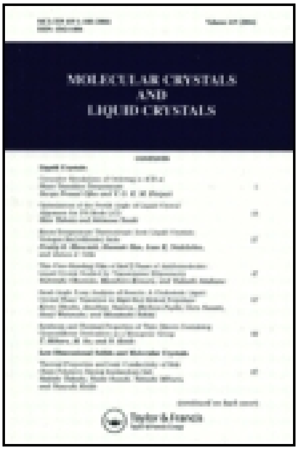

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Physical Studies of Homologous trans-4-ethoxy-4′-n-alkanoyloxyazobenzenes: Birefringence

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Physical Studies of Homologous *trans*-4-ethoxy-4′-*n*-alkanoyloxyazobenzenes: Birefringence.[1]

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The birefringence of a homologous series of nematogenic *trans*-4-ethoxy-4′-*n*-alkanoyloxyazobenzenes has been measured and observed trends correlated with the change in molecular structure represented by the increasing length of the terminal alkane chain. Order parameters calculated from the birefringence and density data on the basis of the isotropic and anisotropic internal field models are compared and discussed. Also the theory fitting the birefringence data to a power series in temperature is discussed. Fractional volume changes calculated for the nematic-isotropic transition using refractive index data are compared to experimentally observed values.

INTRODUCTION

Refractive index and birefringence measurements are readily determined as functions of temperature and provide useful checks on various theoretical treatments of the nematic phase. Very few reports of birefringence data exist in the literature and even fewer report such data for homologous series of liquid crystals.[2,3,4] We report here the refractive index and birefringence data for the homologous series of nematogenic 4-ethoxy-4′-*n*-alkanoyloxyazobenzenes $CH_3CH_2O—C_6H_4N:NC_6H_4OC(:O)(CH_2)_nCH_3$ for $n =$ 3 to 12. The order parameters, calculated for the series using both the isotropic internal field model of Vuks[5] and the anisotropic internal field model of Neugebauer,[6] are compared and discussed in terms of molecular structure. The data is also discussed in light of the theory of Chandrasekhar *et al.* describing the temperature dependence of birefringence as a power series.[7]

TABLE I

Birefringences and refractive indices data for the nematogenic *trans*-4-ethoxy-4′-*n*-alkanoyloxyazobenzenes measured at 589.3 nm.

$T(K)$	n^a	Δn	$T(K)$	n^a	Δn	$T(K)$	n^a	Δn	$T(K)$	n^a	Δn	$T(K)$	n^a	Δn
PENTANOATE $T_{NI} = 400.2$			HEXANOATE $T_{NI} = 401.6$			HEPTANOATE $T_{NI} = 392.3$			OCTANOATE $T_{NI} = 392.8$			NONANOATE $T_{NI} = 387.7$		
354	1.4977	0.286	354	1.4930	0.329	350	1.4949	0.273	360	1.4848	0.279	350	1.4896	0.274
360	1.4982	0.278	360	1.4930	0.321	356	1.4950	0.264	366	1.4893	0.269	356	1.4899	0.264
366	1.4985	0.269	366	1.4931	0.312	362	1.4950	0.255	372	1.4900	0.259	362	1.4905	0.253
372	1.4990	0.259	372	1.4933	0.302	368	1.4950	0.245	378	1.4917	0.247	368	1.4915	0.241
378	1.5002	0.248	378	1.4935	0.287	374	1.4955	0.234	384	1.4950	0.228	374	1.4935	0.223
384	1.5030	0.233	384	1.4944	0.270	380	1.4975	0.216	386	1.4966	0.219	380	1.4968	0.198
388	1.5058	0.220	390	1.4964	0.252	384	1.4995	0.202	388	1.4987	0.216	382	1.4987	0.187
			394	1.4985	0.237	388	1.5026	0.184	390	1.5012	0.187	384	1.5011	0.172
						390	1.5050	0.168	392	1.5042	0.156	386	1.5046	0.150
						392	1.5078	0.135				387	1.5097	0.136
												387.2	1.5145	0.131
												388	1.5555	—
												390	1.5550	—
												392	1.5543	—
												394	1.5537	—

TABLE I (*Continued*)

$T(K)$	n^a	Δn	$T(K)$	n^a	Δn	$T(K)$	n^a	Δn	$T(K)$	n^a	Δn	$T(K)$	n^a	Δn
DECANOATE $T_{NI} = 386.1$			UNDECANOATE $T_{NI} = 383.1$			DODECANOATE $T_{NI} = 382.5$			TRIDECANOATE $T_{NI} = 379.1$			TETRADECANOATE $T_{NI} = 379.4$		
352	1.4852	0.237	356	1.4872	0.222	356	1.4841	0.222	360	1.4830	0.214	360	1.4810	0.215
358	1.4862	0.235	362	1.4875	0.211	362	1.4852	0.210	366	1.4843	0.192	364	1.4826	0.205
364	1.4874	0.231	368	1.4888	0.198	368	1.4868	0.198	370	1.4860	0.177	368	1.4847	0.193
370	1.4889	0.226	374	1.4916	0.180	374	1.4900	0.179	374	1.4884	0.158	372	1.4875	0.179
376	1.4910	0.214	378	1.4948	0.161	378	1.4937	0.161	376	1.4912	0.148	374	1.4891	0.167
380	1.4931	0.199	380	1.4978	0.149	380	1.4966	0.148	378	1.4960	0.133	376	1.4918	0.152
382	1.4954	0.186	381	1.5006	0.141	381	1.4988	0.138	379	1.5010	0.119	377	1.4942	0.138
384	1.5000	0.168	382	1.5060	0.129	382	1.5016	0.121	379.2	1.5056	0.115	380	1.5417	—
385	1.5056	0.156	382.1	1.5078	0.127	384	1.5469	—	380	1.5446	—	384	1.5397	—
385.2	1.5095	0.153	384	1.5508	—	386	1.5458	—	384	1.5423	—	388	1.5376	—
386	1.5538	—	386	1.5497	—	388	1.5448	—	388	1.5400	—	392	1.5355	—
388	1.5533	—	388	1.5486	—	390	1.5437	—	392	1.5377	—			
390	1.5526	—	392	1.5465	—									
394	1.5515	—												

[a] n here is either the ordinary or isotropic refractive index depending on the temperature.

Further, the fractional volumes at the nematic to isotropic transition temperature, T_{NI}, calculated by the method of Haller *et al.*, are compared to experimental values obtained by dilatometry.[8]

EXPERIMENTAL

The ordinary refractive index of the nematic and the isotropic phases was determined at 589.3 nm using a Bausch and Lomb Abbe-3L refractometer attached to a thermostatted circulating oil bath. To prevent possible misalignment problems caused by the epoxies holding the prisms, the maximum safe operating temperature of the Abbe was taken to be 125°C. This maximum prevented measurement of n_0 for some of the compounds in the isotropic phase. The birefringence measurements, also at 589.3 nm, were obtained by measurement of uniformly spaced fringes in a sample contained in a glass wedge.[8] A modified Koeffler hot stage provided the temperature control.

