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Refractive Indices and Optical Anisotropy of Homologous Liquid Crystals

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Refractive Indices and Optical Anisotropy of Homologous Liquid Crystals†

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We have measured as functions of temperature the refractive indices and linear birefringence of seven homologous compounds of *p*, *p'*-di-*n*-alkoxy-azoxybenzenes in the nematic phase. Using the Vuks' model of local-field correction, we have deduced from our results both the microscopic and the macroscopic order parameters. The former agree well with those determined by Pines *et al* from the NMR results. The variations of the various microscopic parameters with the increase of the alkyl chain length are discussed. It is shown that addition of CH_2 groups to the alkyl chain increases the average polarizability much faster than the polarizability anisotropy. Contributions to the polarizability anisotropy from the core and from the alkyl chains respectively are found.

I INTRODUCTION

Among the many interesting properties of liquid crystals, optical birefringence is probably the most important. It is the basis of liquid crystal display as well as other device applications. Physically, the strong optical birefringence arises from alignment of molecules with large molecular anisotropy.[1] The molecular anisotropy reflects not only the geometric shape of the molecules but also anisotropy of their electronic orbitals. With increasing molecular alignment in the nematic phase, the optical birefringence increases accordingly. It can therefore be used as a measure of the nematic order.

As emphasized by the de Gennes,[2] any tensorial property of the nematics can be used to define a nematic order parameter. Thus, we can write the

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refractive indices parallel and perpendicular to the direction of molecular alignment as

$$\begin{aligned} n_{\parallel} &= \bar{n} + \tfrac{2}{3}Q\Delta n \\ n_{\perp} &= \bar{n} - \tfrac{1}{3}Q\Delta n \end{aligned} \tag{1}$$

where $\bar{n}$ is the average refractive index, Q the order parameter, and Δn the birefringence corresponding to full molecular alignment ($Q = 1$). From Eq. (1), the optical birefringence is given by

$$\delta n = n_{\parallel} - n_{\perp} = Q\Delta n. \tag{2}$$

The order parameter Q defined in Eq. (1) is in general not identical to the order parameters defined through other tensorial properties such as electric and magnetic susceptibilities, although all order parameters should range from 0 for random molecular orientation to 1 for perfect alignment. In particular, because of local-field correction due to intermolecular interaction, Q should be different from the microscopic order parameter defined as[2]

$$S = \langle (3\cos^2\theta - 1)/2 \rangle \tag{3}$$

where θ is the angle between the long molecular axis and the average direction of molecular alignment. However, with a given model for local-field correction, there should be a definite relation between Q and S. For example, the Vuks' model gives[3]

$$\delta n = (4\pi/3)\mathcal{N}(\overline{n^2} + 2)\delta\alpha/(n_{\parallel} + n_{\perp}) \tag{4}$$

$$(\Delta\alpha/\bar{\alpha})S = (n_{\parallel} + n_{\perp})\delta n/(\overline{n^2} - 1) \tag{5}$$

where $\delta\alpha = \alpha_{\parallel} - \alpha_{\perp} = S\Delta\alpha$, $\mathcal{N}$ is the number of molecules per unit volume, the superbars indicate average over molecular orientations, $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the average polarizabilities parallel and perpendicular to the direction of alignment respectively, and $\Delta\alpha$ is the polarizability anisotropy at $S = 1$. From Eqs. (2) and (4), we find immediately

$$Q = \frac{(2\bar{n} + \delta n/3Q)}{(2\bar{n} + \delta n/3)} S. \tag{6}$$

Usually, we have $\Delta n \sim 0.4$ and $\bar{n} \sim 1.6$. Then, Eq. (6) shows that for intermediate values of Q or S, the two order parameters can differ by a few percent and Q is not strictly proportional to S.

Several authors have suggested that one can express the temperature dependence of the order parameter S in the form[4,5]

$$S = (1 - T/T^{+})^{\gamma} \tag{7}$$

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where T^+ and γ are constant coefficients. Then, by least-square fitting the results of $(\Delta\alpha/\bar{\alpha})S$ versus T to the form $A(1 - T/T^+)^\gamma$, one can deduce both the absolute values of S and $\Delta\alpha/\bar{\alpha}$. Such an approach, however, has implicitly assumed that $Q = 1$ at $T = 0°K$ and $A = \Delta\alpha/\bar{\alpha}$. These assumptions are not justifiable. In fact, as we shall see later from our work, S can indeed be approximated by $S_0(1 - T/T^+)^\gamma$ but the constant S_0 is different from 1.

