, $\overline{P}_4(c)$, we found that it can not be defined on the same line with Eq. 2, i.e.

$$\overline{P}_4(c) = -\frac{7.445}{n}\sum_i \frac{35\cos^4\theta_i - 30\cos^2\theta_i + 3}{8} \tag{9}$$

in which -7.445 is introduced so as to be $\overline{P}_4(c) = 1$ for all-trans chain which lies along the director. Eq. 9 gives unreasonable value such as larger than 1 or smaller than -1. To investigate physically meaningful definition of higher order parameters of alkyl chain would be an interesting future subject.

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