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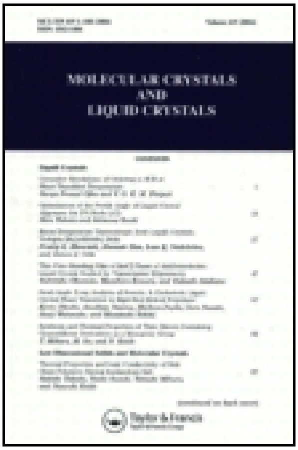

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Birefringence of Some Nematic Compounds

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Birefringence of Some Nematic Compounds

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This paper reports the refractive index and density data and discusses the orientational order parameters in the case of the following eight nematic compounds, viz., (1) *p*(*p*-ethoxyphenylazo) phenyl valerate, (2) *p*(*p*-ethoxyphenylazo)phenyl hexanoate, (3) *p*(*p*-ethoxyphenylazo)phenyl heptanoate, (4) *p*(*p*-ethoxyphenylazo)phenyl undecylenate, (5) 4,4′-bis(hexyloxy)azoxybenzene, (6) 4,4′-bis(heptyloxy)azoxybenzene, (7) anisylidene-*p*-aminophenyl acetate, and (8) anisylidene-*p*-aminophenyl butyrate.

INTRODUCTION

The refractive indices of nematic compounds in their liquid, liquid crystalline and crystalline phases have been used by a number of investigators for the calculation of the orientational order parameters in the nematic phase. The calculation of the polarizabilities and orientational order parameter from the index data involves a knowledge of the nature of the local electric field inside the medium. The problem of the local electric field has been treated mainly from two different approaches, viz., (i) the use of the Vuks formulae[1–3] which assumes an isotropic local field, and (ii) the use of the Neugebauer relation[4–8] obtained from the point dipole approximation, and involving an anisotropic local field. A third approach has also been used by Derzhanski and Petrov[9] and by de Jeu and Bordewijk.[10] In their model it is assumed that the molecule occupies a spheroidal cavity whose volume is equal to the volume available to the molecule and that the spheroid shaped molecule is uniformly polarizable and that the medium surrounding the spheroidal cavity is a homogeneous anisotropic dielectric. Evidently, the basic approximations involved in both the point dipole and the spheroidal-molecule models are of a simplifying nature. Actually, the molecules are of finite size and have

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irregular shapes and consist of groups which are polarizable to different extents. Further, the immediate vicinity of a molecule cannot be approximated by a continuous medium. Therefore, calculations of the cavity field from electrostatic theory by the application of the boundary conditions for a spheroidal cavity are not likely to lead to the true value. However, it is found that the orientational order parameters evaluated through the different approaches mentioned above are reasonably consistent with the values obtained from studies on diamagnetic anisotropy and on the NMR.

The optical anisotropies calculated from the Vuks formulae and the spheroidal molecule model are found to be too high and are difficult to account for, especially in the case of substances with large birefringence. On the other hand, the polarizabilities calculable through the Neugebauer approach agree reasonably well with the estimates of polarizabilities made from bond polarizability data.[8] It may be remarked here that the spheroidal molecule model leads to equations equivalent to the Neugebauer relations in the case of crystals with a parallel alignment of the long axis of the molecules. We have in an earlier paper used the Neugebauer approach to discuss the birefringence data of compounds exhibiting smectic A and B phases.[11] Also, in a recent paper on the optical properties of smectic C phase, Isaert and Billard[12] have shown that in this case also the Naugebauer relation is valid. Under these circumstances, we prefer to use the Neugebauer relation to calculate the polarizabilities and the orientational order parameters in the case of the eight nematic compounds for which the refractive index data are reported here.

EXPERIMENTAL METHODS

The compounds for which the refractive index and density data are reported here, are listed below. The structural formulae of the compounds are shown in Figure 1.

1) *p*(*p*-ethoxyphenylazo) phenyl valerate
2) *p*(*p*-ethoxyphenylazo) phenyl hexanoate
3) *p*(*p*-ethoxyphenylazo) phenyl heptanoate
4) *p*(*p*-ethoxyphenylazo) phenyl undecylenate
5) 4,4′-bis(hexyloxy) azoxybenzene
6) 4,4′-bis(heptyloxy) azoxybenzene
7) anisylidene-*p*-aminophenyl acetate
8) anisylidene-*p*-aminophenyl butyrate.