The thermometric accuracy of the birefringence measurements was estimated to be ±0.1°C. The uncertainty in the birefringence values was on the order of ±2%. For the refractive indices, the temperature uncertainty was estimated to be ±0.3°C. The refractometer, calibrated with a test block yielded n_0 values believed accurate to ±0.0002.

The density measurements were performed with a Lipkin bicapillary pycnometer, the ASTM standard D1481-62 technique on approximately 1 ml sized samples.

The pentanoate, hexanoate, and heptanoate esters were commercially available from Eastman Organic Chemicals and were recrystallized three times before use. The remaining compounds were synthesized as described previously.[9]

RESULTS

Optical Studies. Table I presents the birefringence Δn, ordinary n_0, and isotropic n, refractive indices measured at 589.3 nm as functions of temperature for the ten members of the homologous series here studied. Refractive indices for the isotropic phase of the C_5, C_6, C_7, C_8 homologs could not be measured owing to the temperature limits of the refractometer. The data given in Table I was read off lines drawn through the original data and as such represents a smoothing and an abridgement of the original. The $\bar{n}$ vs T line is generally linear up to about 5° below T_{NI}, and closer, large deviations in a negative direction from linearity are often noted for various members of the series. Such behavior is undoubtedly due to the rapid changes in n_e and n_o coupled with temperature uncertainty. To estimate n at T_{NI} for the C_5, C_6, C_7, C_8 homologs for which no isotropic refractive indices were experimentally available, the quantity

$$(3/4\pi N)[(n^2 - 1)/(n^2 + 2)]$$

evaluated at T_{NI} was found to be linear with carbon numbers 9 through 14 and thus an extrapolation procedure was used to provide the requisite C_5 through C_8 data. This procedure is essentially a plot of $\bar{\alpha}$ vs carbon number and was felt to be more desirable than the extrapolation of $\bar{n}^2 = \frac{1}{3}(n_e^2 + 2n_o^2)$ into the isotropic region since for some compounds the slopes of the nematic phase $\bar{n}$ vs T line were not the same as the slopes from the experimentally-determined isotropic phase n vs T line.

DENSITIES

Density-temperature data for the homologous series is summarized in Table II which presents least square fits to the linear portions of the data. Generally the nematic density is linear to within about 5° of the nematic–isotropic transition temperature. More detailed discussion of the trends exhibited by the density data for the homologous series will be presented in a separate forthcoming article.[10]

TABLE II

Density versus temperature, $\rho = \rho_o + (d\rho/dT)T$, for nematogenic *trans*-4-ethoxy-4′-*n*-alkanoyloxyazobenzenes.

	Nematic phase		Isotropic phase	
Carbons in alkane chain	ρ_o g cm^{-3}	$d\rho/dT$ 10^{-4} g cm^{-3} °C^{-1}	ρ_o g cm^{-3}	$d\rho/dT$ 10^{-4} g cm^{-3} °C^{-1}
5	1.1607	−10.074	1.1438	−9.093
6	1.1418	−9.130	1.1447	−9.827
7	1.1182	−8.629	1.1135	−8.730
8	1.1186	−9.388	1.1140	−9.511
9	1.1079	−9.492	1.1019	−9.413
10	1.0983	−9.512	1.0923	−9.461
11	1.0918	−9.701	1.0817	−9.240
12	1.0875	−9.925	1.0758	−9.327
13	1.0788	−9.760	1.0769	−10.059
14	1.0789	−10.254	1.0595	−8.867

TABLE III

Polarizability anisotropies and extraordinary polarizabilities for nematogenic *trans*-4-ethoxy-4′-*n*-alkanoyloxyazobenzenes calculated using the isotropic internal field model of Vuks and the anisotropic internal field model of Neugebauer presented as functions of carbons in alkane chain (C) for fixed reduced temperatures, ($\Delta T = T - T_{NI}$). Units and magnitudes are in 10^{-24} cm^3, except for γ_e which is unitless.

	Vuks		Neugebauer			Vuks		Neugebauer		
	$\Delta T = -0.5$					$\Delta T = -1.0$				
C	$(\alpha_e - \alpha_o)_V$	$(\alpha_e)_V$	$(\alpha_e - \alpha_o)_N$	$(\alpha_e)_N$	γ_e	$(\alpha_e - \alpha_o)_V$	$(\alpha_e)_V$	$(\alpha_e - \alpha_o)_N$	$(\alpha_e)_N$	γ_e
5	—	—	—	—	—	—	—	—	—	—
6	—	—	—	—	—	—	—	—	—	—
7	14.1 ± .5	54.4 ± .4	16.3 ± .5	56.2 ± .5	2.784	15.2 ± .5	55.3 ± .4	16.4 ± .5	56.3 ± .5	3.050
8	15.4 ± .5	56.8 ± .4	14.4 ± .6	55.1 ± .5	3.200	16.7 ± .5	58.2 ± .4	14.6 ± .6	56.3 ± .5	3.333
9	14.2 ± .5	58.4 ± .5	10.6 ± 1.8	56.1 ± 1.3	3.992	15.4 ± .5	59.0 ± .5	14.6 ± 1.0	60.0 ± .8	3.584
10	16.3 ± .5	62.2 ± .5	—	—	—	17.5 ± .5	62.8 ± .5	15.3 ± 1.4	59.1 ± 1.0	4.210
11	13.5 ± .5	62.4 ± .5	—	—	—	14.9 ± .5	62.7 ± .5	16.2 ± 1.0	63.3 ± .7	3.420
12	14.9 ± .6	63.8 ± .5	17.2 ± .8	66.2 ± .6	3.092	16.2 ± .6	64.5 ± .5	17.5 ± .8	66.5 ± .7	3.240
13	14.7 ± .6	65.5 ± .5	13.9 ± 1.6	66.5 ± 1.2	3.627	16.0 ± .6	66.0 ± .5	17.8 ± .8	68.5 ± .7	3.225
14	—	—	—	—	—	—	—	—	—	—
	$\Delta T = -2.0$					$\Delta T = -3.0$				
5	—	—	—	—	—	—	—	—	—	—
6	—	—	—	—	—	—	—	—	—	—
7	16.6 ± .5	56.2 ± .4	16.7 ± .5	56.6 ± .5	3.193	17.5 ± .5	56.9 ± .4	16.9 ± .5	56.7 ± .5	3.300
8	18.4 ± .5	59.7 ± .4	15.0 ± .6	56.7 ± .6	3.656	19.6 ± .5	60.7 ± .4	15.4 ± .7	57.1 ± .6	3.815
9	16.9 ± .5	60.0 ± .5	15.2 ± .8	60.5 ± .7	3.550	17.9 ± .5	60.9 ± .5	15.4 ± .8	60.8 ± .6	3.654
10	19.0 ± .5	63.7 ± .5	15.8 ± .9	61.2 ± .7	3.760	20.2 ± .5	64.4 ± .5	16.2 ± .7	62.0 ± .6	3.750
11	16.4 ± .5	63.3 ± .5	18.0 ± .7	65.0 ± .6	3.255	17.4 ± .5	63.8 ± .5	18.9 ± .7	65.8 ± .6	3.171
12	17.6 ± .6	65.5 ± .5	18.2 ± .8	67.0 ± .6	3.329	18.6 ± .6	66.3 ± .5	18.8 ± .7	67.4 ± .6	3.338
13	17.3 ± .6	66.7 ± .5	19.5 ± .8	69.8 ± .6	3.153	18.2 ± .6	67.3 ± .5	20.8 ± .7	70.5 ± .6	3.093
14	—	68.6 ± .6	18.6 ± .8	70.8 ± .7	3.241	19.6 ± .6	70.1 ± .6	18.9 ± .9	71.1 ± .7	3.400

