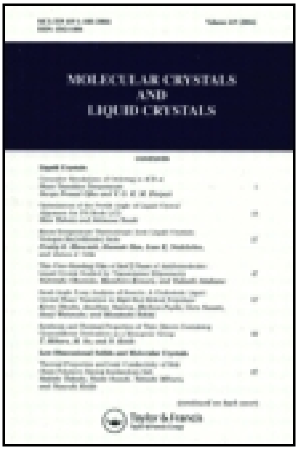

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Hindered Rotation as the Cause of Change in Polarizability Tensor Scalar of Mesogenic Molecules

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Hindered Rotation as the Cause of Change in Polarizability Tensor Scalar of Mesogenic Molecules

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In investigations of molecular order parameters $S = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle$ for liquid crystal materials, it is usually assumed that the scalar of the polarizability tensor $\alpha_\parallel + 2\alpha_\perp = \alpha_s$ of a molecule is constant. In this work the temperature dependence of the scalar of the polarizability tensor of low molecular weight liquids and of liquid crystal materials in their nematic and isotropic phases was calculated using their densities and refractive index data. The polarizability tensor scalar of mesogenic molecules is a nonlinear function of temperature, suggesting the existence of hindered rotation in the molecules in liquid crystals. The densities and refractive indixes of the low molecular weight liquids were measured, while those for the liquid crystal materials were taken from the literature. A new parameter $\lambda = \frac{d\alpha_s}{dT}$ was introduced, which gives information about the hindered rotation of one part relative to another part of the molecule in a liquid crystal. It was found that there are two causes of change in the polarizability tensor scalar of a liquid crystal molecule.

INTRODUCTION

Until now it has been believed that liquid crystal molecules have a rigid rod shape. This assumption has been the basis of most physical investigations of liquid crystals, especially those of their order parameters S.[1–10] This assumption led to the conclusion that the values of the polarizability tensor scalar $\alpha_\parallel + 2\alpha_\perp = \alpha_s$ of a molecule in the solid phase of a liquid crystal material are equal to those in the mesophase. However this assumption is incorrect, because the molecules of all liquid crystal materials have single bonds in their structures. These single bonds allow the possibility of rotation of one part of a molecule relative to another. For example, the molecules of *p*-azoxyanizole (PAA) have single bonds between azo-groups and benzene rings, and between the benzene rings and the oxygen atoms. The double bonds of the azo-groups do not however allow rotations of the nitrogens in the *p*-azoxyanizole molecule. Moreover, in a PAA molecule there are other possibilities for hindered rotation of remaining parts of the molecule. In this case, the hindered rotations of local groups are associated with change in the mesophase temperature. Change in temperature of a liquid crystal may produce a change in the conformation of molecules in three-dimensional space. This change in turn leads to a change in the polarizability tensor scalar. The polarizability tensor of each molecule of a liquid crystal is asymmetrical and its scalar $\alpha_{\parallel} + 2\alpha_{\perp} = \alpha_s$ is a constant in all coordinate systems.

In this work, we assume that the molecule of a liquid crystal can change its three-dimensional conformation with increase in temperature, and that its polarizability tensor scalar is also changed. In order to prove this hypothesis we investigated the values of the polarizability tensor scalar of two low molecular weight liquids (cyclohexanone and N_1N-dimethylformamide) because their molecules do not have the possibility of hindered rotation.