Experimentally, δn can be measured with very high accuracy.[4] If we neglect the temperature dependence of Δn, then $\delta n(T)$ gives directly the variation of nematic order with temperature. On the other hand, if a particular local field model is chosen and $n_\parallel(T)$ and $n_\perp(T)$ are measured, we should be able to find the temperature dependence of Q and S without making other assumptions. The absolute values of Q and S, however, have to come from other measurements.

There already exist in the literature a number of reports on the measurements of refractive indices and optical birefringence of liquid crystals and their temperature dependence.[5] From these measurements, the order parameters were deduced and compared with those obtained from other measurements. One would expect that these measurements carried out on a homologous series of liquid crystals could yield valuable information about the effects of molecular structure on refractive indices, optical anisotropy, and molecular ordering. However, no such measurements have yet been reported.

In this paper, we present the results of refractive index measurements on the homologous series of *p,p'*-di-*n*-alkoxy-azoxybenzenes. We first describe in Section II the experimental arrangement, sample preparation, and experimental results. We then deduce the order parameters as functions of temperature for the homologous nematics and compare them with the microscopic order parameters deduced from nuclear magnetic resonance (NMR) measurements.[6] In Section III, we discuss the results and show how the increase of alkoxy chain length on the molecules affects the average molecular polarizability and the polarizability anisotropy.

II EXPERIMENT

We used the wedge method to measure the refractive indices and linear birefringence of the nematics.[4,7] As shown in Figure 1, the wedge was made of two glass plates with a 0.015 in. tungsten wire as the spacer to give an apex angle β of 0.0210 radian. The glass plates were coated with a surfectant (Dow Corning XZ 2-2024) and rubbed along the wedge axis. The nematic sample introduced into the wedge had its director parallel to the wedge axis. The wedged sample was then mounted on an enclosed hot stage which had a

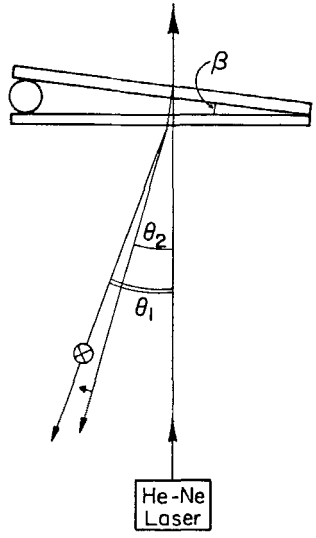

FIGURE 1 Schematic of the wedged sample.

temperature uniformity and stability of $\sim 0.1°C$ at an operating temperature of $\sim 130°C$. It was put under a microscope between crossed polarizers and illuminated by a He–Ne laser beam. The alignment direction of the nematic was 45° from the polarizer axes.

As seen in Figure 1, the incoming laser beam produced two reflected beams at angles θ_1 and θ_2 respectively from the sample. They were polarized parallel and perpendicular to the wedge axis respectively. The refractive indices $n_\parallel$ and $n_\perp$ could then be deduced from the Snell's law $n_{\parallel,\perp} = \sin\theta_{1,2}/\sin 2\beta$ if θ_1 and θ_2 were measured. At the same time, we could use the microscope to photograph the interference fringes in the beam transmitted through the sample. From the observed fringe spacing d, we could deduce the linear birefringence

$$\delta n = \lambda/\beta d \tag{8}$$

where λ is the He–Ne laser wavelength.