	$\Delta T = -5.0$					$\Delta T = -10.0$				
5	—	—	—	—	—	—	—	—	—	—
6	—	—	—	54.6 ± .4	3.740	23.1 ± .4	59.9 ± .4	17.5 ± .4	55.2 ± .4	3.760
7	18.8 ± .5	57.9 ± .4	17.5 ± .5	57.1 ± .5	3.369	20.9 ± .4	59.4 ± .4	18.5 ± .4	57.8 ± .4	3.395
8	21.5 ± .5	62.1 ± .4	16.1 ± .8	57.7 ± .6	4.110	24.0 ± .5	64.0 ± .4	17.7 ± .5	58.9 ± .5	3.888
9	19.7 ± .5	62.3 ± .5	15.9 ± .7	61.2 ± .6	3.760	22.5 ± .5	64.5 ± .5	17.1 ± .6	62.0 ± .5	3.827
10	21.8 ± .5	65.6 ± .5	17.1 ± .7	62.6 ± .6	3.739	24.1 ± .5	67.8 ± .5	18.9 ± .6	63.8 ± .5	3.751
11	18.9 ± .5	64.8 ± .5	20.0 ± .6	66.5 ± .6	3.135	21.4 ± .5	66.6 ± .5	21.6 ± .5	67.4 ± .5	3.201
12	20.0 ± .6	67.4 ± .5	19.8 ± .7	68.1 ± .7	3.337	22.4 ± .6	69.1 ± .5	21.7 ± .5	69.9 ± .6	3.301
13	19.6 ± .6	68.4 ± .5	22.2 ± .7	71.4 ± .7	3.030	22.5 ± .6	70.5 ± .5	23.3 ± .5	72.2 ± .6	3.137
14	21.2 ± .6	71.9 ± .5	19.7 ± .8	71.6 ± .7	3.520	24.7 ± .6	74.2 ± .5	21.5 ± .7	72.8 ± .6	3.573
	$\Delta T = -15.0$					$\Delta T = -20.0$				
5	20.3 ± .4	56.0 ± .4	18.2 ± .4	53.8 ± .4	3.356	21.4 ± .4	56.8 ± .4	19.4 ± .4	54.5 ± .4	3.291
6	24.5 ± .4	61.1 ± .4	18.6 ± .4	55.7 ± .4	3.720	25.8 ± .4	62.2 ± .4	19.2 ± .4	56.2 ± .4	3.743
7	22.5 ± .4	60.6 ± .4	19.4 ± .4	58.3 ± .4	3.416	23.7 ± .4	61.5 ± .4	20.1 ± .4	58.8 ± .4	3.424
8	25.4 ± .5	65.1 ± .4	19.0 ± .5	59.9 ± .5	3.805	26.4 ± .5	65.8 ± .4	20.1 ± .5	60.5 ± .5	3.721
9	24.4 ± .5	66.0 ± .5	18.2 ± .6	62.7 ± .5	3.838	25.8 ± .5	67.1 ± .5	19.2 ± .5	63.3 ± .5	3.820
10	25.2 ± .5	68.1 ± .5	20.6 ± .5	64.9 ± .5	3.621	25.7 ± .5	68.4 ± .5	22.2 ± .5	65.9 ± .5	3.451
11	22.5 ± .5	67.8 ± .5	22.9 ± .5	68.2 ± .5	3.179	24.4 ± .5	68.8 ± .5	23.9 ± .5	68.9 ± .5	3.139
12	24.0 ± .6	70.2 ± .5	23.2 ± .5	70.4 ± .5	3.254	25.3 ± .6	71.2 ± .5	24.5 ± .5	71.2 ± .5	3.198
13	24.8 ± .6	72.4 ± .5	24.0 ± .5	72.6 ± .5	3.251	26.9 ± .6	74.1 ± .5	24.4 ± .5	72.8 ± .5	3.375
14	26.6 ± .6	75.6 ± .6	23.2 ± .6	74.0 ± .6	3.494	28.2 ± .6	76.8 ± .6	24.8 ± .6	75.1 ± .6	3.408

DISCUSSION

Order parameters and models for the internal field of the nematic phase Two models are commonly used to describe the internal polarization field of a nematic mesophase, the isotropic model of Vuks and the anisotropic model of Neugebauer.[5,6] The isotropic internal field model yields the following Lorenz–Lorentz type expressions relating the extraordinary and ordinary refractive indices to the corresponding polarizabilities

$$\frac{n_e^2 - 1}{\bar{n}^2 + 2} = \frac{4\pi}{3} N_N \alpha_e \tag{1a}$$

$$\frac{n_o^2 - 1}{\bar{n}^2 + 2} = \frac{4\pi}{3} N_N \alpha_o \tag{1b}$$

where N_N is the number density (#/cm^3) of the nematic phase and, α_e and α_o are the extraordinary and ordinary polarizabilities of the nematic phase respectively. Noting that $\bar{\alpha} = \frac{1}{3}(\alpha_e + 2\alpha_o)$ and that the order parameter S_V can be defined as

$$S_V = \frac{(\alpha_e - \alpha_o)_V}{(\alpha_\parallel - \alpha_\perp)_V}$$

where $(\alpha_\parallel - \alpha_\perp)_V \equiv \Delta\alpha$ refers to the anisotropy of the uniaxial nematic molecule, Eqs. (1a) and (1b) can be rearranged after Haller *et al.* to yield[11]

$$\frac{n_e^2 - 1}{\bar{n}^2 + 2} = \frac{4\pi}{3} N_N(\bar{\alpha} + \tfrac{2}{3} S_V \Delta\alpha) \tag{2a}$$

$$\frac{n_o^2 - 1}{\bar{n}^2 + 2} = \frac{4\pi}{3} N_N(\bar{\alpha} - \tfrac{1}{3} S_V \Delta\alpha) \tag{2b}$$

