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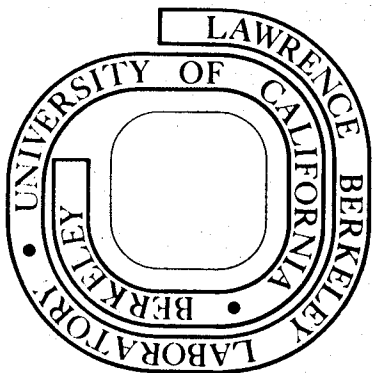
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MEASUREMENTS OF dc KERR CONSTANTS FOR A
HOMOLOGOUS SERIES OF NEMATIC COMPOUNDST. Bischofberger,[†] Robert Yu,^{**} and Y. R. Shen^{*}Physics Department, University of California
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ABSTRACT

The dc Kerr constants of seven p,p'-di-n-alkoxy-azoxybenzene homologous compounds have been measured as functions of temperature in the isotropic phase. The observed pretransitional behavior near the isotropic-nematic transition is consistent with the phenomenological model of Landau-de Gennes with the Onsager's local-field correction included in the dielectric tensor. The dc polarizability anisotropy and the average orientation of the permanent dipole with respect to the long molecular axis are deduced from the experimental results. Their variations with increase of methylene groups in the alkyl chains are discussed.

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I. Introduction

Liquid crystalline materials are composed of highly anisotropic molecules. Therefore, the field-induced birefringence in such materials is often very strong.¹⁻³ Even in the isotropic phase, the Kerr effect in a liquid crystal can be larger than in CS_2 by more than one order of magnitude. Measurements of both dc and optical Kerr constants for several liquid crystalline materials have been reported in the literature.^{2,3} The difference between dc and optical Kerr effects is that the permanent dipoles on the molecules contribute only to the former but not to the latter. In all cases, the Kerr constant shows a critically divergent pretransitional behavior as the temperature approaches the isotropic-to-nematic transition.

As pointed out by de Gennes,⁴ the pretransitional effect due to molecular ordering in a nematic liquid crystal can be described by the Landau's model for phase transition. According to the model, the field-induced birefringence should vary with temperature as $(T - T^*)^{-1}$, where T^* is a fictitious second-order transition temperature. This explains successfully the results of both the magnetic-field-induced birefringence¹ and the optical Kerr effect,³ but measurements of the dc Kerr effect have indicated that this simple temperature dependence does not hold.² Taking into account the permanent dipole contribution and using Onsager's model⁵ for local-field correction in Maier and Meier's mean-field theory,⁶ one can however find a modified temperature dependence which agrees well with the results.⁷ In fact, from the temperature dependence of the results, one can deduce the relative contributions of permanent and induced dipoles to the dc Kerr constant.

In the present paper, we report the results of our recent measurements on the dc Kerr constants as functions of temperature for seven homologous compounds of p,p'-di-n-alkoxy-azoxybenzenes (PAA) ($C_n H_{2n+1} O - C_6 H_4 - N_2 O - C_6 H_4 - O C_n H_{2n+1}$ with $n = 1, 2, \dots, 7$). So far as we know, this is the first time the dc Kerr constants for a homologous series of compounds are measured. In Sec. II, we review the theory of dc Kerr effect. We show that by using Onsager's local-field correction in the Landau-de Gennes model, the explicit expression with the correct temperature dependence for the Kerr constant can be derived. In Sec. III, we describe the experimental arrangement, sample preparation, and experimental results. Finally, in Sec. IV, we compare the results with theory, and find the relative contributions of permanent and induced dipoles to the Kerr constants. Then, since the relevant parameters in the expression for the Kerr constant are known from other measurements, we can deduce the values of anisotropy in dc polarizabilities and orientation of the permanent dipole for each compound. The variation of these values as functions of the number of methylene groups is discussed.