In our experiment, the samples of azoxybenzene derivatives

$$(C_NH_{2N+1}O—C_6H_4—N_2O—C_6H_4—C_NH_{2N+1}O \quad \text{with } N = 1, 2, \ldots, 7)$$

were purchased from Kodak Co. and recrystallized before use. The nematic-isotropic transition temperatures T_K remained constant during the measurement and were measured to an accuracy of $\pm 0.05°K$. The accuracy of the

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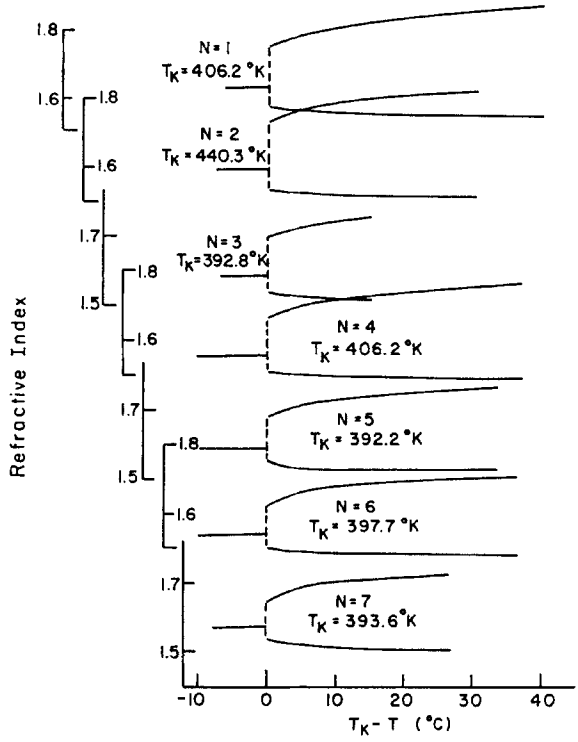

FIGURE 2 Refractive indices of the seven azoxybenzene derivatives ($N = 1, 2, \ldots, 7$) as functions of temperature. T_K is the isotropic-nematic transition temperature. For $T < T_K$, the upper and lower branches of the curves refer to optical polarizations parallel and perpendicular to the molecular alignment respectively.

refractive index measurements was better than $\pm 0.3\%$. The spacing of the interference fringes was determined by averaging over 20 ± 0.1 fringes. This led to a δn accurate to $<0.5\%$.

The results of our measurements of $n_{\parallel}$ and $n_{\perp}$ versus temperature for the seven homologous nematic liquid crystals are presented in Figure 2. The directly measured linear birefringence data δn versus T are shown in Figure 3. In all cases, $n_{\parallel} - n_{\perp}$ from the refractive index measurements and δn from the linear birefringence measurements agree well within the experimental accuracy. Our results on the $N = 1$ and $N = 2$ compounds agree very well with those reported earlier.[8]

As we mentioned in the last section, one can define a macroscopic order parameter $Q = \delta n/\Delta n$. With a given model of local field correction, Q is then related to the microscopic order parameter S. Here, we adopted the Vuks'

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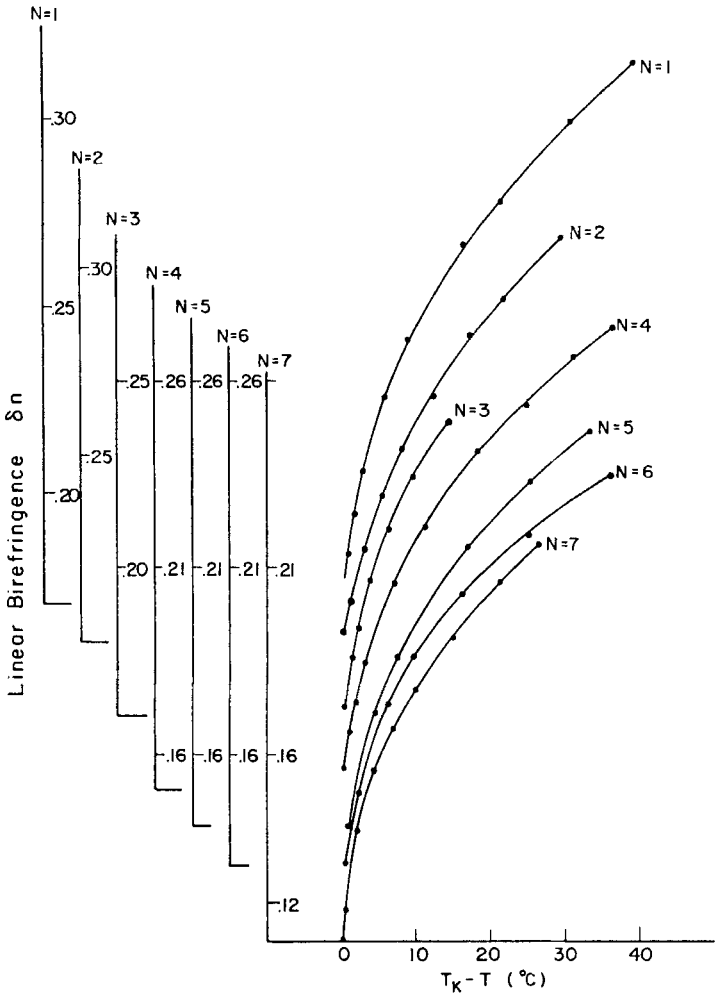