The first four compounds were obtained from Eastman Kodak, USA., the next two from E. Merck, W. Germany and the other two were from

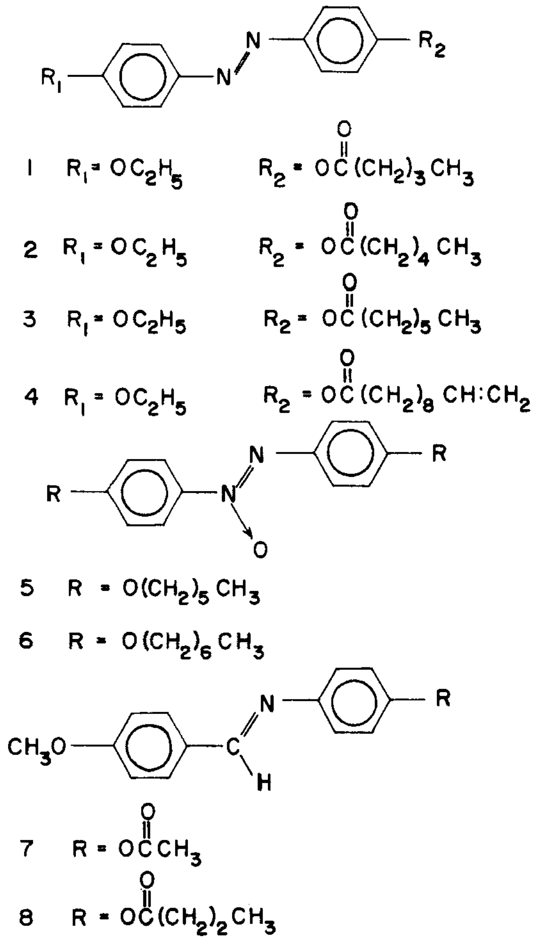

FIGURE 1 Structural formulae of the eight compounds. The serial numbers in the figure correspond to the numbers in the list of the compounds given in text.

Riedel De Haen AG, W. Germany. For use in our experiments, the compounds were purified by recrystallization from benzene solutions. The refractive index measurements were made using a goniometer spectrometer, the specimen being inside a hollow prism of small angle (4 to 5°). The experimental techniques adopted by us are the same as employed by a number of earlier investigators.[13,14] The oriented samples were prepared by rubbing the inner face of the prism along the desired direction of orientation, prior to the introduction of the sample into the prism. The refractive indices were

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determined at different temperatures for different wavelengths in the visible region of the spectrum. The refractive indices of compounds 5 and 6 in their nematic phase have been determined by Hanson and Shen[3] for λ 6328 Å and by de Jeu and Bordewijk[10] for λ 6328 Å and λ 5461 Å. Our data are for the wavelengths λ 5893 Å, λ 5780 Å and λ 5461 Å. There is broad agreement between the data obtained by us and the other investigators.

For five of the compounds, it was possible to determine the refractive indices (at 28°C) in the crystalline phase also, using specially prepared oriented specimens. Two sets of specimens were prepared in the case of each compound. In the first case, the sample in the nematic phase (with the long axes of the molecules oriented parallel to the refracting edge of the prism) was cooled in a high magnetic field applied parallel to the direction of the molecular orientation and was allowed to crystallize slowly. With this crystalline sample the refractive index for light polarized parallel to the refracting edge was very high and for light polarized perpendicular to the refracting edge, the index was low. These refractive indices may be denoted by n_3 and n_1 respectively. In the second case, the sample in the nematic phase with the long axes of the molecules oriented perpendicular to the refracting edge (and parallel to the surfaces of the prism), was cooled and allowed to crystallize slowly in a magnetic field applied parallel to the direction of molecular orientation. With the second sample, the refractive index for light polarized perpendicular to the refracting edge was very high and equal to n_3, whereas the index for vibrations parallel to the refracting edge was found to be low (and slightly different from n_1) and this index is here denoted by n_2. In the case of both the crystalline specimens, the optic axes of the medium were lying too close to the refracting surface of the prism for observation of the interference figures between crossed polars. Under the circumstances, n_3 appears to be a good estimate of the refractive index for light polarized parallel to the long axes of the molecules, (i.e., $n_3 = n_{\parallel}$). The index $n_{\perp}$ for light polarized perpendicular to the long axes of the molecules is tentatively assumed to be given by the relation $n_{\perp}^2 = (n_1^2 + n_2^2)/2$. The above identification is further justified by the fact that if one uses the Born relation[11,15] to calculate the mean polarizabilities, they agree to within about 1% of the values obtained from the Lorenz–Lorentz relation using the index data for the liquid phase.