Equations (2a) and (2b) can be solved to yield $S_V \Delta\alpha$ as a function of temperature and molecular structure. Table III presents calculated $S_V \Delta\alpha$, that is $(\alpha_e - \alpha_o)_V$, values as function of carbons in alkane chain for fixed values of reduced temperature $\Delta T = T - T_{NI}$. Some of this data is plotted in Figure 1. If it is assumed that the plot of $S_V \Delta\alpha$ vs $\ln|\Delta T|$ can be extrapolated to $T = 0$ and at $T = 0$, S_V equals unity, $(\alpha_\parallel - \alpha_\perp)_V$ can be estimated, and hence S_V itself calculated for T other than zero.[11,12] Table IV gives the values of $(\alpha_\parallel - \alpha_\perp)_V$ obtained by this procedure and Table V presents the order parameter S_V as a function of reduced temperature for the homologs in the series.

Treating the internal field as anisotropic requires the introduction of two new parameters γ_e and γ_o which describe the anisotropy of the medium

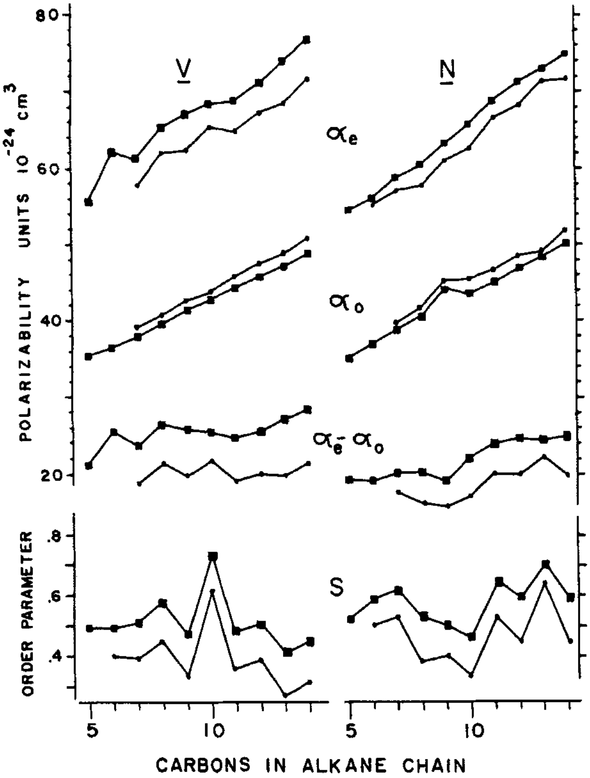

FIGURE 1 Polarizabilities and order parameters calculated by the isotropic internal field model of Vuks (V) and by the anisotropic internal field model of Neugebauer (N) for two reduced temperatures $T - T_{NI} = -20$ (■) and $T - T_{NI} = -5$ (●) as functions of carbons in the alkane chain of the nematogenic *trans*-4-ethoxy-4′-*n*-alkanoyloxyazobenzenes.

immediately surrounding a single molecule in the nematic phase. The resulting Lorenz–Lorentz type expressions are

$$n_e^2 - 1 = \frac{4\pi N_N \alpha_e}{(1 - \gamma_e \alpha_e N_N)} \tag{3a}$$

$$n_o^2 - 1 = \frac{4\pi N_N \alpha_o}{(1 - \gamma_o \alpha_o N_N)} \tag{3b}$$

where γ_e and γ_o are the internal field constants in the extraordinary and ordinary directions respectively and are subject to the condition $\gamma_e + 2\gamma_o = 4\pi$.[12,13] For the isotropic phase the normal Lorenz-Lorentz relationship is given as

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N\bar{\alpha} = \frac{4\pi}{9} N(\alpha_e + 2\alpha_o) \tag{4}$$

TABLE IV

Anisotropy of the molecular polarizability as a function of alkane chain length for homologous *trans*-4-ethoxy-4′-*n*-alkanoyloxy-azobenzenes in units of 10^{-24} cm^3.

Carbons in alkane chain	$(\alpha_\parallel - \alpha_\perp)_N$[a]	$(\alpha_\parallel - \alpha_\perp)$[b]	$(\alpha_\parallel - \alpha_\perp)_V$[c]
5	31.5	36.5	36.2
6	27.9	37.3	43.3
7	27.8	38.0	38.0
8	32.0	38.8	39.0
9	31.9	39.8	44.9
10	39.5	40.3	30.5
11	32.0	41.1	41.3
12	35.8	41.9	41.4
13	29.8	42.8	53.5
14	35.8	43.7	50.9

[a] Extrapolated from $(\alpha_e - \alpha_o)$ data obtained using anisotropic model of Neugebauer.

[b] Obtained from bond polarizability data.

[c] Extrapolated from $(\alpha_e - \alpha_o)$ data obtained using isotropic model of Vuks.

where recalling n is the refractive index of the isotropic phase. Taking $\bar{\alpha}$ in any phase to be independent of temperature, [Eqs. (3a), (3b) can be rewritten to give for the nematic phase

$$\frac{1}{\alpha_e} + \frac{2}{\alpha_o} = \frac{4\pi}{3} N_N \frac{n_e^2 + 2}{n_e^2 - 1} + \frac{2(n_o^2 + 2)}{n_o^2 - 1} \tag{5}$$

Combining Eqs. (3a), (3b), (4) and (5) with the restriction on γ_e and γ_o yields results for α_e, α_o, γ_e, γ_o.

Maier and Saupe used the anisotropic model of Neugebauer but defined a single internal field parameter $\mathbf{a}$ which modified the Lorenz–Lorentz equations to give[14]

$$\frac{n_e^2 - 1}{n_e^2 + 2 - 2\mathbf{a}(n_e^2 - 1)} = \frac{4\pi}{3} N_N \alpha_e. \tag{6a}$$

$$\frac{n_e^2 - 1}{n_o^2 + 2 + \mathbf{a}(n_o^2 - 1)} = \frac{4\pi}{3} N_N \alpha_o. \tag{6b}$$

Again assuming $\bar{\alpha}$ independent of phase and temperature, Eqs. (6a) and (6b) can be combined with Eq. (4) to yield $\mathbf{a}$ with which α_e and α_o may then be calculated. The relationship between $\mathbf{a}$ and γ_e is $2a = (1 - 3\gamma_e/4\pi)$. As a test for consistency, γ_e and γ_o calculated via (3a), (3b) and (4) were compared to $\mathbf{a}$ calculated with Eqs. (6a) and (6b). The agreement between the calculations is, to significant figures, exact. In Table III are also presented the Neugebauer

TABLE V

Order parameters for the homologous nematogenic *trans*-4-ethoxy-4′-*n*-alkanoyloxyazobenzenes, calculated using the isotropic internal field model of Vuks (S_V, S'_V) and the anisotropic internal field model of Neugebauer (S_N, S'_N) presented as functions of reduced temperature ($\Delta T = T - T_{NI}$) for the series.