FIGURE 3 Linear birefringence δn of the seven azoxybenzene derivatives as functions of temperature.

local-field model.[3] Knowing $\delta n(T)$, $n_{\parallel}(T)$, and $n_{\perp}(T)$, we could find from Eqs. (5) and (6) the relative values of S and Q versus T, realizing that $\Delta\alpha/\bar{\alpha}$ should be essentially independent of temperature. Then, for each sample, we normalized our S value at a temperature sufficiently far below T_K (where T_K is the nematic-isotropic transition temperature) against the absolute S value obtained by Pines *et al.* from measuring the chemical shifts of the ^{13}C NMR

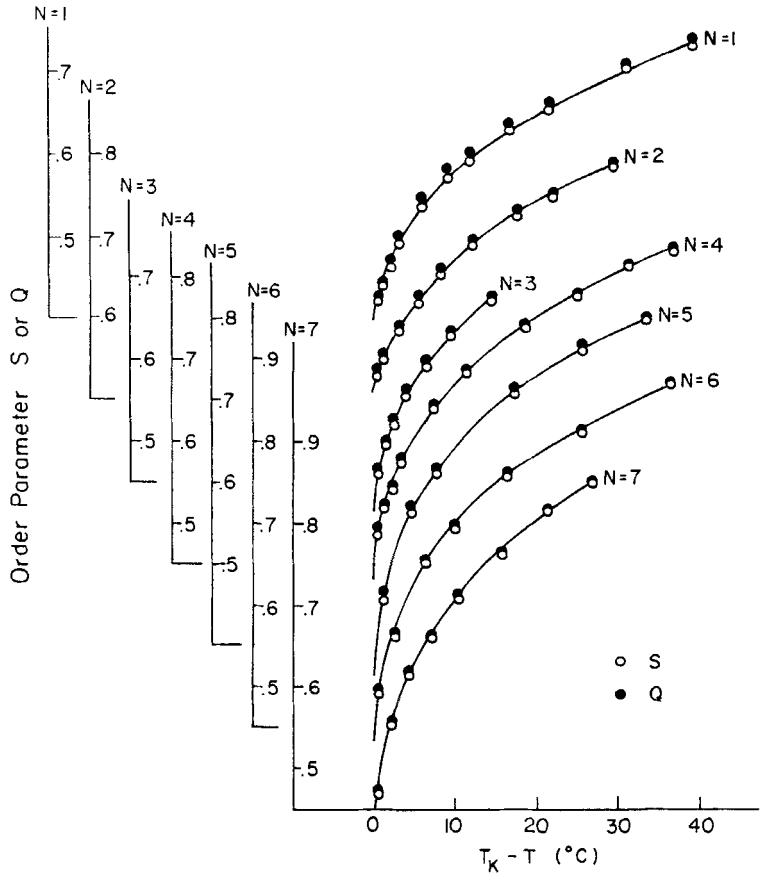

FIGURE 4 Microscopic order parameter S and macroscopic order parameter Q versus temperature for the seven azoxybenzene derivatives.

spectra.[6] The results of S and Q versus T thus obtained are shown in Figure 4. As an example, we compare our $S(T)$ results for PAA with those of Pines *et al.* obtained from NMR in Figure 5(a). We also show in Figure 5(b) $Q(T)$ and $\delta n(T)/\Delta n(T_0)$ for PAA, where T_0 is arbitrarily chosen to be 31°K below T_K.