II. Theory

We use the formalism of Landau-de Gennes⁴ to describe the dc Kerr effect. The applied dc electric field \vec{E}^{dc} induces some molecular alignment even in the isotropic fluid. The degree of molecular alignment can be described by a macroscopic tensorial order parameter \vec{Q} which is defined by the relation

$$\epsilon_{ij} = \bar{\epsilon} \delta_{ij} + \frac{2}{3}(\Delta\epsilon)Q_{ij}, \quad (1)$$

where ϵ_{ij} is the dc dielectric tensor, $\bar{\epsilon} = \frac{1}{3} \sum_i \epsilon_{ii}$, $\Delta\epsilon$ is the anisotropy in ϵ_{ij} when all molecules are perfectly aligned in one direction, say \hat{x} , such that $Q_{xx} = -2Q_{yy} = -2Q_{zz} = 1$. By this definition, \vec{Q} is a symmetric traceless tensor. In the absence of the applied field, Q_{ij} is zero for an isotropic fluid.

Let $F(Q_{ij})$ be the free energy per unit volume of the fluid. In the isotropic phase, the field-induced ordering is often much smaller than 1. It is therefore a good approximation to expand $F(Q_{ij})$ into power series of Q_{ij} and retain only the lower order terms. We have the so-called Landau expansion

$$F = F_0 + \frac{1}{2} a(T - T^*) Q_{ij} Q_{ji} - (1/8\pi) \epsilon_{ij} E_i^{dc} E_j^{dc}, \quad (2)$$

where F_0 is independent of Q and a is a constant independent of temperature. The field-induced ordering Q_{ij} can then be obtained from minimization of F , i.e., $\partial F / \partial Q_{ji} = 0$. With \vec{E}^{dc} along \hat{x} , we find

$$Q_{xx} = -2Q_{yy} = (1/18\pi) (\Delta\epsilon) (E^{dc})^2 / a(T - T^*). \quad (3)$$

Using Onsager's model for local-field correction, Maier and Meier⁶ have derived an expression for $\Delta\epsilon$ which includes contributions from both induced and permanent dipoles.

$$\Delta\epsilon = 4\pi N [\Delta\alpha + F\mu^2 (3 \cos^2 \beta - 1) / 2kT] hF, \quad (4)$$

where N is the number of molecules per unit volume, $\Delta\alpha$ is the anisotropy

in the dc molecular polarizability, μ is the permanent dipole, β is the average angle the permanent dipole makes with the long axis of the molecule, $F = 1/(1 - \bar{\alpha}f)$ is the factor describing the reaction field, $\bar{\alpha}$ is the average molecular polarizability, $f = 8\pi N(\bar{\epsilon} - 1)/3(2\bar{\epsilon} + 1)$, and $h = 3\bar{\epsilon}/(2\bar{\epsilon} + 1)$ is the factor describing the cavity field. According to the model, the local-field effect is accounted for by the product hF .

Although Q_{ij} is defined through the dc dielectric tensor in Eq. (1), we expect that it also describes the induced anisotropy in the optical dielectric constant very well.^{1,8} The field-induced optical birefringence in the isotropic fluid can therefore be written as

$$\delta n(\omega) = (2\pi/n_\omega)\Delta\chi(\omega)Q_{xx}, \quad (5)$$

where n_ω is the linear refractive index, $\Delta\chi(\omega)$ is the anisotropy in the optical susceptibility tensor, and ω is the optical frequency. From Eqs. (3), (4), and (5) and from the definition of the dc Kerr constant $B = (\omega/2\pi c)\delta n/(E^{dc})^2$, we find

$$B = (2\omega/9c)(NhF/n_\omega)(\Delta\chi/a)[\Delta\alpha + F\mu^2(3\cos^2\beta - 1)/2kT]/(T - T^*). \quad (6)$$

As seen in the above equation, the induced-dipole part (the $\Delta\alpha$ term) and the permanent-dipole part (the μ^2 term) have different temperature dependence. If the various parameters, N , h , F , n_ω , $\Delta\chi$, a , and T , in Eq. (6) are known for a given medium, then from the temperature dependence of B , we can deduce $\Delta\alpha$ and $\mu^2(3\cos^2\beta - 1)$. If in addition μ is also known, we can find the angle β which describes the orientation of the permanent

dipole with respect to the long molecular axis. For elongated molecules of nematic compounds, $\Delta\alpha$ is always positive, but the permanent-dipole term in Eq. (6) can be either positive or negative depending on β .