EXPERIMENTAL

The values of the polarizability tensor scalar of the low molecular weight liquids were obtained by using the Lorenz-Lorentz equation

$$\alpha_{\parallel} + 2\alpha_{\perp} = \alpha_s = \frac{(n^2 - 1)9M}{(n^2 + 2)4d\pi N_A}, \qquad (1)$$

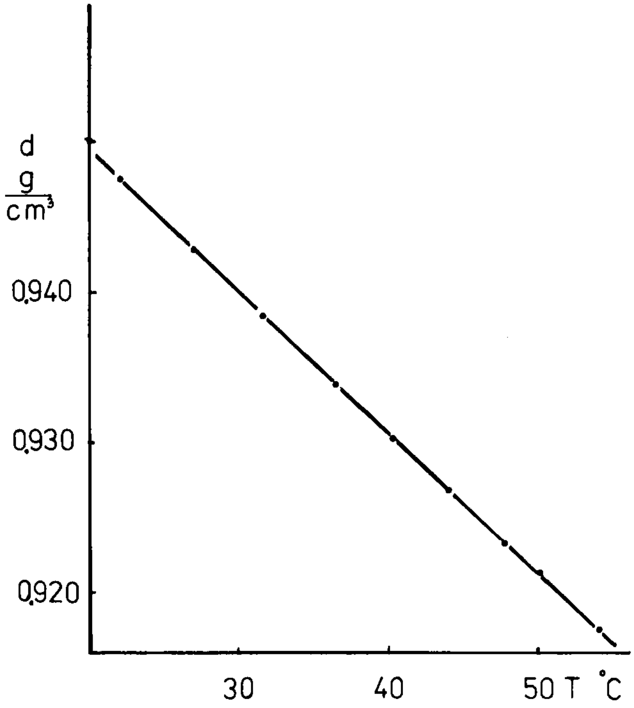

FIGURE 1 Density of *N,N*-dimethylformamide (DMF) as a function of temperature.

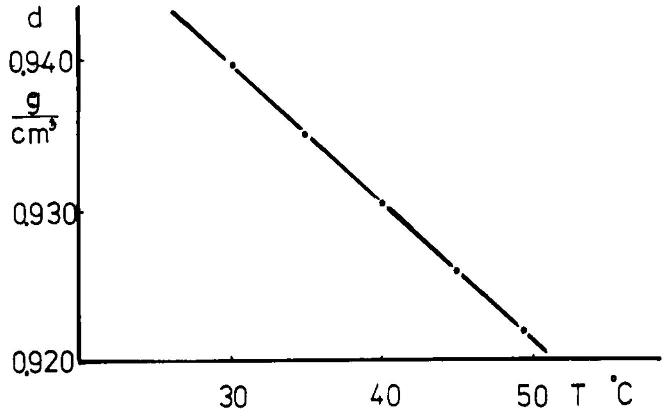

FIGURE 2 Temperature dependence of density of cyclohexanone.

where n is the refractive index of the liquid, d is its density, M is its molecular weight and N_A is the Avogadro number. Measurements of density and refractive index for cyclohexanone and dimethylformamide were made with an accuracy 10^{-4}. Density measurements were made by a method described elsewhere,[11] and an Abbé refractometer was employed to determine refractive indices. The results are shown in Fig. 1–4 and in Tables I and II.

The figures reveal that all the curves for the temperature dependence of density and refractive index are linear. From the density and refractive index data, the values of the polarizability tensor scalar $\alpha_{\parallel} + 2\alpha_{\perp} = \alpha_1 + 2\alpha_2 = \alpha_s$ were calculated for the two substances. The calculated values are listed in Tables I and II and shown in Fig. 5 and 6. It is seen from these figures that the polarizability tensor scalar of a low molecular weight liquid is practically independent of temperature. We assume that the small slope of the linear temperature dependence is not connected with the possibility of rotation of parts of the molecules. This effect is

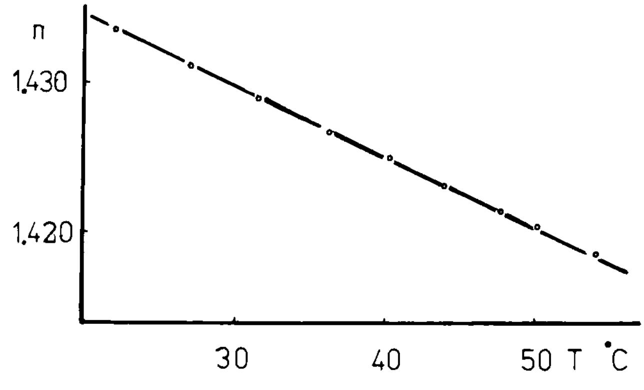

FIGURE 3 Refractive index for sodium light of dimethylformamide (DMF) as a function of temperature.