In the process of deducing S, we also obtained values of $\Delta\alpha/\bar{\alpha}$ for the seven homologous compounds. They are listed in Table I and plotted in Figure 6 together with the order parameters $S(T_K)$ deduced from extrapolation of the curves in Figure 4.

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TABLE I

Values of $\Delta\alpha/\bar{\alpha}$, T_K, $S(T_K)$, $dV/V\,dT$, $\bar{\alpha}$, and $\Delta\alpha$ for the azoxybenzene derivatives with $N = 1, 2, \ldots, 7$.

N	1	2	3	4	5	6	7
$\Delta\alpha/\bar{\alpha}$	0.830	0.797	0.746	0.704	0.636	0.603	0.545
T_K(°K)	406.2	440.3	392.8	406.2	392.2	397.7	393.6
$S(T_K)$[a]	0.40	0.517	0.395	0.475	0.358	0.437	0.431
$S(T_K)$[b]	0.37	0.487	0.396	0.436	0.410	0.485	0.432
$dV/V\,dT(°C^{-1})$[a]	7.8×10^{-4}	9.4×10^{-4}	8.0×10^{-4}	8.9×10^{-4}	8.2×10^{-4}	7.1×10^{-4}	5.4×10^{-4}
$dV/V\,dT(°C^{-1})$[c]	8.2×10^{-4}	9.6×10^{-4}	—	—	—	—	—
$\bar{\alpha}(\times 10^{-24})$	31.9	36.5	39.8	43.7	49.5	51.0	57.4
$\Delta\alpha(\times 10^{-24})$	26.5	29.1	29.7	30.8	31.5	30.8	31.3

[a] This work
[b] Pines *et al* (Ref. 6)
[c] Ref. 9

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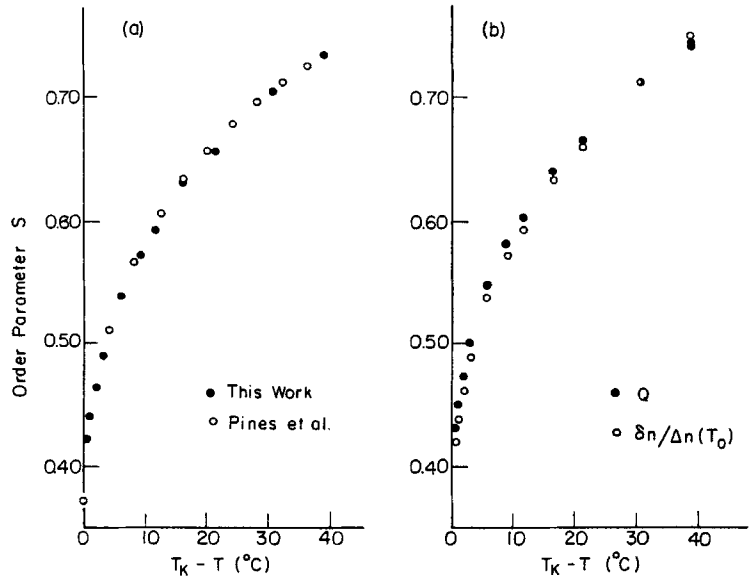

FIGURE 5 (a) Comparison of microscopic order parameters obtained in this work for *p*-azoxyanisole (PAA) with those of Pines *et al.* in Ref. 6. (b) Comparison of Q versus T with δn versus T for PAA.