Measurements of the densities in the crystalline phase were carried out, using the floatation technique. The densities in the liquid and nematic phases were determined using a density bottle and also by using a capillary tube and were corrected for the thermal expansion of glass. The refractive index and density data for the different compounds are presented in Tables I to IX. The average errors in the measurements of the temperatures, densities and refractive indices are estimated to be ±0.2°C, ±0.001 gm/cm^3 and ±0.001 respectively.

TABLE I

Densities and refractive indices of *p*(*p*-ethoxyphenylazo)phenyl valerate (t_c = 128°C)

	ρ in	5461 Å		5780 Å		5893 Å		6563 Å	
$t_c - t$	gm/cm^3	n_e	n_o	n_e	n_o	n_e	n_o	n_e	n_o
−0.8 (liquid)	1.053	1.604		1.593		1.589		1.575	
1.0	1.058	1.743	1.541	1.726	1.533	—	—	—	—
4.0	1.062	1.766	1.532	1.743	1.525	1.737	1.522	1.715	1.514
10.0	1.068	1.792	1.525	1.766	1.518	1.761	1.516	1.734	1.509
15.5	1.074	1.808	1.521	1.782	1.514	1.777	1.512	1.748	1.506
23.5	1.081	1.827	1.517	1.801	1.511	1.795	1.509	1.764	1.503
30.0	1.086	1.839	1.515	1.813	1.509	1.806	1.507	1.775	1.501
35.5	1.090	1.847	1.514	1.822	1.508	1.814	1.507	1.783	1.501
41.0	1.094	1.855	1.513	1.829	1.508	1.821	1.506	1.791	1.500
48.0	1.099	1.862	1.512	1.837	1.507	1.829	1.505	1.797	1.500

TABLE II

Densities and refractive indices of *p*(*p*-ethoxyphenylazo)phenyl hexanoate (t_c = 126°C)

	ρ in	5461 Å		5780 Å		5893 Å		6563 Å	
$t_c - t$	gm/cm^3	n_e	n_o	n_e	n_o	n_e	n_o	n_e	n_o
−0.5 (liquid)	1.044	1.600		1.587		1.584		1.570	
4.0	1.051	1.753	1.528	1.731	1.520	1.728	1.519	—	—
8.0	1.055	1.768	1.522	1.747	1.516	1.740	1.515	—	—
12.5	1.059	1.781	1.518	1.759	1.512	1.752	1.511	1.726	1.503
16.0	1.062	1.790	1.516	1.768	1.510	1.761	1.509	1.734	1.501
19.5	1.065	1.799	1.514	1.776	1.509	1.768	1.507	1.742	1.500
24.0	1.069	1.809	1.512	1.786	1.507	1.778	1.505	1.751	1.498
28.5	1.073	1.819	1.511	1.795	1.506	1.788	1.504	1.760	1.497
32.0	1.076	1.825	1.510	1.801	1.505	1.794	1.503	1.766	1.497
37.0	1.080	1.834	1.509	1.809	1.504	1.802	1.502	1.774	1.496
40.0	1.083	1.841	1.509	1.815	1.504	1.809	1.502	1.779	1.496
44.5	1.086	1.849	1.508	1.824	1.503	1.817	1.502	1.786	1.496
48.5	1.090	1.855	1.508	1.829	1.503	1.822	1.502	1.791	1.495
52.5	1.093	1.864	1.507	1.837	1.502	1.831	1.501	1.800	1.495

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TABLE III

Densities and refractive indices of *p*(*p*-ethoxyphenylazo)phenyl heptanoate (t_c = 119°C)