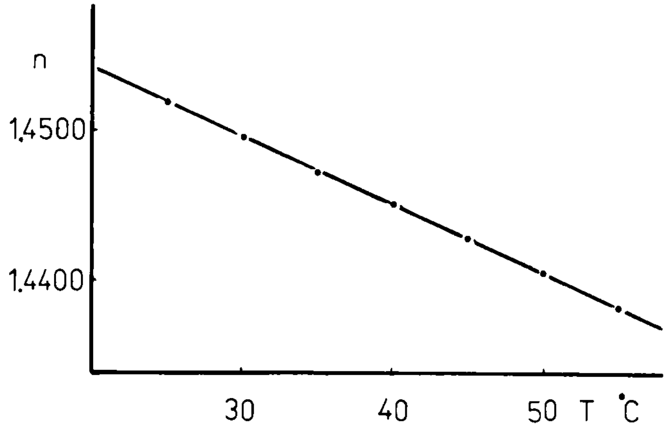

FIGURE 4 Temperature dependence of refractive index for sodium light of cyclohexanone.

TABLE I

Density (d) and refractive index data for sodium light (n_o) and polarizability tensor scalars (α_s) for *N,N*-dimethylformamide (DMF).

	T °C	d g/cm^3	n_o	α_s 10^{24} cm^3
1	22	0.9476	1.4335	23.86
2	27	0.9430	1.4311	23.86
3	31.6	0.9386	1.4290	23.87
4	36.3	0.9341	1.4268	23.88
5	40	0.9303	1.4250	23.89
6	44	0.9259	1.4232	23.91
7	46	0.9250	1.4223	23.89
8	50	0.9215	1.4204	23.89
9	54	0.9175	1.4186	23.90
10	56	0.9156	1.4178	23.91

TABLE II

Density (d) and refractive index data for sodium light (n_o) and polarizability tensor scalars (α_s) for cyclohexanone.

	T °C	d g/cm^3	n_o	α_s 10^{24} cm^3
1	20	0.9490	1.4540	33.30
2	25	0.9445	1.4519	33.33
3	30	0.9398	1.4496	33.35
4	35	0.9352	1.4473	33.36
5	40	0.9306	1.4452	33.39
6	45	0.9260	1.4429	33.41
7	50	0.9214	1.4406	33.42
8	55	0.9168	1.4384	33.44
9	60	0.9123	1.4360	33.45
10	65	0.9078	1.4339	33.47
11	70	0.9032	1.4316	33.50

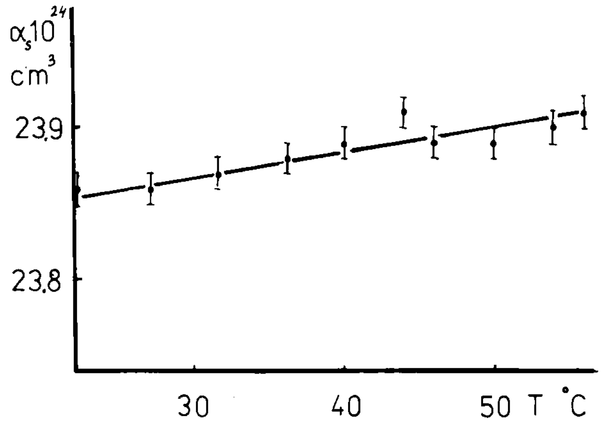

FIGURE 5 Temperature dependence of the polarizability tensor scalar of dimethylformamide (DMF).

probably due to the rotational excitation of the molecules, caused by thermal collisions.