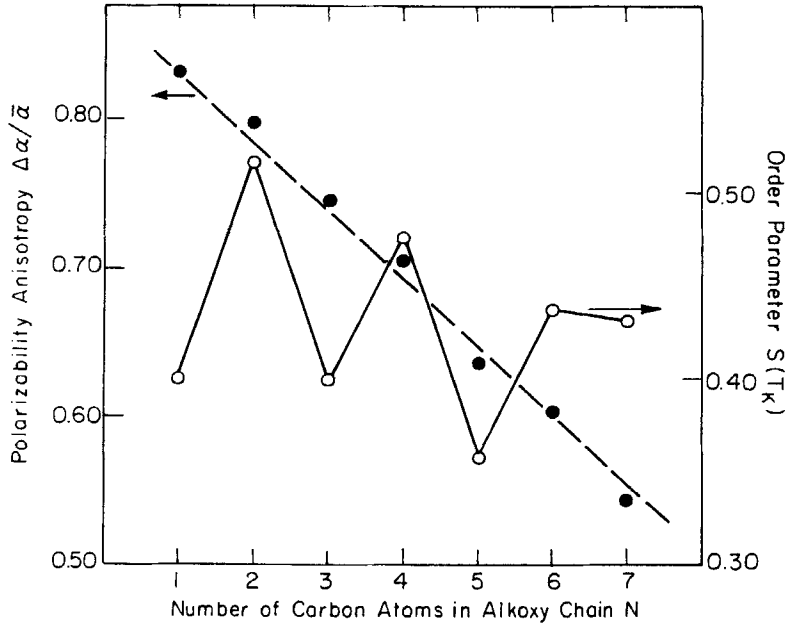

FIGURE 6 Variations of $\Delta\alpha/\bar{\alpha}$ and $S(T_K)$ with the number of carbon atoms in the alkyl chain of the *p*, *p*′-di-*n*-alkoxy-azoxybenzene homologous series.

III DISCUSSION

The highly accurate measurements of refractive indices and linear birefringence enables us to obtain the temperature variation of the order parameters with very good accuracy. The relative accuracy of S and Q shown in Figure 4 is certainly within 1%. The absolute values of S and Q depend on calibration of S at one temperature against measurements of Pines *et al.* which were accurate to within $\pm 3\%$.

In deducing the values of S and Q, we have used the Vuks' local-field model. We can check the validity of this model by comparing our S versus T curves with those of Pines *et al.*[6] The NMR experiment of Pines *et al.* measures the chemical shifts of ^{13}C spectra from which the microscopic order parameter can be deduced. As shown in Figure 5(a) for PAA, our results are in excellent agreement with theirs. Aside from the point at T_K, the highest discrepancy is about 1% and is certainly within the experimental uncertainty. The same is true for all the other homologous compounds we have studied. This shows that the Vuks' model is adequate for the present application of local-field correction.

Figure 4 shows a clear difference between the macroscopic order parameter Q and the microscopic order parameter S. The difference is due to local-field correction which is governed by Eq. (6) in the Vuks' model. In all cases, Q is larger than S by 0.5–2%, as it should be.

One may think that the temperature dependence of Δn in Eq. (2) should be negligible so that the linear birefringence δn versus T measures directly Q versus T. Actually, this is not true as can be seen in Figure 5(b) comparing Q with $\delta n/\Delta n(T_0)$ for PAA where $T_0 = T_K - 30.8°C$. The discrepancy between Q and $\delta n/\Delta n(T_0)$ is however less than 3%. This is also true for all the homologous compounds. The variation of Δn over a temperature range of 40°C is about 4%. It is presumably due to thermal expansion of the medium. The latter can be estimated from the expression

$$\mathcal{N}\bar{\alpha} = (3/4\pi)(\overline{n^2} - 1)/(\overline{n^2} + 2) \tag{9}$$

since $\bar{\alpha}$ should be independent of temperature. As an example, we show $\mathcal{N}\bar{\alpha}$ versus T for PAA in Figure 7. From the results, we can deduce the thermal expansion coefficient $dV/V\,dT$. We have listed the values of $dV/V\,dT$ for the seven homologous compounds in Table I. The first two agree well with those reported in the literature.[9]

For all the seven homologous compounds, we can fit our data of S versus T by an equation of the form

$$S = S_0(1 - T/T^+)^\gamma \tag{10}$$

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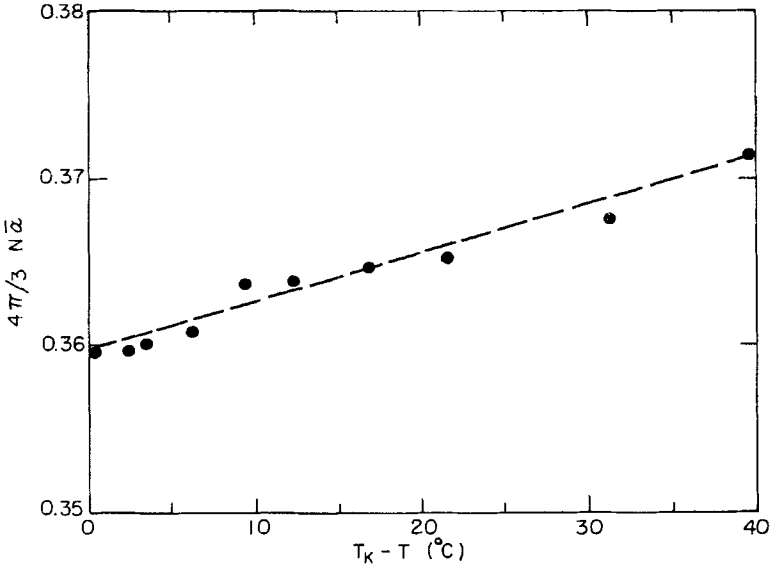