$t_c - t$	ρ in gm/cm^3	5461 Å		5780 Å		5893 Å	
		n_e	n_o	n_e	n_o	n_e	n_o
−1.0 (liquid)	1.040	1.589		1.577		1.574	
4.0	1.046	1.723	1.527	1.703	1.519	1.698	1.517
6.0	1.048	1.735	1.522	1.712	1.516	1.708	1.514
9.0	1.051	1.746	1.518	1.724	1.512	1.719	1.510
13.0	1.055	1.758	1.514	1.737	1.509	1.730	1.507
19.0	1.060	1.773	1.511	1.752	1.505	1.745	1.503
21.5	1.062	1.779	1.510	1.758	1.504	1.750	1.502
25.0	1.065	1.787	1.508	1.765	1.503	1.757	1.501
28.0	1.067	1.793	1.507	1.771	1.502	1.763	1.500
34.0	1.072	1.804	1.506	1.781	1.501	1.774	1.499
39.0	1.076	1.813	1.505	1.789	1.500	1.783	1.499

TABLE IV

Densities and refractive indices of *p*(*p*-ethoxyphenylazo)phenyl undecylenate (t_c = 110°C)

$t_c - t$	ρ in gm/cm^3	5461 Å		5780 Å		5893 Å	
		n_e	n_o	n_e	n_o	n_e	n_o
−0.5 (liquid)	1.037	1.575		1.565		1.562	
2.0	1.042	1.691	1.524	1.674	1.516	1.668	1.514
6.0	1.046	1.710	1.514	1.694	1.508	1.685	1.506
9.5	1.050	1.724	1.510	1.707	1.504	1.699	1.502
14.5	1.055	1.739	1.506	1.722	1.501	1.715	1.498
17.0	1.058	1.746	1.504	1.728	1.500	1.721	1.498
20.5	1.062	1.754	1.503	1.736	1.499	1.730	1.497
25.0	1.067	1.764	1.503	1.745	1.498	1.739	1.496
30.0	1.072	1.775	1.501	1.755	1.497	1.749	1.496
35.0	1.078	1.785	1.501	1.764	1.497	1.758	1.495
40.0	1.083	1.795	1.500	1.773	1.496	1.767	1.495
44.0	1.086	1.803	1.500	1.780	1.496	1.773	1.494

TABLE V

Densities and refractive indices of 4,4′-bis(hexyloxy) azoxybenzene
(t_c = 127°C)

$t_c - t$	ρ in gm/cm^3	5461 Å n_e	5461 Å n_o	5780 Å n_e	5780 Å n_o	5893 Å n_e	5893 Å n_o
−1.0 (liquid)	0.976	1.576		1.569		1.566	
3.0	0.986	1.698	1.521	1.688	1.516	1.682	1.515
10.8	0.992	1.726	1.515	1.713	1.510	1.707	1.509
14.5	0.996	1.738	1.513	1.724	1.508	1.718	1.507
19.5	1.000	1.752	1.511	1.736	1.507	1.731	1.505
21.5	1.002	1.758	1.510	1.742	1.506	1.737	1.504
27.5	1.007	1.767	1.509	1.753	1.504	1.747	1.503
30.0	1.009	1.769	1.508	1.756	1.504	1.751	1.503

TABLE VI

Densities and refractive indices of 4,4′-bis(heptyloxy) azoxybenzene
(t_c = 122°C)

$t_c - t$	ρ in gm/cm^3	5461 Å n_e	5461 Å n_o	5780 Å n_e	5780 Å n_o	5893 Å n_e	5893 Å n_o
−1.0 (liquid)	0.968	1.571		1.564		1.561	
3.0	0.976	1.683	1.522	1.668	1.518	1.666	1.516
5.0	0.978	1.689	1.518	1.675	1.514	1.673	1.512
9.5	0.983	1.703	1.512	1.690	1.509	1.686	1.507
13.3	0.987	1.714	1.509	1.701	1.506	1.696	1.504
16.5	0.990	1.722	1.507	1.710	1.504	1.704	1.502
20.5	0.995	1.732	1.504	1.717	1.501	1.712	1.500
26.0	0.999	1.739	1.502	1.724	1.500	1.718	1.499

TABLE VII

Densities and refractive indices of anisylidene-*p*-aminophenyl acetate (t_c = 110°C)