Values for the density and refractive indices of nematic liquid crystals are available in the literature.[1,7,8,12,13] Here we used the density and refractive index data for *p*-azoxyanizole (PAA) reported by Price and Wendorff[12] and Brunet-Germain,[1] respectively. The same data for three other mesogens, 4-*n*-pentylphenyl 4-methoxybenzoate (I), 4-*n*-pentylphenyl 4-*n*-hexyloxybenzoate (II) and 4-*n*-hexyloxy-

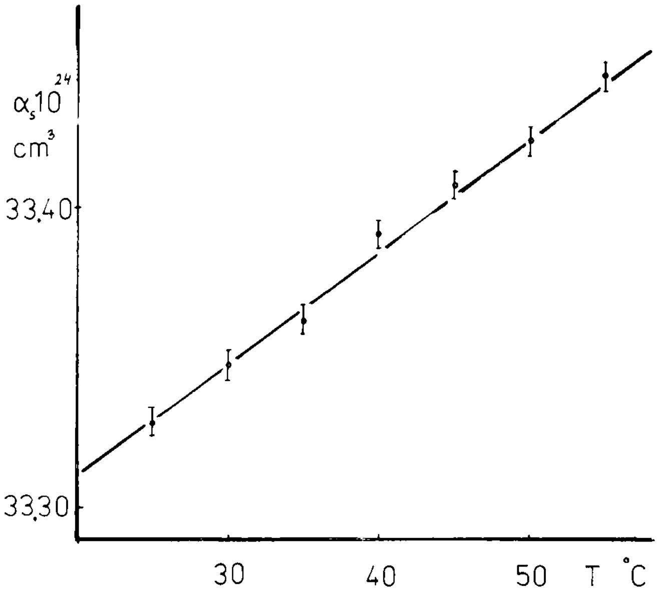

FIGURE 6 Temperature dependence of polarizability tensor scalar of cyclohexanone.

TABLE III

Densities (d), refractive indices (n_e and n_o) for sodium light and polarizability tensor scalars (α_s) for p-azoxyanizole PAA.[1,12]

	T °C	d g/cm^3	n_e	n_o	α_s 10^{24} cm^3
1	95	1.1943	1.888	1.558	94.78
2	100	1.1890	1.880	1.558	94.95
3	105	1.1837	1.870	1.559	95.14
4	110	1.1784	1.860	1.560	95.32
5	115	1.1735	1.849	1.561	95.44
6	120	1.1680	1.837	1.563	95.66
7	125	1.1624	1.823	1.567	95.98
8	130	1.1570	1.804	1.572	96.19
9	134	1.1488	1.779	1.581	96.75

phenyl 4-n-butyloxybenzoate (III), were taken from the work of Ibrahim and Haase.[13] All these data are collected in Tables III–VI.

The polarizability tensor scalar of the molecule of a liquid crystal was calculated from the equation developed for the theory of the polarizability of liquid crystals by Maier and Saupe.[14] According to this theory, the main polarizability components of a liquid crystal layer may be expressed by the equations

$$\begin{aligned} \alpha_1 &= \bar{\alpha} + (\alpha_\parallel - \alpha_\perp)\tfrac{2}{3}S \\ \alpha_2 &= \bar{\alpha} - (\alpha_\parallel - \alpha_\perp)\tfrac{1}{3}S \end{aligned} \qquad (2)$$

where $\bar{\alpha} = \dfrac{\alpha_\parallel + 2\alpha_\perp}{3}$ is the mean polarizability of the molecule of a liquid crystal, $\alpha_\parallel$ and $\alpha_\perp$ are the main polarizability tensor components of the molecule, and S is the molecular order parameter of the liquid crystal. The main polarizability components α_1 and α_2 of a liquid crystal layer can be obtained from the Lorenz-Lorentz

TABLE IV

Densities (d), refractive indices (n_e and n_o[13]) for sodium light and polarizability tensor scalars (α_s) for 4-n-pentylphenyl 4-methoxybenzoate.[13]