FIGURE 7 Variation of $4\pi\mathcal{N}\bar{\alpha}/3$ with temperature for *p*-azoxyanisole.

where S_0, γ, and T^+ are constants to be determined. We have listed the values of S_0, γ, and $T^+ - T_K$ for all the compounds in Table II. Contrary to what has been suggested,[4,5] we find in no case does $S_0 = 1$. As mentioned in Section I, this means that from the refractive index measurements only, it is not possible to obtain the absolute values of the order parameter S and the polarizability anisotropy $\Delta\alpha/\bar{\alpha}$. We note, however, that the exponent γ for all compounds except $N = 3$ falls in a narrow range between 0.181 and 0.192. The physical meaning of such a coincidence is not clear to us.

The values of $T^+ - T_K$ show a zigzag variation as N varies from 1 to 7. This actually reflects the well known zigzag behavior of $S(T_K)$ among the homologous compounds resulting from the cogwheel configuration of the alkyl chains. From either Eq. (10) or simple extrapolation of the curves in Figure 4 to T_K, we can obtain $S(T_K)$ for all compounds. They are plotted in Figure 6 showing explicitly the zigzag behavior. We compare our values of $S(T_K)$ with those of Pines *et al.*[6] in Table I. The discrepancy of $\sim 10\%$ is mainly due to inaccuracy in our extrapolation procedure and partly due to the larger uncertainty in the measurements of Pines *et al.* at T_K.

Figure 6 also shows that $\Delta\alpha/\bar{\alpha}$, the anisotropy of molecular polarizability normalized against the average polarizability, decreases almost linearly with the number of carbon atoms in the alkyl chain or with the increase of chain length. This suggests that the polarizability anisotropy $\Delta\alpha$ mainly comes

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TABLE II

Values of S^0, γ, and $T^+ - T_K$ obtained by least-square fitting of our data on S versus T to the form $S = S_0(1 - T/T^+)^\gamma$ for the azoxybenzene derivatives with $N = 1, 2, \ldots, 7$.

N	1	2	3	4	5	6	7
S_0	1.13 ± 0.03	1.27 ± 0.03	1.11 ± 0.03	1.32 ± 0.02	1.24 ± 0.02	1.34 ± 0.02	1.4 ± 0.04
γ	0.189 ± 0.008	0.182 ± 0.008	0.155 ± 0.01	0.192 ± 0.008	0.181 ± 0.007	0.189 ± 0.006	0.188 ± 0.01
$T^+ - T_K$(°K)	1.8 ± 0.3	3.3 ± 0.5	0.5 ± 0.2	2.0 ± 0.2	0.4 ± 0.2	1.1 ± 0.2	0.8 ± 0.2

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from the core (azoxybenzene) contribution. The covalent bond electrons in the alkyl chain, on the other hand, contribute more to the average polarizability than to the anisotropy. As a result, the addition of the CH_2 groups to the alkyl chain increases $\bar{\alpha}$ much more than $\Delta\alpha$, and so $\Delta\alpha/\bar{\alpha}$ decreases with with N. We can find $\bar{\alpha}$ and $\Delta\alpha$ explicitly if $\mathcal{N}$ is known. It turns out that the molar volumes of the seven homologous compounds studied here have actually been measured by Linsert.[11] Therefore, from Eq. (9) and our results on $\overline{n^2}$ and $\Delta\alpha/\bar{\alpha}$, we can deduce the values of $\bar{\alpha}$ and $\Delta\alpha$ separately. They are listed in Table I and plotted in Figure 8. As N increases from 1 to 7, $\bar{\alpha}$ increases almost linearly by a factor of 1.8 while $\Delta\alpha$ shows a saturable increase of a factor of 1.18. The saturation of $\Delta\alpha$ at larger N is presumably because the waggling end segment of the chain is more disordered than the core. By assuming an order parameter S_A which varies along the alkyl chain, Marčelja[10] has calculated S_A/S as a function of N. We can then write