III. Experiment

The dc Kerr effect was measured at 6328 Å by using a 1-mW He-Ne laser as the light source. A low-frequency sinusoidal wave generator followed by a high-voltage power amplifier were used to drive the Kerr cell. The length of the cell and the separation of the electrodes were $L = 1$ cm and $d = 0.2$ cm, respectively. The cell was between a set of crossed polarizers. The beam passing through the analyzer due to induced birefringence in the cell was detected by a photomultiplier and was displayed on an oscilloscope to be measured.

The sample of azoxybenzene derivatives were purchased from Eastman Kodak Co. and were purified by recrystallization from saturated solutions in various solvents.³ The recrystallized sample was placed in a square optical cell (Kerr cell), which was evacuated for several hours to remove atmospheric H_2O , O_2 and the residual solvent. They showed a sharp isotropic-nematic transition and the transition temperature T_k , given in Table I, remained constant with time. During the measurements the cell was kept under vacuum and was placed in a thermocontrolled oven. The temperature of the sample could be stabilized within 0.02° C.

The Kerr constant B of a sample at a given temperature was obtained from the slope of the measured induced birefringence as a linear function of $(E^{dc})^2$. A typical example is shown in Fig. 1. In our experiment, we have obtained B as a function of T for the seven azoxybenzene derivatives with $n = 1, 2, \dots, 7$ denoting the number of methylene groups in the alkyl

chain. The results are shown in Fig. 2. We note that PAA ($n = 1$) is the only homologue whose dc Kerr constant changes in sign in the temperature range we studied. This was first reported by Tsvetkov and Ryumtsev.² All other compounds in the homologous series have a negative dc Kerr constant, indicating that the permanent-dipole contribution dominates over the induced-dipole part.

The solid lines in Fig. 2 were derived from Eq. (6) by a least square fit to the data. The value of T^* for each compound was obtained by plotting the data as B^{-1} versus T and extrapolating the curve to $B^{-1}(T = T^*) = 0$. Then, from $(T - T^*)B$ versus T^{-1} , the induced-dipole and permanent-dipole contributions could be deduced from the point where the line intersects the ordinate and from the slope of the line respectively. At $T = T^0$, the two contributions are equal and $B(T^0) = 0$. The values of T^* and T^0 we obtained for the seven homologous compounds are listed in Table I. We find our values of $(T_k - T^*)$ for these compounds are in very good agreement with those deduced earlier from the optical Kerr measurements.³

It happens that the various parameters N ,⁹ $\bar{\epsilon}$,¹⁰ $\Delta\chi$,³ a ,³ and n_ω ,⁸ in Eq. (6) are known from previous measurements for the PAA series. Therefore, from Eq. (6) and the results in Fig. 2, we can deduce the values of $\Delta\alpha$ and $\mu(1 - 3 \cos^2\beta)^{1/2}$ for these compounds. They are listed in Table I and also plotted as a function of the number n of methylene groups in the alkyl chain in Fig. 3. The accuracy of these values has suffered from accumulating uncertainties in the parameters we used in the calculations. An error of about $\pm 15\%$ is typical.

IV. Discussion

The increase of alkyl chain length by addition of methylene groups

modifies the physical behavior of the homologous compounds in many ways.^{3,8} In Fig. 3, the anisotropy $\Delta\alpha$ in the dc molecular polarizability increases smoothly with increase of the alkyl chain length. No saturation of $\Delta\alpha$ at large n is found. This is in contrast to the behavior of the optical polarizability anisotropy $\Delta\alpha_{\text{opt}}$ which shows an obvious saturation at large n .⁸ The difference can be explained as follows. Because their lower transition frequencies are closer to the optical frequency, the core (azoxybenzene) electrons contribute much more to the optical $\Delta\alpha_{\text{opt}}$ than the bond electrons in the alkyl chains. Therefore, the increase of $\Delta\alpha_{\text{opt}}$ with n appears to be saturated. On the other hand, since the transition frequencies of both the core electrons and the bond electrons in the chain are far away from zero frequency, their contributions to the dc $\Delta\alpha$ are not very different and hence the increase of $\Delta\alpha$ with n is unsaturated.