	T °C	d g/cm^3	n_e	n_o	α_s 10^{24} cm^3
1	29	1.0860	1.6490	1.5134	100.95
2	31	1.0790	1.6460	1.5138	101.51
3	33	1.0766	1.6430	1.5140	101.61
4	35	1.0745	1.6390	1.5146	101.64
5	37	1.0724	1.6335	1.5154	101.61
6	39	1.0700	1.6280	1.5170	101.84
7	41	1.0680	1.6200	1.5190	101.85
8	42	1.0660	1.6130	1.5220	102.02
9	42.7	1.0626	—	1.5506	102.19
10	44	1.0614	—	1.5500	102.21
11	47.7	1.0582	—	1.5482	102.24
12	52.7	1.0538	—	1.5460	102.32

equation

$$\frac{(n_e^2 - 1)3M}{(n_e^2 + 2)d4\pi N_A} = \alpha_1; \qquad \frac{(n_o^2 - 1)3M}{(n_o^2 + 2)d4\pi N_A} = \alpha_2, \tag{3}$$

where n_e and n_o are the extraordinary and ordinary refractive indices of the layer of liquid crystal.

In the literature, there are also equations due to Vuks[15] and Neugebauer[16] relating density, refractive index and polarizability for liquid crystals. However, the existing equations of Lorenz-Lorentz, Vuks, and Neugebauer are only attempts to describe the dependence of polarizability of molecules on refractive index. Of these, Neugebauer's equation is rarely used because of difficulties in the calculations. In the case of the isotropic liquid state, Vuks equation is equivalent to the Lorenz-Lorentz equation, but for the liquid crystal state, Vuks equation may yield values of α_s different from those obtained by the Lorenz-Lorentz equation. In this work however, we are interested in knowing the temperature dependence of α_s, and not the absolute values of α_s. For this purpose we used the Lorenz-Lorentz equation.

Equations 2 and 3 give the values of the polarizability tensor scalar of the mesogenic molecule as a function of refractive index, density and molecular weight. This function has a mathematical form

$$\left[\frac{(n_e^2 - 1)}{(n_e^2 + 2)} + \frac{2(n_o^2 - 1)}{(n_o^2 + 2)}\right]\frac{3M}{d4\pi N_A} = \alpha_{\parallel} + 2\alpha_{\perp} = \alpha_s; \tag{4}$$

Taking the appropriate data from Tables III–VI in equation (4), the polarizability tensor scalar for each of our four liquid crystal materials was calculated as a function of temperature. The results are illustrated in Figures 7–10.

The above figures show that the polarizability tensor scalar α_s increases with increase in temperature. However the changes in α_s are more marked in the nematic

TABLE V

Densities (d), refractive indices (n_e and n_o[13]) for sodium light and polarizability tensor scalars (α_s) for 4-*n*-pentylphenyl 4-*n*-hexyloxybenzoate.[13]

	T °C	d g/cm^3	n_e	n_o	α_s 10^{24} cm^3
1	50	1.019	1.613	1.490	132.79
2	51	1.018	1.611	1.490	132.79
3	53	1.016	1.607	1.490	132.75
4	55	1.015	1.602	1.491	132.73
5	57	1.012	1.598	1.492	132.99
6	59	1.009	1.592	1.493	133.14
7	61	1.007	1.583	1.496	133.23
8	62	1.005	1.577	1.498	133.37
9	63	1.002	—	1.522	133.39
10	65	1.001	—	1.521	133.30
11	68	0.998	—	1.520	133.49
12	73	0.994	—	1.518	133.59

TABLE VI

Densities (d), refractive indices (n_e and n_o[13]) for sodium light and polarizability tensor scalars (α_s) for 4-*n*-hexyloxyphenyl 4-*n*-butyloxybenzoate.[13]