$$\Delta\alpha = \Delta\alpha_0 + (S_A/S)N\Delta\alpha_A \tag{11}$$

where $\Delta\alpha_0$ comes from the core and $\Delta\alpha_A$ from each CH_2 group in the chain.

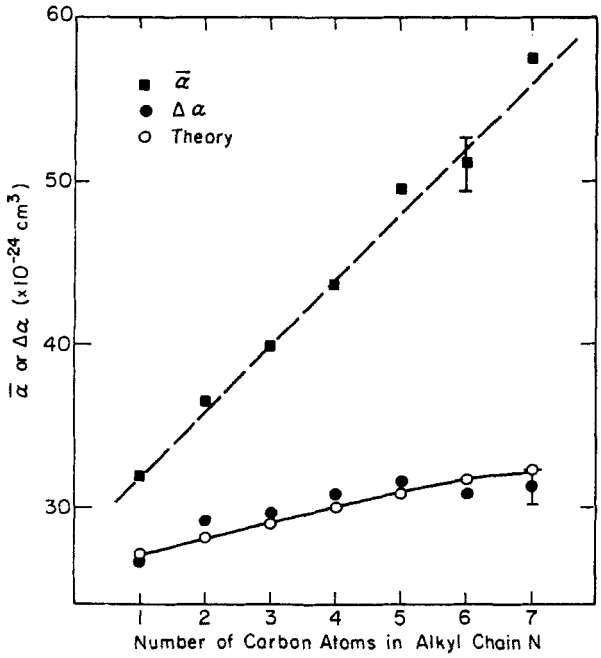

FIGURE 8 Variations of $\bar{\alpha}$ and $\Delta\alpha$ with the number of carbon atoms in the alkyl chain of the *p*, *p'*-di-*n*-alkoxy-azoxybenzene derivatives. The solid line is a theoretical fit using Eq. (11).

Using Marčelja's values of S_A/S, we can fit the data of $\Delta\alpha$ versus N with Eq. (11) in Figure 8, but the result suggests that Marčelja's values of S_A/S do not decrease fast enough with N. The least-square fit gives $\Delta\alpha_0 = 25.6 \times 10^{-24}$ and $\Delta\alpha_A = 2.06 \times 10^{-24}$

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IV CONCLUSION

Highly accurate measurements of refractive indices and optical anisotropy together with a local-field model enables us to deduce the temperature dependence of both microscopic and macroscopic order parameters with very good accuracy. We have made these measurements on seven homologous compounds of $C_NH_{2N+1}O—C_6H_4—N_2O—C_6H_4—OC_NH_{2N+1}$ with $N = 1, \ldots, 7$. Using the Vuks' model for local-field correction and calibrating the microscopic parameter at one temperature against that obtained by Pines *et al.* from NMR measurements, we have deduced as functions of temperature absolute values of both microscopic and macroscopic order parameters for these compounds. They agree very well with the results of Pines *et al.* on the temperature dependence of the microscopic order parameters. This shows that the Vuks' model is adequate in the present application. Our results also indicate that the use of linear birefringence $\delta n(T)$ as a direct measure of the temperature dependence of the order parameter could lead to a few percent error.

We have shown that for all the homologous compounds, the microscopic order parameter S as a function of temperature can be described by a simple equation $S = S_0(1 - T/T^+)^\gamma$, but S_0 is not equal to 1 as has been suggested by others. Our results on the homologous series also yield information about the effects of molecular structure on the optical properties. We have found that with increasing N from 1 to 7 in the C_NH_{2N+1} alkyl chain the average polarizability increases by a factor of 1.8 while the polarizability anisotropy only increases by a factor of 1.18. Using Marčelja's calculation, we have also been able to deduce separately the contributions to the polarizability anistropy from the core and from the CH_2 groups in the chain.

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