	Pentanoate				Hexanoate				Heptanoate				Octanoate				Nonanoate			
ΔT	S_V[a]	S'_V[a]	S_N[b]	S'_N[b]	S_V	S'_V	S_N	S'_N	S_V	S'_V	S_N	S'_N	S_V	S'_V	S_N	S'_N	S_V	S'_V	S_N	S'_N
−20.0	0.59[c]	0.59	0.62	0.54	0.59	0.68	0.69	0.52	0.61	0.61	0.72	0.53	0.68	0.68	0.63	0.52	0.57	0.64	0.60	0.48
−15.0	0.56	0.56	0.58	0.50	0.57	0.66	0.67	0.50	0.58	0.58	0.70	0.51	0.65	0.65	0.59	0.49	0.54	0.61	0.57	0.46
−10.0	0.52	0.52	0.53	0.46	0.53	0.62	0.63	0.47	0.54	0.54	0.67	0.49	0.62	0.62	0.55	0.45	0.50	0.56	0.53	0.42
−5.0	—	—	—	—	0.50	0.58	0.60	0.45	0.49	0.49	0.63	0.46	0.55	0.55	0.48	0.40	0.43	0.49	0.50	0.40
−2.0	—	—	—	—	—	—	—	—	0.42	0.42	0.61	0.45	0.47	0.47	0.43	0.35	0.37	0.42	0.48	0.38
−1.0	—	—	—	—	—	—	—	—	0.38	0.38	0.59	0.43	0.44	0.44	0.41	0.34	0.34	0.38	0.44	0.35
	Decanoate				Undecanoate				Dodecanoate				Tridecanoate				Tetradecanoate			
−20.0	0.84	0.64	0.56	0.55	0.58	0.58	0.75	0.58	0.61	0.60	0.69	0.59	0.51	0.64	0.81	0.56	0.55	0.64	0.70	0.57
−15.0	0.83	0.63	0.52	0.51	0.56	0.56	0.71	0.55	0.58	0.57	0.65	0.56	0.47	0.59	0.80	0.56	0.52	0.61	0.65	0.53
−10.0	0.79	0.60	0.49	0.48	0.52	0.52	0.68	0.53	0.55	0.54	0.61	0.52	0.42	0.53	0.78	0.54	0.49	0.57	0.60	0.49
−5.0	0.72	0.54	0.44	0.43	0.46	0.46	0.63	0.49	0.49	0.48	0.55	0.47	0.37	0.46	0.74	0.52	0.42	0.49	0.55	0.45
−2.0	0.62	0.47	0.38	0.37	0.40	0.40	0.56	0.44	0.42	0.41	0.50	0.43	0.33	0.41	0.66	0.46	0.35	0.41	0.51	0.42
−1.0	0.58	0.44	0.29	0.28	0.37	0.37	0.49	0.38	0.38	0.38	0.48	0.41	0.29	0.36	0.60	0.42	0.32	0.37	0.49	0.40

[a] $S_V = (\alpha_e - \alpha_o)_V/(\alpha_\parallel - \alpha_\perp)_V$; $S'_V = (\alpha_e - \alpha_o)_V/(\alpha_\parallel - \alpha_\perp)$

[b] $S_N = (\alpha_e - \alpha_o)_N/(\alpha_\parallel - \alpha_\perp)_N$; $S'_N = (\alpha_e - \alpha_o)_N/(\alpha_\parallel - \alpha_\perp)$

[c] Uncertainty of ±0.04 is valid for entire table and estimated taking a typical error of 2% in $(\alpha_e - \alpha_o)$ and 5% error in $\alpha_\parallel - \alpha_\perp$.

model values of $(\alpha_e - \alpha_o)_N$ and $(\alpha_e)_N$ as function of carbon chain length for fixed temperatures. Assuming a plot of $\ln(\alpha_e/\alpha_o)$ vs $\ln|\Delta T|$ can be extrapolated to $T = 0$, and that the value of α_e/α_o at $T = 0$ is just $\alpha_{\parallel}/\alpha_{\perp}$, the relationship $3\bar{\alpha} = \alpha_{\parallel} + 2\alpha_{\perp}$ can be used to obtain $\alpha_{\parallel}$ and $\alpha_{\perp}$, hence $(\alpha_{\parallel} - \alpha_{\perp})_N$ and finally the order parameter S_N from $(\alpha_e - \alpha_o)_N/(\alpha_{\parallel} - \alpha_{\perp})_N$. The values of $(\alpha_{\parallel} - \alpha_{\perp})_N$ obtained by this extrapolation procedure are given in Table IV which also affords a comparison with those values for $(\alpha_{\parallel} - \alpha_{\perp})_V$. Table V also presents the structure and temperature dependence of the order parameter S_N for comparison with S_V.

Trends in the polarizability anisotropies calculated by the two models are shown in Figure 1. A regular odd–even effect is seen plotting $(\alpha_e - \alpha_o)_V$ versus carbon number, the effect being even more pronounced at smaller relative temperatures. Moreover for a given relative temperature the $(\alpha_e - \alpha_o)_V$ values seem to alternate between two values 20.8 and 19.5 for $\Delta T = -5.0$, suggesting perhaps the occurrence of only two types of conformations in the nematic phase, each of which is such that increasing the chain length does not much affect the resultant polarizability anisotropy. The values of $(\alpha_e - \alpha_o)_N$, on the other hand, show no regular odd–even trend, and if there is any trend evident at all, it is one of a very gradual increase of polarizability anisotropy with carbon chain length. However, such an increase is what would be expected for a conformation in which the molecule was stretched with the methylene carbons following some type of zig-zag pattern. Physically some type of elongated conformation seems more intuitively satisfactory for a molecular description of the nematic phase, and by such inference, the $\alpha_e - \alpha_o$ values calculated assuming the anisotropic field provide some evidence for the superiority of the Neugebauer model.