	T °C	d g/cm^3	n_e	n_o	α_s 10^{24} cm^3
1	31	1.033	1.615	1.496	127.22
2	34	1.030	1.612	1.496	127.13
3	36	1.029	1.608	1.497	127.14
4	38	1.027	1.604	1.497	127.29
5	41	1.025	1.599	1.498	127.20
6	43	1.022	1.596	1.498	127.38
7	45	1.018	1.592	1.498	127.63
8	47	1.016	1.583	1.501	127.71
9	48	1.014	1.577	1.503	127.85
10	48.5	1.013	—	1.527	127.93
11	50	1.013	—	1.526	127.86
12	53.5	1.008	—	1.524	127.95
13	58.5	1.005	—	1.522	127.93

phases of the liquid crystal materials than in the low molecular weight liquids. In Fig. 8–10, one should also note that the temperature dependence of the polarizability tensor scalar of a liquid crystal material in the isotropic liquid state is linear and similar to that for a low molecular weight liquid. Moreover, the changes in the polarizability tensor scalar of the nematic phases are much greater than those for the isotropic liquid states. Thus, it may be inferred that there is hindered rotation in parts of the molecules of liquid crystal materials only in the temperature intervals of their nematic phases. It is also suggested that hindered rotation of parts of molecules may lead to the formation of mesophases.

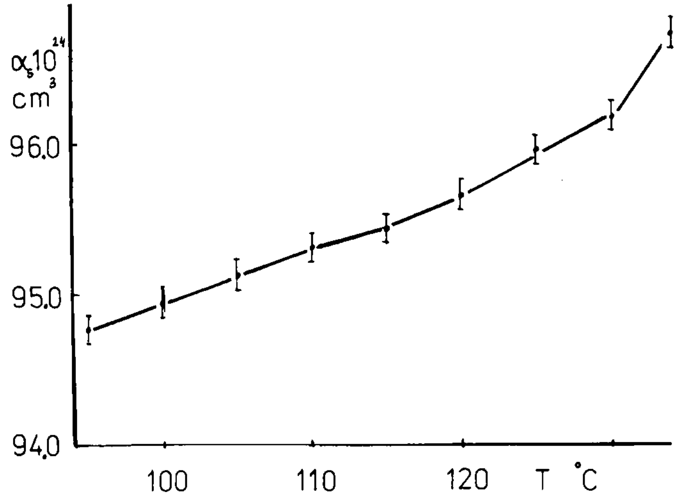

FIGURE 7 Polarizability tensor scalar of p-azoxyanizole *v* temperature.

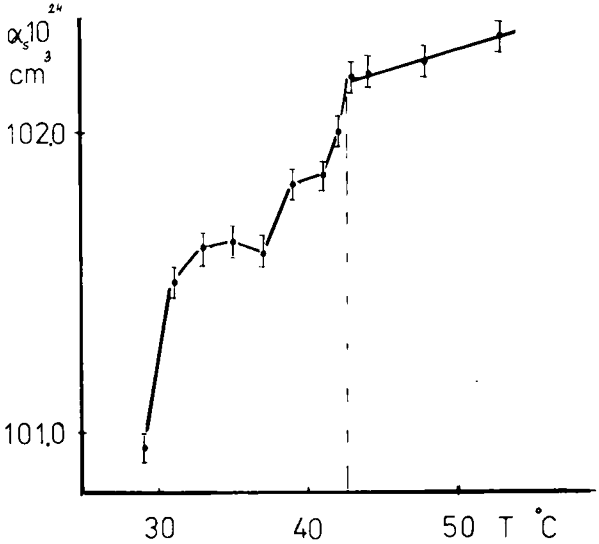

FIGURE 8 Temperature dependence of the scalar of the polarizability tensor of 4-*n*-pentylphenyl 4-methoxybenzoate.

