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Electro-optical properties of 4,4'-bis-[ω -(4-cyanobiphenyl-4'-yloxy)alkyloxy]biphenyls nematics

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Electro-optical properties of nematics of the trimer series 4,4'-bis-[ω -(4-cyanobiphenyl-4'-yloxy)alkyloxy]biphenyls have been investigated by the method of orientational elastic deformations in electric fields. The number n of CH_2 groups in the oxyalkyl fragment was varied from $n=2$ to $n=10$. A strong odd–even effect was observed in the optical anisotropy Δn and in the values of the threshold potential V_0 for the trimer nematics. These effects are, respectively, caused by oscillations of the degree of inter- and intra-molecular orientational order when n is varied. The great difference in the dependences of Δn and V_0 on n is discussed and compared with data for dimers.

1. Introduction

The molecules of low molecular weight liquid crystals (LCs) usually consist of a rigid core (mesogenic core) and one or two adjoining flexible (often alkyl) terminal groups. Although the active components favouring the formation of a mesophase with orientational intermolecular long range order, are the mesogenic cores of molecules, flexible fragments can also play an important role in determining mesophase properties. This role is particularly pronounced in odd–even effects [1] which are manifested in periodical changes of the thermal [1, 2], optical [3, 4], mechanical [5], and other properties [6] of liquid crystals when the terminal chain lengths in their molecules are varied. These experimental data have been quantitatively explained by theory in which the flexibility and conformational states of terminal alkyl chains have been taken into account [7]. It has been shown that the observed odd–even effects are due to changes in the degree of orientational order in the terminal chains of the molecules and, correspondingly, in the mesophase as a whole. These results have also been confirmed by data from NMR spectroscopy [8, 9].

However, another class of low molecular weight liquid crystals is also known. Their molecules consist of two (or three) rigid mesogenic parts joined by flexible spacers [1, 10, 11]. For these liquid crystals, the odd–even effect is manifested very dramatically in the periodicity of changes in temperature [1], enthalpy and entropy of

the nematic–isotropic phase transition [10, 11], as well as in the degree of orientational order of the mesophases [12].

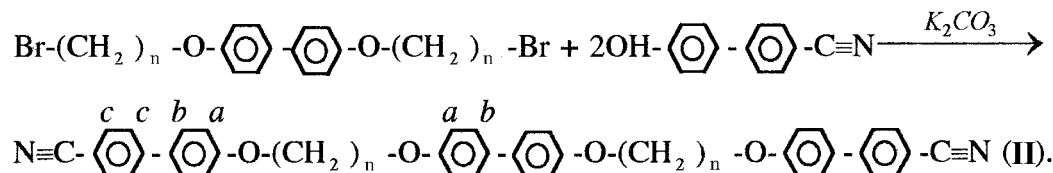
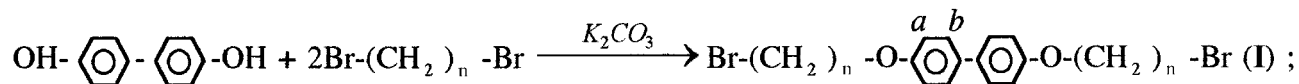
The properties of dimers (4,4'-bis-cyanobiphenyl-yloxyalkanes, BCBOA) have been investigated for solutions [13] and for the nematic phase by the methods of NMR spectroscopy [12] and molecular electro-optics [14]. A strong odd–even effect was detected for these compounds. It was manifested in the thermal and electro-optical characteristics of their melts and solutions, as well as in strong oscillations of the degree of intermolecular orientational order S with variation of the flexible core length in the molecule. It has also been shown [13, 14] that electro-optical and dielectric characteristics of dimers both in solution and in the mesophase are mainly determined by *intramolecular* orientational polar order which is retained (and is even slightly enhanced) in the mesophase under the influence of the nematic potential of the medium.