The α_e values calculated by either model increase linearily with carbon number showing a small odd–even effect again more pronounced at low reduced temperatures and greater in magnitude for the Vuks model calculation. The alternation in $(\alpha_e - \alpha_o)_V$ must apparently come entirely from $(\alpha_e)_V$, since the variation of $(\alpha_o)_V$ is essentially monotonically linear. The $(\alpha_o)_V$ values change only slightly less than $(\alpha_o)_N$ with increasing chain length, and thus each model calculates a similar contribution to the ordinary polarizability, describing then the variations in $(\alpha_e - \alpha_o)$ to the extraordinary polarizability.

The molecular polarizability anisotropies obtained by the extrapolation procedure mentioned above as well as those calculated by addition of bond polarizabilities are given in Table IV. The calculated $\alpha_{\parallel} - \alpha_{\perp}$ values were arrived at by using the experimental value of $\alpha_{\parallel}$ for PAP, subtracting the contributions due to O^{2-} and the ethyl fragment, and then adding the estimated polarizability due to the alkane chain using the isotropic bond polarizability values in accord with the method described by Subramhanyam *et al.*[12] Once estimating $\alpha_{\parallel}$ and again assuming $\bar{\alpha}$ independent of phase and temperature, $\alpha_{\parallel} - \alpha_{\perp} = 1.5(\alpha_{\parallel} - \bar{\alpha})$ where $\bar{\alpha}$ was calculated from the isotropic phase data at T_{NI}. The trend in $\alpha_{\parallel} - \alpha_{\perp}$ calculated from bond polarizabilities is quite regular and in good agreement with literature values for similar compounds. As seen in Table IV the $(\alpha_{\parallel} - \alpha_{\perp})_V$ values agree much better with the bond polarizability values than do the extrapolated $(\alpha_{\parallel} - \alpha_{\perp})_N$ values. The extrapolated values for the C_{10} decanoate homolog seem anomalously out of place. The absence of actual data for the true $\alpha_{\parallel} - \alpha_{\perp}$ does not allow any conclusive comments to be made either on the validity of the extrapolation procedures or which model is indeed better. The apparent better agreement with the Vuks model might be fortuitous and highly dependent on assumptions made in using the bond polarizabilities to calculate $\alpha_{\parallel} - \alpha_{\perp}$.

Given the three estimates for the molecular polarizability $\alpha_{\parallel} - \alpha_{\perp}$, $(\alpha_{\parallel} - \alpha_{\perp})_V$, and $(\alpha_{\parallel} - \alpha_{\perp})_N$, several order parameters can be calculated from the $(\alpha_e - \alpha_o)$ data. Four possibilities labeled S_V, S'_V, S_N and S'_N are defined and presented in Table V. Figure 1 presents an abridgement of the order parameter data given in Table V. The plots $(\alpha_e - \alpha_o)_{V,N}$ in Figure 1 are also just exactly $S'_{V,N}$ apart from the constant, common divisor $(\alpha_{\parallel} - \alpha_{\perp})$. Since there can be but one molecular polarizability anisotropy per compound, the best order parameters to compare would be those calculated on a common basis. Given the reasonableness of the $(\alpha_{\parallel} - \alpha_{\perp})$ values calculated from bond polarizabilities, S'_V and S'_N appear to be the values most reasonable to discuss. However, this statement really says that the properties of the order parameters are, comparing except for actual magnitude, determined by the $(\alpha_e - \alpha_o)$ values. Thus comparing the S'_V or $(\alpha_e - \alpha_o)_V$ values with the S'_N or $(\alpha_e - \alpha_o)_N$ values reveals a regular odd–even effect for S'_V. This observation is in agreement with Chang *et al.* who have noted, using a Vuks treatment, an odd–even alternation of order parameter with chain length for a short homologous series of Schiff bases.[3] Hanson and Shen also calculate an order parameter that exhibits an odd–even alternation using the Vuks equations for a homologous series of azoxybenzenes.[4] The order parameters based on the Neugebauer model appear to be different. The S_N values show a regular odd–even effect especially for low relative temperature and high carbon numbers, but the S'_N values barely show any odd–even effect and then only at low relative temperatures and again long alkyl chains. The studies of Pines *et al.* using ^{13}C NMR techniques, which are independent of the models discussed here, have demonstrated that the order parameters of a homologous series of azoxybenzenes do indeed show marked odd–even effects.[15] Thus the observation of the more pronounced odd–even effect via the Vuks model might be evidence for its superiority.

The argument might be made that the uncertainties in the order parameters are too large to conclude very much, but this is not true by virtue of the fact that an order parameter has its temperature and structure properties determined by the error in the $(\alpha_e - \alpha_o)$ values. Clearly even with the uncertainties in these values, either model supports an alternation of structure although the alternation is calculated to be less pronounced in the Neugebauer model. However, neither model seems to agree with the hypothesis that the nematic order parameter is a universal constant dependent only on temperature.

Again if it is assumed that $\alpha_{\|} - \alpha_{\perp}$, whatever its value, is temperature independent, the temperature dependence of the order parameter is entirely determined by the $(\alpha_e - \alpha_o)$ values. Thus in Figure 2 which presents $(\alpha_e - \alpha_o)$, $(n_e - n_o)$, and S'_N, and S'_N data as a function of reduced temperature for the C_{13} tridecanoate homolog

$$\frac{dS'_V}{dT} = \frac{1}{\alpha_{\|} - \alpha_{\perp}} \frac{d(\alpha_e - \alpha_o)_V}{dT} \quad \text{and} \quad \frac{dS'_N}{dT} = \frac{1}{\alpha_{\|} - \alpha_{\perp}} \frac{d(\alpha_e - \alpha_o)_N}{dT}$$

and what can be noted is that dS'_N/dT is smaller and more closely linear than dS'_V/dT except for very small ΔT, in which case S'_N varies much more rapidly than S'_V with temperature. The anisotropic model is apparently much more sensitive to the rapid density and refractive index changes for temperatures close to T_{NI}. The birefringence appears to be roughly parallel in curvature to $(\alpha_e - \alpha_o)_V$ (at least more so than to $(\alpha_e - \alpha_o)_N$), and thus, the temperature dependence of the order parameter could be roughly estimated by simply that of the birefringence. In fact Hanson and Shen, for example, present equations describing the relationship between the birefringence and the order parameter.[4] Further, if the birefringence is plotted versus carbons in the alkane chain for various reduced temperatures, distinct odd–even alternations are observed. Since, following the work of Hanson and Shen, the order parameter is proportional to the birefringence, the order parameter should alternate with chain length, a result not obvious using the anisotropic internal field.