In order to illustrate the change in the three-dimensional conformation of the molecule of a liquid crystal material in the interval of the nematic phase and in the isotropic liquid, we introduced a new parameter $\lambda = \frac{d\alpha_s}{dT}$. In the isotropic liquid state, $\lambda = 0.0013\ 10^{-24}$ cm^3/°C for dimethylformamide and $\lambda = 0.0036\ 10^{-24}$ cm^3/°C for cyclohexanone. For the investigated liquid crystal materials, the following values of λ were found for the isotropic liquids: $\lambda_4 = 0.013\ 10^{-24}$ cm^3/°C, $\lambda_5 = 0.0208\ 10^{-24}$ cm^3/°C and $\lambda_6 = 0.008\ 10^{-24}$ cm^3/°C.

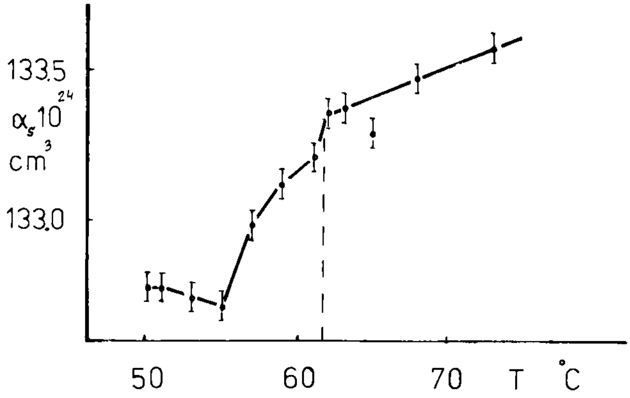

FIGURE 9 Temperature dependence of the polarizability tensor scalar of 4-*n*-pentylphenyl 4-*n*-hexyloxybenzoate.

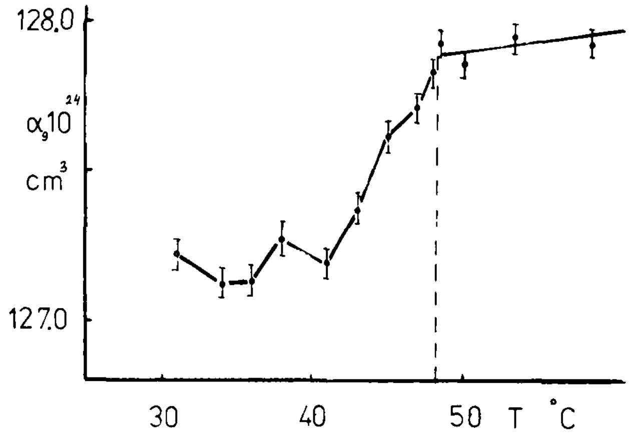

FIGURE 10 Temperature dependence of the polarizability tensor scalar of 4-*n*-hexyloxyphenyl 4-*n*-butyloxybenzoate.

Each value of the λ parameter is constant for the isotropic liquid phase. The values of λ for investigated liquid crystal materials are not however constant over the temperature interval of the nematic phase. A mean value of $\bar{\lambda}$ can be calculated for these liquid crystal materials over the temperature interval of the nematic phase, taking the end value of α_s of this interval. The calculated $\bar{\lambda}$ values for our liquid crystal materials are as follows: $\bar{\lambda}_3 = 0.0512\ 10^{-24}$ cm^3/°C, $\bar{\lambda}_4 = 0.0813\ 10^{-24}$ cm^3/°C, $\bar{\lambda}_5 = 0.048\ 10^{-24}$ cm^3/°C, $\bar{\lambda}_6 = 0.037\ 10^{-24}$ cm^3/°C.

From the above data it follows that the $\bar{\lambda}$ values for the nematic phase are greater than the values of λ for the isotropic phases of mesogens and for low molecular weight liquids. The maximum difference $(\bar{\lambda} - \lambda)$ proves the existence of hindered rotation of parts of the molecule of a liquid crystal material in the temperature interval of its nematic phase. The fact that the λ values of low molecular weight liquids and of liquid crystal materials in their isotropic phases are constant implies that the change in the polarizability tensor scalar in the isotropic liquid phase is connected with the rotational excitation of molecules, caused by thermal collisions.

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