The permanent-dipole factor $\mu(1 - 3 \cos^2 \beta)^{1/2}$ also shows a smooth increase with the alkyl chain length. Maier and Baumgartner¹¹ have measured the permanent dipole moment μ of these homologous compounds in highly diluted solution of benzene. Their values are shown in Fig. 4. As expected, μ is essentially independent of the alkyl chains since it is known to come from the N_2O group in the core. Using these values for μ , we can then deduce the angle β . In all cases, we have found a β value which is between 45° and 90° . This is a confirmation on the correctness of our theoretical analysis since otherwise the deduced value of β could be physically unreasonable. We have plotted our values of β as a function of n in Fig. 4. For $n = 1$ and 6 , these values are in good agreement with those calculated from the dielectric dispersion measurements¹⁰ (also shown in Fig. 4). For larger n , the angle β between the permanent dipole and the long mole-

cular axis is closer to 90° . The addition of methylene groups to the alkyl chains presumably creates a more balanced average local field at the core to align the permanent dipole more closely towards the normal of the molecular plane.

Since β is larger than 60° , the permanent dipoles like to align the long molecules nearly perpendicular to the applied field while the induced dipoles like to align the molecules parallel to the field. The competition between the two gives rise to the possible change of sign of the dc Kerr constant as it varies with temperature. This is experimentally observed in PAA. For the other homologous compounds, as β increases with n , the permanent-dipole contribution becomes larger and dominates over the induced-dipole contribution leading to the negative Kerr constants in a wide temperature range above T_k .

In conclusion, we have shown that with the Onsager's local-field correction, the phenomenological theory of Landau-de Gennes gives a correct temperature dependence of the dc Kerr effect. From the experimental results, we can deduce the dc polarizability anisotropy and the average orientation of the permanent dipole with respect to the long molecular axis. The effects of addition of methylene groups to the alkyl chains on these quantities have been observed.

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FIGURE CAPTIONS

- Fig. 1 Typical results of measurement on the induced birefringence versus the square of the applied dc electric field for PAA at $T = 415.4^\circ \text{ K}$. The slope of the line yields a Kerr constant $B = 0.73 \cdot 10^{-6} \text{ cm}^2/\text{erg}$.
- Fig. 2 Experimental results of $(T - T_k^*)B$ vs. T^{-1} for the azoxybenzene derivatives $n = 1, 2, \dots, 7$. The solid curves are calculated from Eq. (6). The arrows indicate the isotropic-nematic transition temperature T_k .
- Fig. 3 Variations of $\Delta\alpha$ and $\mu(1 - 3 \cos^2\beta)^{1/2}$ with the number n of carbon atoms in the alkyl chain of $\text{C}_n\text{H}_{2n+1}^0 - \text{C}_6\text{H}_4 - \text{N}_2\text{O} - \text{C}_6\text{H}_4 - \text{OC}_n\text{H}_{2n+1}$.
- Fig. 4 Variations of the permanent dipole μ , given by Ref. 11, and the angle β with the number of carbon atoms in the alkyl chain of $\text{C}_n\text{H}_{2n+1}^0 - \text{C}_6\text{H}_4 - \text{N}_2\text{O} - \text{C}_6\text{H}_4 - \text{OC}_n\text{H}_{2n+1}$. The open circles are values of β obtained from dielectric dispersion measurements in Ref. 9.