In the present paper, liquid crystalline trimers (4,4'-bis-[ω -(4-cyanobiphenyl-4'-yloxy)alkyloxy]biphenyls, BCBOAOB) (see scheme 1) were investigated for the nematic phase by the method of orientational elastic deformations in electric fields. The aim of this work was to study the effect of the length of flexible chain fragments on the optical and electro-optical characteristics of BCBOAOB nematics. A comparative analysis of the results obtained for BCBOAOB and BCBOA was also carried out. Therefore, it was possible to follow the dependence of mesophase characteristics on the number of mesogenic groups in the molecule.

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Scheme 1.



Scheme 2.

2. Experimental

2.1. Synthesis and materials

The syntheses of BCBOAOB (II) were carried out in two stages according to scheme 2 presented above, using two successive Williamson reactions

The melting temperatures of the 4,4'-bis- ω -bromoalkoxybiphenyls (I) are given in table 1. All reagents—except the α,ω -dibromoalkanes (C₆–C₁₀) and 4,4'-dihydroxybiphenyl (Merck Ltd)—from the Reakhim Company (Russia) were distilled before use and purified according to standard procedures.

Elemental analysis was carried out in the analytical laboratory of the Institute of Macromolecular Compounds of the Russian Academy of Sciences. NMR spectra were recorded using a Bruker AC 200 instrument, and the IR spectra using a Bruker IFS-88 spectrometer.

4,4'-Bis- ω -bromoheptyloxybiphenyl (I) was synthe-

Table 1. The melting temperatures T_m of 4,4'-bis- ω -bromoalkoxybiphenyls.

n	$T_m/^\circ\text{C}$
2	163
3	130
4	129
5 ^a	72
6	115
7 ^b	64
8	106
9	81
10	103

^a Formed a smectic phase with isotropization temperature

$T_{is} = 85^\circ\text{C}$.

^b Formed a smectic phase with $T_{is} = 83^\circ\text{C}$.

sized as follows. A mixture of 1,7-dibromoheptane (2.06 g, 8 mmol), 4,4'-dihydroxybiphenyl (0.74 g, 4 mmol), and 3 g of K₂CO₃ in 25 ml of cyclohexanone was stirred under reflux for 4 h. Subsequently the reaction mixture was poured into light petroleum and left overnight. The solid material was filtered off and extracted with boiling hexane. The product precipitated from hexane and was recrystallized again from hexane. The yield was 1.87 g (87%). ¹H NMR (CDCl₃, δ): 7.47 b(d, 4H); 6.92 a(d, 4H); 3.98 OCH₂ (t, 4H); 3.51 BrCH₂ (t, 4H); 1.86 (m, 8H); 1.40 (m, 12H). Calculated (C₂₆H₃₆O₂Br₂): C 57.78, H 6.72, Br 29.59%. Found: C 57.83, H 6.61, Br 29.67%.

For the synthesis of BCBOAOB (II, n = 7), a mixture of 4-cyano-4'-hydroxybiphenyl (1 g, 5.2 mmol), I (1.86 g, 3.45 mmol), and 3 g of K₂CO₃ in 25 ml of cyclohexanone was stirred under reflux for 6 h, and subsequently poured into 200 ml of water. The residue was filtered off, dried, extracted for 12 h with octane in a Soxhlet extraction apparatus and reprecipitated twice from chloroform solution using methanol. The yield was 1.66 g (63%). ¹H NMR (CDCl₃, δ): 7.66 c(q, 8H); 7.42–7.52 b(m, 8H); 6.94 a(t, 8H); 4.01 OCH₂ (t, 8H); 1.85 (m, 8H); 1.40 (m, 12H). $\nu_{\text{CN}} = 2227 \text{ cm}^{-1}$ (in KBr). Calculated (C₅₂H₅₂O₄N₂): C 81.22, H 6.82, N 3.64%. Found: C 81.15, H 6.75, N 3.51%.

Trimers with even n were synthesized according to an analogous scheme. BCBOAOBs with an even number of methylene units were recrystallized from DMF. For BCBOAOB (II, n = 2), yield was 30%. ¹H NMR (DMF-d₇, δ): 7.70 c(q, 8H); 7.45–7.60 b(m, 8H); 7.09 a(t, 8H); 3.98 OCH₂ (broad singlet, 8H). $\nu_{\text{CN}} = 2227 \text{ cm}^{-1}$ (in KBr). Calculated (C₄₇H₄₂O₄N₂): C 80.78, H 6.06, N 4.01%. Found: C 80.53, H 6.15, N 3.85%.