$t_c - t$	ρ in gm/cm^3	4358 Å n_e	4358 Å n_o	5461 Å n_e	5461 Å n_o	5780 Å n_e	5780 Å n_o	5893 Å n_e	5893 Å n_o
−0.6 (liquid)	1.122	1.651		1.596		1.589		1.586	
4.0	1.133	1.830	1.569	1.738	1.532	1.726	1.527	1.721	1.525
9.0	1.136	1.840	1.564	1.749	1.529	1.736	1.524	1.731	1.522
13.5	1.139	1.854	1.560	1.757	1.526	1.744	1.521	1.740	1.519
19.0	1.142	1.867	1.556	1.768	1.524	1.754	1.518	1.749	1.517
23.0	1.144	1.877	1.553	1.775	1.522	1.761	1.517	1.756	1.516
26.0	1.146	1.884	1.552	1.780	1.521	1.766	1.517	1.762	1.516

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TABLE VIII

Densities and refractive indices of anisylidene-*p*-aminophenyl butyrate (t_c = 113°C)

$t_c - t$	ρ in gm/cm^3	4358 Å		5461 Å		5780 Å		5893 Å	
		n_e	n_o	n_e	n_o	n_e	n_o	n_e	n_o
−0.8 (liquid)	1.070	1.635		1.587		1.580		1.578	
7.0	1.079	1.776	1.569	1.698	1.535	1.689	1.529	1.686	1.528
10.0	1.081	1.793	1.565	1.712	1.532	1.700	1.527	1.697	1.525
13.0	1.084	1.807	1.562	1.722	1.530	1.709	1.525	1.706	1.523
18.0	1.087	1.824	1.559	1.735	1.527	1.721	1.523	1.717	1.521
24.0	1.092	1.841	1.555	1.747	1.525	1.733	1.522	1.729	1.519
28.0	1.094	1.850	1.554	1.754	1.524	1.741	1.521	1.737	1.519
34.0	1.099	1.862	1.552	1.765	1.523	1.752	1.520	1.747	1.518
41.5	1.104	1.874	1.550	1.777	1.523	1.764	1.519	1.759	1.517
49.5	1.111	1.886	1.549	1.788	1.522	1.775	1.518	1.771	1.516
57.0	—	1.897	1.548	1.799	1.521	—	—	—	—

TABLE IX

Density and refractive index data for the crystalline state at 28°C

Substance	ρ in gm/cm^3	λ in Å	n_1	n_2	n_3
p(*p*-ethoxyphenylazo) phenyl valerate	1.226	5461	1.484	1.569	2.120
		5780	1.481	1.563	2.076
		5893	1.481	1.561	2.064
p(*p*-ethoxyphenylazo) phenyl hexanoate	1.210	5461	1.498	1.549	2.066
		5780	1.493	1.546	2.036
		5893	1.491	1.544	2.025
p(*p*-ethoxyphenylazo) phenyl heptanoate	1.190	5461	1.494	1.540	2.001
		5780	1.493	1.537	1.966
		5893	1.493	1.536	1.958
p(*p*-ethoxyphenylazo) phenyl undecylenate	1.160	5461	1.466	1.522	1.931
		5780	1.465	1.516	1.898
		5893	1.465	1.514	1.891
anisylidene-*p*-aminophenyl butyrate	1.220	5461	1.505	1.559	1.977
		5780	1.502	1.556	1.958
		5893	1.502	1.555	1.952

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RESULTS AND DISCUSSION

The calculation of the polarizabilities in the nematic, liquid and the crystalline phases are made by using the following relations (see for example Subramhanyam *et al.*[8]). Neugebauer relation for the nematic phase:

$$\frac{1}{\alpha_e} + \frac{2}{\alpha_o} = \frac{4\pi N_n}{3}\left[\frac{n_e^2 + 2}{n_e^2 - 1} + \frac{2(n_o^2 + 2)}{n_o^2 - 1}\right]. \tag{1}$$

Lorenz–Lorentz relation for the liquid phase:

$$\bar{\alpha} = \frac{\alpha_{\|} + 2\alpha_{\perp}}{3} = \frac{\alpha_e + 2\alpha_o}{3} = \frac{3}{4\pi N_l}\left(\frac{n^2 - 1}{n^2 + 2}\right). \tag{2}$$