TABLE I

Values of T_k , T^* , T^0 , $\Delta\alpha$ and $\mu(1 - 3 \cos^2\beta)^{\frac{1}{2}}$ for azoxybenzene derivatives with $n = 1, 2, \dots, 7$ deduced from our experiment.

n	1	2	3	4	5	6	7	
T_k	404.8	436.3	393.2	403.2	391.4	396.7	392.6	°K
T^*	402.3	432.8	390.5	398.4	387.0	395.7	391.9	°K
T^0	409.8	452.5	404.4	419.8	415.5	435.0	432.3	°K
$\Delta\alpha \times 10^{24}$	37.0	37.3	39.4	42.3	46.2	50.7	54.0	cm ³
$\mu(1 - 3 \cos^2\beta)^{\frac{1}{2}}$	1.49	1.60	1.61	1.73	1.84	2.01	2.09	Debye

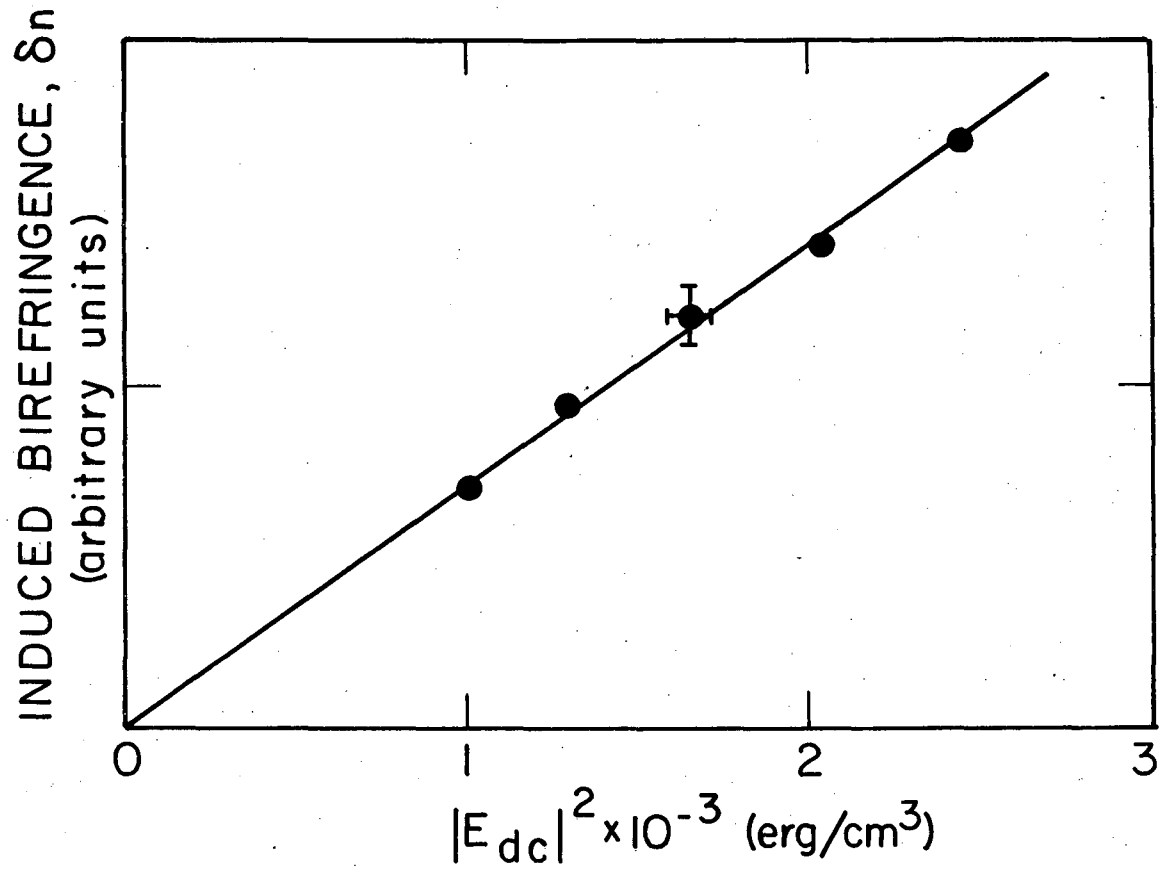


FIGURE 1

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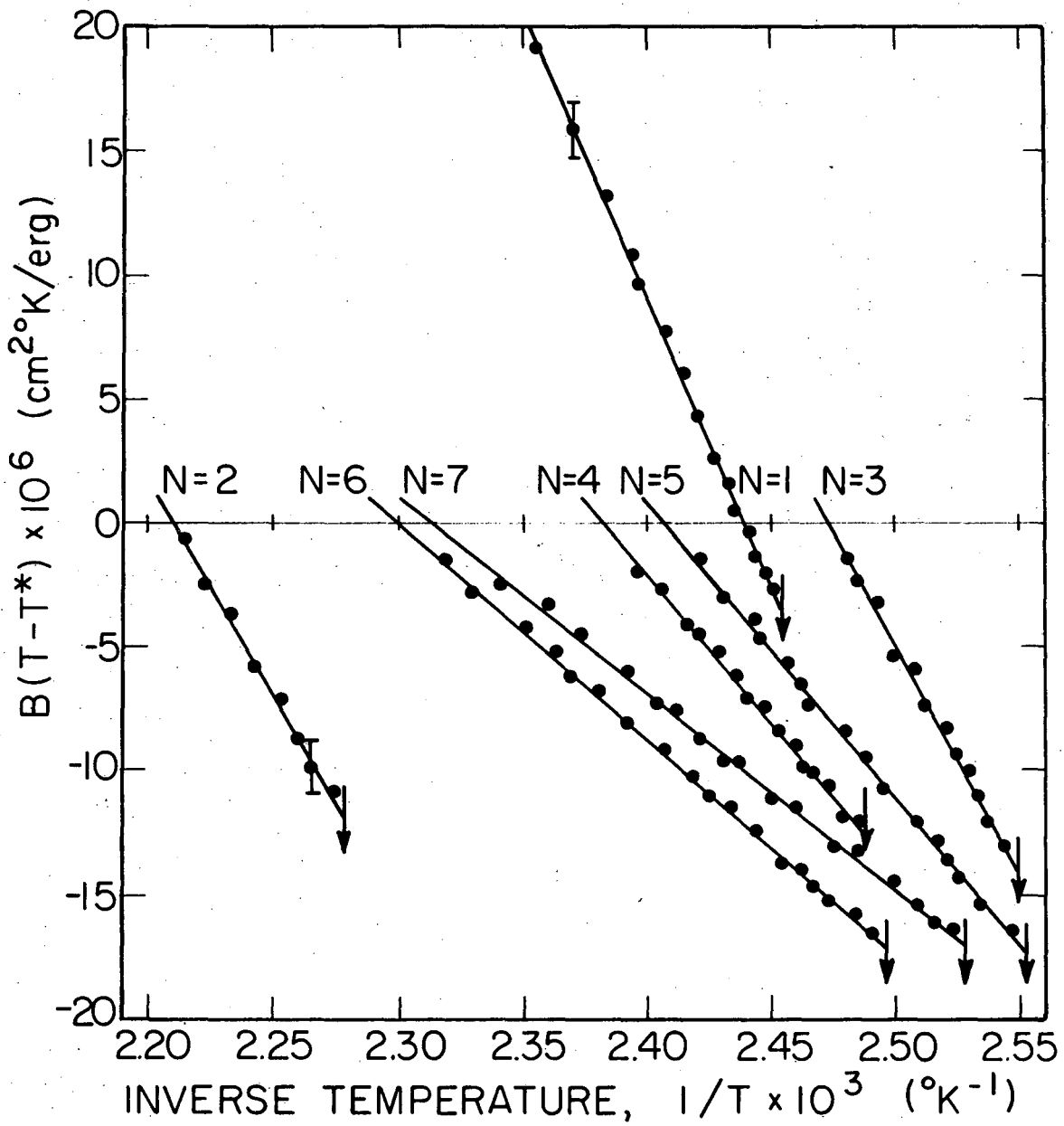