A few comments on the magnitude and trends of the parameters γ_e and γ_o, introduced by the anisotropic field model, are in order. First $\gamma_e < \gamma_o$ and $\gamma_e < 4\pi/3$, its expected value for a completely isotropic field. For a given member of the homologous series the variation of γ_e with temperature generally exhibits a maximum within 2° of T_{NI}. This maximum has been observed before.[12] Curiously, however, for members of the series with an odd number of carbons in the terminal alkane chain, just before T_{NI}, the γ_e increases very markedly. Further at fixed relative temperatures γ_e (hence γ_o also) shows an odd–even effect which is more pronounced for the lower members of the homologous series. Perhaps the lack of dramatic odd–even

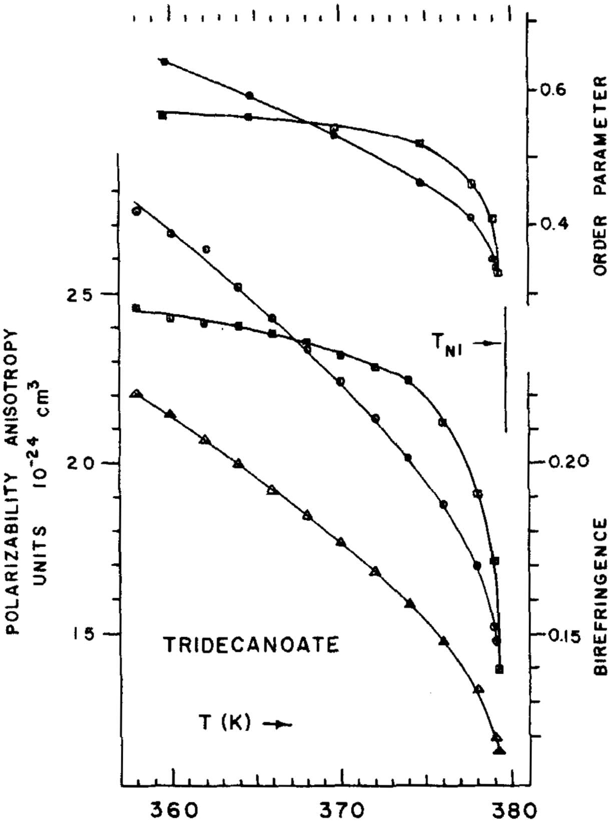

FIGURE 2 Polarizabilities (Vuks (○); Neugebauer (□)), order parameters, and birefringence (△) for the nematogenic *trans*-4-ethoxy-4′-*n*-tridecanoyloxyazobenzene as a function of temperature.

effects for the values of $(\alpha_e - \alpha_o)_N$ and S_N can be explained by suggesting that such effects appear instead in the anisotropic field parameters γ_e and γ_o.

Neither model appears demonstrably better than the other on the basis of the above calculations. Again the anisotropic field model is more intuitively appealing but does not offer any more profound insight for its required additional computational efforts than the simpler isotropic model which actually appears to agree with experiment at times more consistently.

Theory of birefringence Chandrasekhar *et al.* wrote for the birefringence a power series in temperature given by

$$x = (n_e^2 - n_o^2)[\rho_{NI}/\rho]^4 \approx AT^{-1} + BT^{-2} + CT^{-3} + DT^{-4} \qquad (7)$$

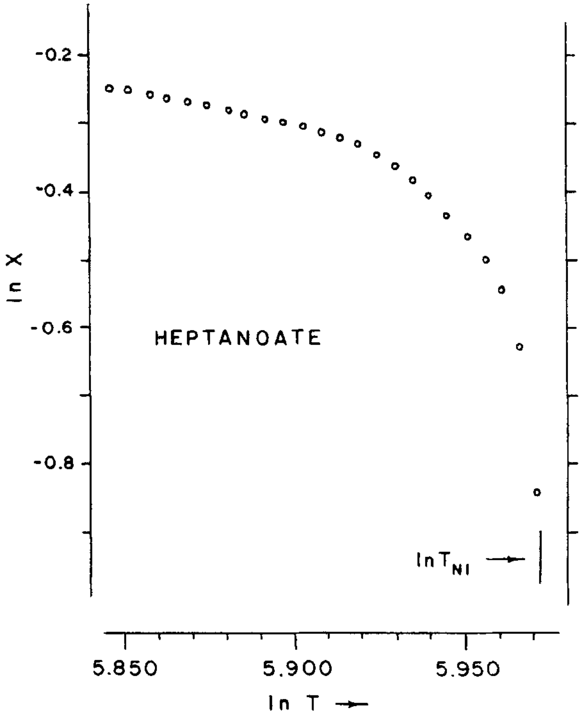

FIGURE 3 Plot of the birefringence function $\ln(n_e^2 - n_o^2)(\rho_{NI}/\rho)^4$, ($\ln x$), vs $\ln T$ for nematogenic *trans*-4-ethoxy-4′-*n*-heptanoyloxyazobenzene.

where A is a function of repulsion and first order dispersion forces, B is a function of the second order dispersion forces, C depends on dipole dispersion cross terms and D depends on dipole forces.[7] The slope of $\ln x$ vs $\ln T$ suggests the relative contributions of the various forces to the observed birefringence, since for example, if $B \approx C \approx D \approx 0$, then the slope $d \ln x/d \ln T$ is approximately $|1|$, while in the case of $A \approx B \approx C \approx 0$, the slope is about $|4|$. In Figure 3 is given a typical plot of $\ln x$ vs $\ln T$ for the C_7 heptanoate member of the homologous series. At large reduced temperatures the terms involving A and B appear to be the most important, that is, repulsion and dispersion forces are dominant. Closer to T_{NI}, however, the dipole–dipole interactions appear to dominate. Figure 4 presents a summary of the $\ln x$ vs $\ln T$ data as a function of homologous series for various reduced temperatures. For the lower homologs, those with short alkane chains, the slopes are all about unity at large reduced temperature but tend to increase negatively with chain length. Thus long chains even at temperatures far removed from T_{NI} appear to require different forces to account for the birefringence of the nematic state. For intermediate temperatures ($\Delta T = -10$) slopes vary from