Neugebauer relation for the crystalline phase:

$$\frac{1}{\alpha_{\|}} + \frac{2}{\alpha_{\perp}} = \frac{4\pi N_c}{3}\left[\frac{n_{\|}^2 + 2}{n_{\|}^2 - 1} + \frac{2(n_{\perp}^2 + 2)}{n_{\perp}^2 - 1}\right], \tag{3}$$

with $n_{\|}^2 = n_3^2$ and $n_{\perp}^2 = (n_1^2 + n_2^2)/2$. In the above N_n, N_l, and N_c refer to the number of molecules per unit volume in the nematic, liquid and crystalline phases respectively, and α_e and α_o are the effective average polarizabilities of the molecules for the electric vector respectively parallel and perpendicular to the optic axis of the medium. $\alpha_{\|}$ and $\alpha_{\perp}$ refer to the principal polarizabilities of the molecule parallel and perpendicular to the long axis respectively. The orientational order parameter S is related to the polarizabilities by the equation, $S = (\alpha_e - \alpha_o)/\Delta\alpha$, where $\Delta\alpha = (\alpha_{\|} - \alpha_{\perp})$ is the optical anisotropy. α_e and α_o are readily calculated from Eq. 1 and Eq. 2 remembering $\alpha_e > \alpha_o$. We wish to remark that the values of $(\alpha_e - \alpha_o)$ calculated by using the Neugebauer relation (or by using the other approaches) exhibit an almost linear relationship with the corresponding values of $(n_e^2 - n_o^2)$. However, it should be mentioned that this feature is only approximately true and may not hold in general.

With regard to the calculation of $\Delta\alpha$ one can use Eq. 2 and Eq. 3. In Table X, are shown the values of $\Delta\alpha$ calculated from the refractive index data in the

TABLE X

Anisotropy of polarizabilities calculated from the index data for λ 5893 Å and the values used in our calculations of S-factors

Substance	1	2	3	4	5	6	7	8
$\Delta\alpha \times 10^{24}$ (cm^3) from index data	30.8	32.0	30.8	35.8	—	—	—	23.0
$\Delta\alpha \times 10^{24}$ (cm^3) used in our calculations of S factors	31.3	32.0	31.9	35.8	29.3	29.4	22.4	23.0

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crystalline phase for five compounds. Equation (3) is based on the assumption that all the molecules are aligned parallel to one another in the crystalline phase. If the molecules are not aligned exactly parallel, the calculated value of $\Delta\alpha$ is likely to be smaller than the true value of the optical anisotropy of the molecule. It is found that the values of $\Delta\alpha$ calculated in the case of the compounds 2 and 4 (i.e., the hexanoate and undecylenate esters) lead to values of S-factors which are in reasonable agreement with the values determined from NMR studies by Watkins and Johnson,[16] confirming that the values of $\Delta\alpha$ calculated from the index data for the compounds 2 and 4 are reliable. The compounds 1, 2 and 3 have the same central rigid portion and differ from one another, only in that the number of methylene end groups are different in the three cases. If it is assumed that the contribution of the central rigid portion of the molecules to $\Delta\alpha$ is the same in all the three cases, then it follows that the values of $\Delta\alpha$ in the case of the valerate, hexanoate and heptanoate esters will be different owing to the different contributions to $\Delta\alpha$ arising from the different end groups in the three cases. The contributions of the end groups to $\Delta\alpha$ in the three cases can be calculated from the anisotropies of bond polarizabilities[17] for λ 5893 Å, assuming that the molecules have the all-*trans* conformation. From the calculations it emerges that the values of $\Delta\alpha$ in the case of valerate and heptanoate esters should be less than that of hexanoate ester by 0.7×10^{-24} cm^3 and 0.1×10^{-24} cm^3 respectively. Therefore, the values of $\Delta\alpha$ for the valerate and heptanoate esters are estimated to be 31.3×10^{-24} cm^3 and 31.9×10^{-24} cm^3 respectively and these values are used in our calculation of the S-factors in the case of compounds 1 and 3. It may be noticed from Table 10 that the values of $\Delta\alpha$ calculated from the index data in the case of valerate and heptanoate esters are only slightly lower than our estimated values.