FIGURE 2

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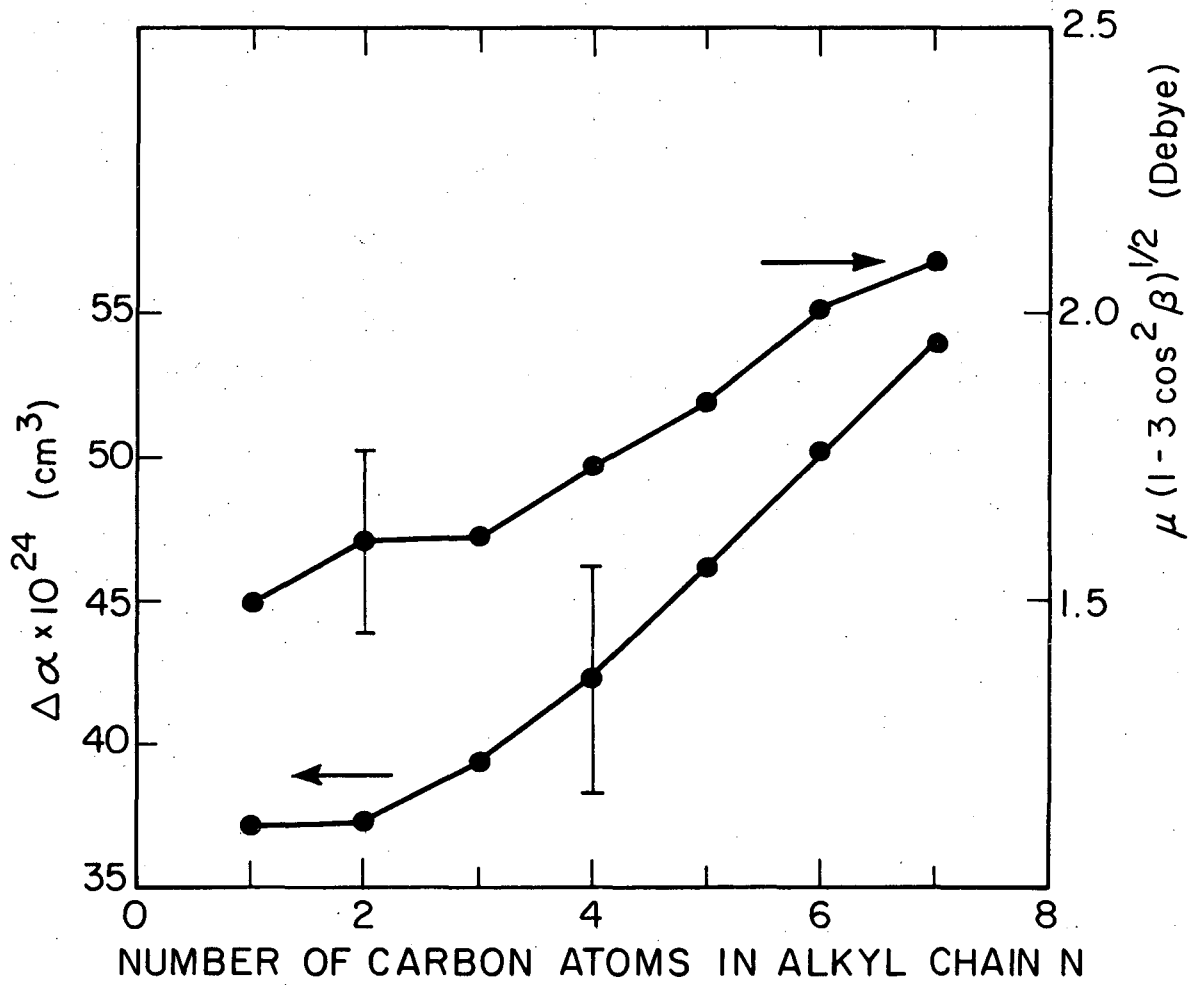