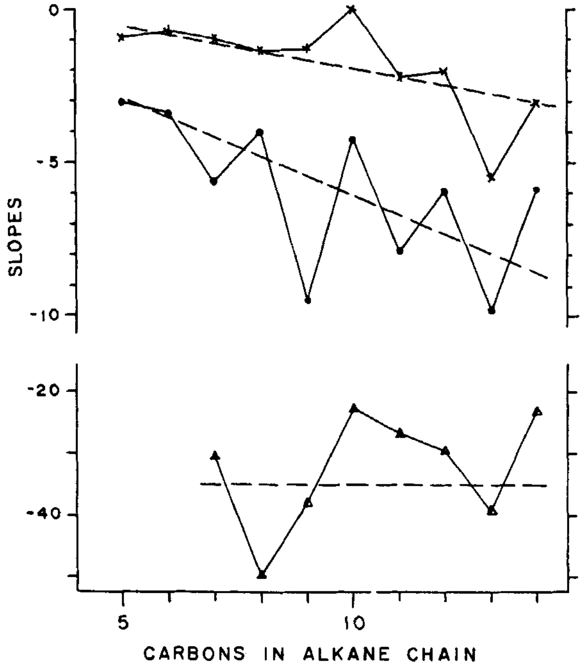

FIGURE 4 Slopes of the birefringence function ln $(n_e^2 - n_o^2)(\rho_{NI}/\rho)^4$ plotted vs ln T for three reduced temperatures $T - T_{NI} = -30$ (×), -10 (●), -2 (△) as a function of carbons in the alkane chain of nematogenic *trans*-4-ethoxy-4′-*n*-alkanoyloxyazobenzenes.

about 3 to 7 suggesting predominately the influence of dipole–dipole forces, whose influence again increases with increasing alkane chain length. For small reduced temperatures $\Delta T = -2$, the slopes are considerably larger than predicted by the theory, and given the uncertainties involved in estimating the slopes in this region, practically independent of chain length. What occurs near T_{NI} to contribute to such large slopes is the loss of the assumed temperature independence of the coefficients A, B, C, and D. Within this theory, then, no reliable conclusions can be made concerning the trend of intermolecular forces with structure near T_{NI}.

Fractional volume changes Haller *et al.* suggested that refractive index data can be used to estimate the fractional volume change at T_{NI}.[8] The method assumes the variation of $(\bar{n}^2 - 1)/(\bar{n}^2 + 2)$ with temperature to be a measure of the change of density with temperature under the assumption that the total polarizability $\bar{\alpha}$ is essentially independent of temperature, that is

$$R = \frac{\bar{n}^2 - 1}{\bar{n}^2 + 2} = \frac{4\pi}{3} N\bar{\alpha} \tag{8}$$

TABLE VI

Fractional volume changes at the nematic to isotropic transition point for the homologous series of nematogenic *trans*-4-ethoxy-4′-*n*-alkanoyloxyazobenzenes. $\Delta V/V \equiv 1 - V_I/N_N$

Carbons in alkane chain	$\Delta V/V$ (calc'd)[a]	$\Delta V/V$ (obsv'd)[b]
5	-0.2×10^{-3}	-4.3×10^{-3}
6	-9.7	-6.0
7	-3.1	-6.0
8	-0.1	-6.1
9	-13.1	-5.0
10	-21.5	-5.5
11	$+4.4$	-5.1
12	$+0.3$	-5.3
13	$+11.3$	-5.2
14	-5.1	-4.9

[a] Calculated from refractive index data using the method of Haller, *et. al.* Ref. 8.

[b] Observed from dilatometry experiments.

then

$$dR/dT = \frac{4\pi}{3}\bar{\alpha}dN/dT \tag{9}$$

The fractional volumes calculated by extrapolating the linear portions of R in the nematic range to T_{NI}, as well as R in the isotropic range are given in Table VI. Also given in Table VI are the fractional volumes calculated from the density data by extrapolation of the linear density regions to T_{NI}. From comparison of the results, obviously the extrapolation procedure using refractive index data cannot be relied upon to yield good estimates of either magnitude of sign of the correct volume change. The most likely cause for the discrepancy is the neglect of the temperature change of the polarizability. Rewriting Eq. (9) to include variation of $\bar{\alpha}$ with T gives

$$\frac{dR}{dT} = \frac{4\pi}{3}\bar{\alpha}\frac{dN}{dT} + \frac{4\pi}{3}N\frac{d\bar{\alpha}}{dT} \tag{10}$$

Table VII gives some pertinent isotropic data for the C_{11} undecanoate homolog. The temperature variation calculated for R by Eq. (9), that is, the first term on the right hand side of Eq. (10) is given in the last column of Table VII. The observed slope of R versus T is $-2.54 \times 10^{-4}\,\mathrm{K}^{-1}$, in considerable disagreement with the calculated value of $\approx -3.02 \times 10^{-4}$

TABLE VII

Isotropic refractive index and density as a function of temperature for nematogenic *trans*-4-ethoxy-4′-*n*-undecanoyloxyazobenzene.

T (K)	N $(10^{21}\ \mathrm{cm}^3)$[a]	R[b]	$\bar{\alpha}$ $(10^{-24}\ \mathrm{cm}^3)$[c]	$\frac{4\pi}{3}\bar{\alpha}\frac{dN}{dT}$ $(10^{-4}\ \mathrm{K}^{-1})$
382	1.4393	0.3194	52.98	−3.015
384	1.4365	0.3190	53.02	−3.017
386	1.4339	0.3184	53.01	−3.016
388	1.4311	0.3179	53.03	−3.018
390	1.4284	0.3174	53.05	−3.019
392	1.4257	0.3169	53.07	−3.020

[a] $dN/dT = -1.3586 \times 10^{18}\ \mathrm{cm}^{-3}\ \mathrm{K}^{-1}$ assuming linear
[b] $dR/dT = -2.543 \times 10^{-4}\ \mathrm{K}^{-1}$ assuming linear
[c] $d\bar{\alpha}/dT = 8.000 \times 10^{-27}\ \mathrm{cm}^3\ \mathrm{K}^{-1}$ assuming linear

K^{-1}. However, the second term in Eq. (10) can be estimated as

$$\frac{4\pi}{3} N \frac{d\bar{\alpha}}{dT} = \frac{4\pi}{3}(1.43 \times 10^{21}\ \mathrm{cm}^{-3})(8.00 \times 10^{-27}\ \mathrm{cm}^3\ \mathrm{K}^{-1})$$

$$\approx 0.48 \times 10^{-4}\ \mathrm{K}^{-1}$$

taking N to be the mid-range value. This now gives

$$\frac{dR}{dT} = -3.02 \times 10^{-4}\ \mathrm{K}^{-1} + 0.48 \times 10^{-4}\ \mathrm{K}^{-1} = -2.54 \times 10^{-4}\ \mathrm{K}^{-1}$$

which is now in agreement with the observed value. Thus the temperature variation of the polarizability is almost 20% of the variation of the refractive index and to omit it when using the refractive index extrapolation procedures for the fractional volumes can indeed lead to large errors of magnitude and sign. Moreover, as seen in Table VII, the total average polarizability does vary with temperature and, in fact, the temperature variation should be estimated in calculating the ordinary and extraordinary polarizabilities of the nematic phase. Fortunately, however, the error introduced by the neglect of the polarizability's temperature variation is small enough to be ignored in such calculations, especially when simply discussing rough trends with structure and temperature.

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