The hexyloxy and heptyloxy compounds (5 and 6) and PAA are homologous compounds. The value of $\Delta\alpha$ in the case of PAA, calculated from the index data,[8,18] is known to be 25.6×10^{-24} cm^3. The contributions to $\Delta\alpha$ by the end groups in the hexyloxy and heptyloxy compounds are again calculable from the anisotropies of bond polarizabilities and by assuming the all-*trans* conformation for the molecules. Taking into account the value of $\Delta\alpha$ for PAA and the end group contributions in the case of the hexyloxy and heptyloxy compounds, the values of $\Delta\alpha$ in these two cases are calculated to be 29.3×10^{-24} cm^3 and 29.4×10^{-24} cm^3 respectively and these values are used in the calculation of S-factors.

The value of $\Delta\alpha$ in the case of compound 8, calculated from the index data for λ 5893 Å is found to be 23.0×10^{-24} cm^3. This value is in close agreement with the value of 22.5×10^{-24} cm^3 for MBBA obtainable from the index data for λ 5893 Å in the nematic phase and the S-factors from NMR studies in the case of MBBA,[19] because the molecular structures in these two cases are quite similar. Therefore, the value of $\Delta\alpha$ obtained from the index data in the case of compound 8 appears to be reliable. In the case of compound 7, which is homologous with compound 8, the value of $\Delta\alpha$ is estimated to be 22.4×10^{-24} cm^3, after taking into account from bond polarizability data the difference which should arise in the value of $\Delta\alpha$ in the case of the compounds 7 and 8 owing to the different end groups in the two cases.

It may be mentioned here that in the case of compounds 2, 4 and 8 the calculated S-factors from the index data for the different wavelengths at any given temperature are in agreement to within one percent of their mean value. In the case of the other compounds also similar agreement is obtainable provided one finds the values of $\Delta\alpha$ for the other wavelengths by assuming the S-factors calculated for λ 5893 Å at any one temperature. The calculated values of S-factors are graphically represented in Figures 2, 3 and 4. From Figure 2 it emerges that in the case of compounds 1 to 4, all of which have the same central group but different end groups, the S-factors at the same value of $(t_c - t)$ lie very close to one another as is predicted by the theory due to

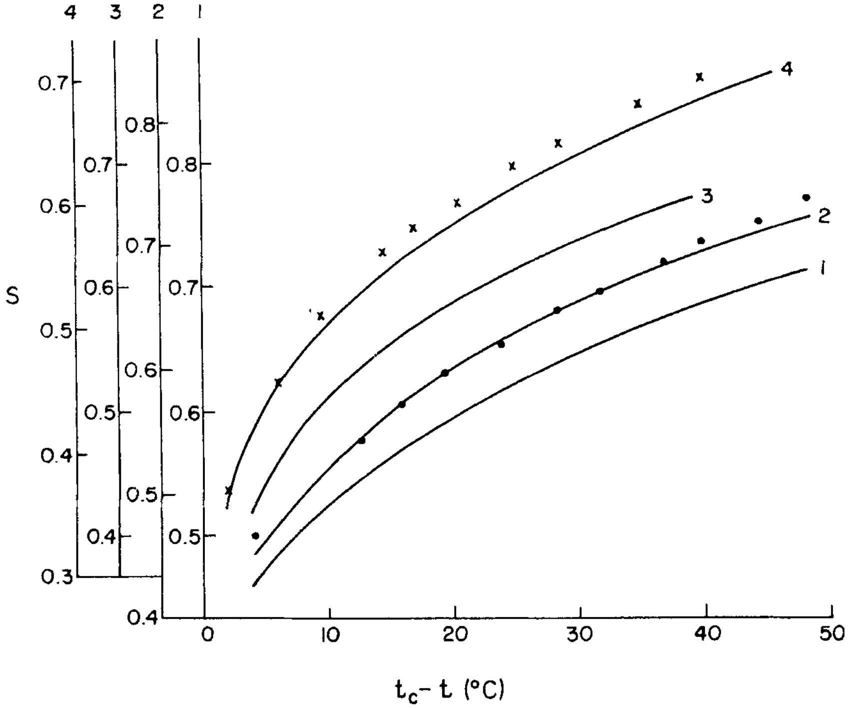

FIGURE 2 Orientational order parameter versus $(t_c - t)$ for the first four compounds. Solid line: present work; solid circles and crosses refer to the S factors from NMR studies (Ref. 16), for the compounds 2 and 4 respectively.