FIGURE 3

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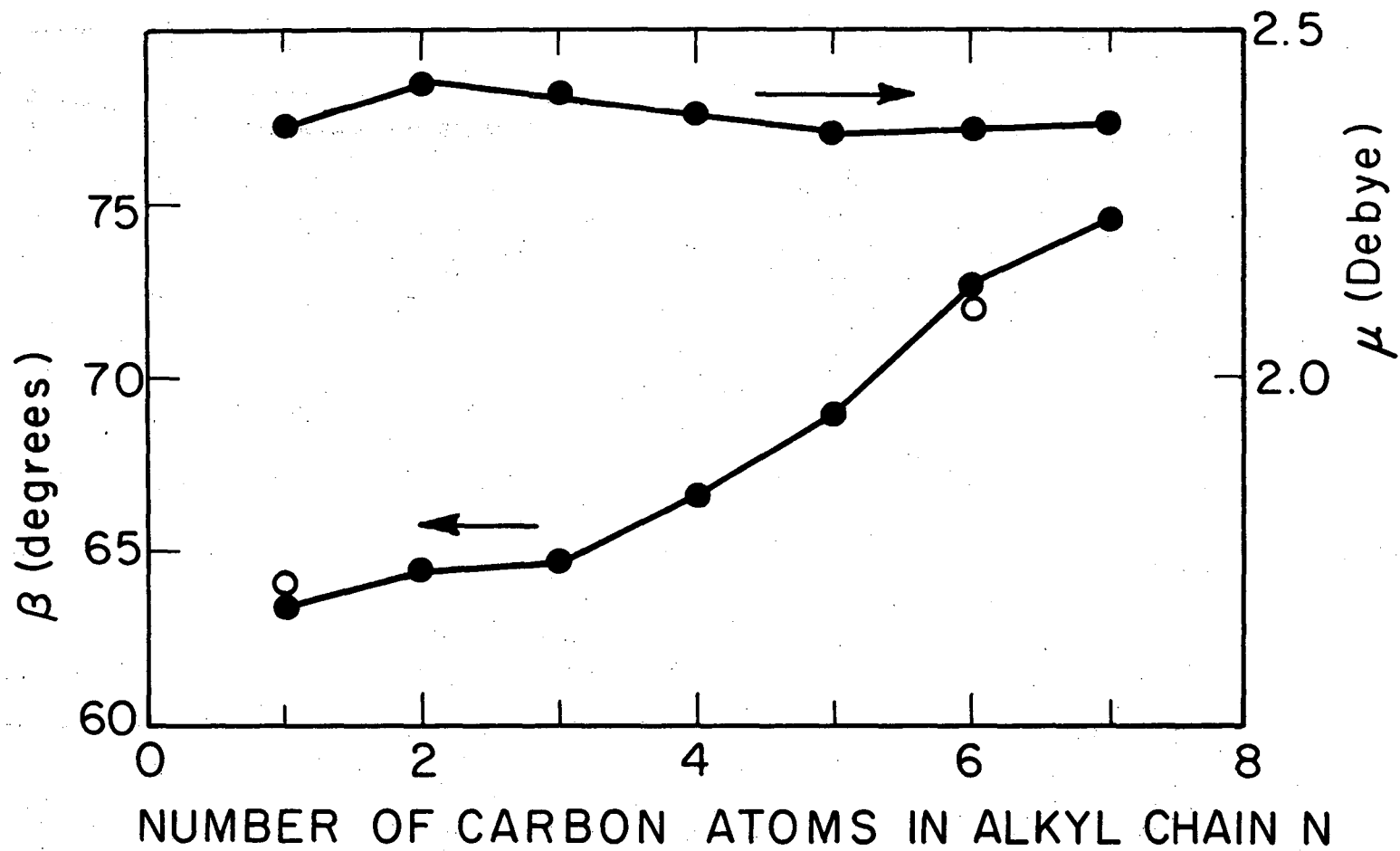


FIGURE 4

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