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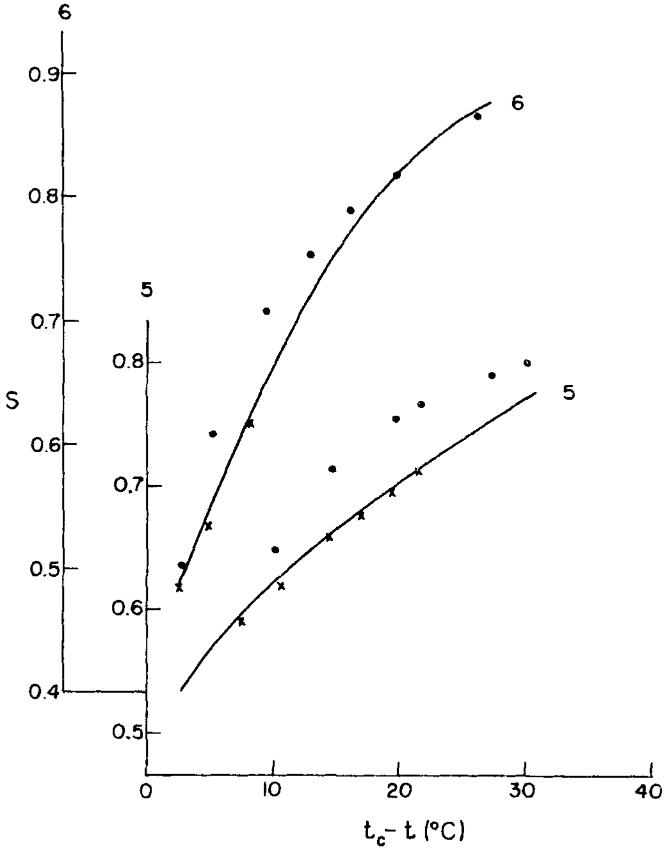

FIGURE 3 Orientational order parameter versus ($t_c - t$) for the compounds 5 and 6. Solid line: present work; solid circles and crosses refer to data from Ref. 3 and Ref. 22 respectively.

Maier and Saupe.[20,21] However, such similarity is not observed in the case of compounds 5 and 6. It is found that in the case of compound 6 [4,4′-bis(heptyloxy)azoxybenzene], that at low temperatures, the orientational order parameters are quite high, consistent with the fact that this compound undergoes a phase transition to the smectic mesophase at 95°C. The values of the *S*-factors in the case of compounds 5 and 6 may be seen from Figure 3 to be in reasonable agreement with the values obtained by Hanson and Shen[3] and by de Jeu and Claassen.[22] It is also found from Figures 2 and 4 that the *S*-factors, in the case of compounds 1, 7 and 8 and MBBA, exhibit a similar temperature variation, the corresponding values for the same ($t_c - t$) being approximately close to one another, as may be expected from the similarity of their molecular structures.

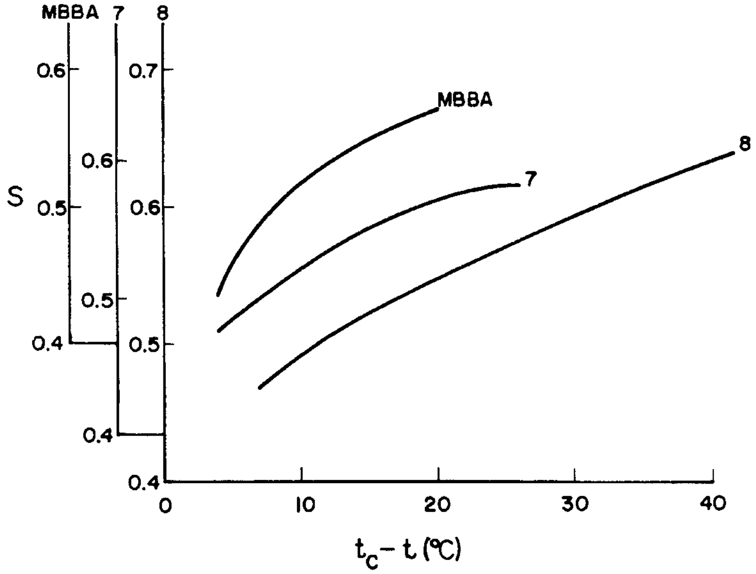

FIGURE 4 Orientational order parameter versus ($t_c - t$) for MBBA (Ref. 19) and for the compounds 7 and 8.

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