The number n of CH₂ groups in the spacer of the molecules of BCBOAOB was varied from 2 to 10. All

Table 2. Electro-optical properties of BCBOAOB nematics at different temperatures ΔT .

n	$T_{NI}/^{\circ}C$	$T_m/^{\circ}C$	$\Delta T/^{\circ}C$	Δn	V_0/V			
2	329	251	5.5	0.279	16.3			
			10.5	0.300	14.2			
			16.5	0.307	13.7			
			22.5	0.314	14.3			
			29.5	0.323	13.7			
			36.5	0.323	13.9			
			43.5	0.337	12.1			
			49.5	0.346	12.9			
			3	196.5	165	5	0.207	1.28
11	0.217	1.30						
18.5	0.231	1.47						
26	0.239	1.58						
34	0.248	1.69						
42	0.255	1.77						
50	0.260	1.82						
58	0.268	2.08						
66	0.268	2.47						
4	299	223	5.5	0.265	2.19			
			8	0.273	2.19			
			14	0.294	2.17			
			20	0.294	2.34			
			26	0.301	2.36			
			33.5	0.301	2.43			
			39.5	0.311	2.58			
			47.5	0.319	2.45			
			56	0.319	2.71			
			5	210	153	4.5	0.179	1.14
						11.5	0.184	1.07
18.5	0.184	1.22						
24	0.206	1.30						
31	0.205	1.27						
37.5	0.212	1.31						
45	0.218	1.40						
52.5	0.228	1.44						
60	0.228	1.38						
66.5	0.234	1.44						
75	0.234	1.66						
84	0.240	1.82						
6	255	188				4.5	0.255	—
			13.5	0.259	1.62			
			17	0.260	1.96			
			22	0.264	2.03			
			26.5	0.269	1.92			
			31.5	0.273	1.87			
			36.5	0.279	1.93			
7	201	142	4.5	0.149	0.94			
			10.5	0.160	1.07			
			16.5	0.169	1.14			
			23	0.183	1.20			
			29.5	0.189	1.14			
			36	0.195	1.22			
			42.5	0.202	1.26			
			49	0.207	1.48			
			56	0.211	1.53			
			64.5	0.218	1.61			
			71	0.218	1.44			
			77.5	0.222	1.73			
			84.5	0.222	2.04			

Table 2. (continued).

n	$T_{NI}/^{\circ}C$	$T_m/^{\circ}C$	$\Delta T/^{\circ}C$	Δn	V_0/V
8	233	181	13.5	0.228	1.50
			16	0.233	1.59
			20.5	0.239	1.72
			24.5	0.248	1.66
			27	0.264	1.79
			29.5	0.263	1.63
			33	0.264	1.73
			35.5	0.265	—
			39.5	0.279	—
			42	0.273	—
9	192	137	4.5	0.146	0.86
			11	0.158	1.05
			18.5	0.178	1.11
			26	0.190	1.27
			35.5	0.195	1.30
			44.5	—	1.53
			52.5	0.210	1.69
			60.5	0.212	1.70
10	206	162	9	0.218	2.70
			12.5	0.228	2.86
			16	0.231	2.65
			19.5	0.239	2.76

BCBOAOBs obtained exhibit thermotropic nematic mesomorphism. Their isotropization, T_{NI} and melting, T_m temperatures determined by polarizing optical microscopy are given in table 2. The same data are shown in figure 1 in the form of the dependence of T_{NI} on n. The values of T_{NI} obtained for BCBOAOBs are close to those reported in [11]. The dependence of T_{NI} on n exhibits a distinct periodicity, thus illustrating the odd-even effect in thermal characteristics of these compounds.

2.2. Electro-optical measurements

Electro-optical characteristics of the BCBOAOBs were studied in planar/concave layers up to 5×10^{-3} cm

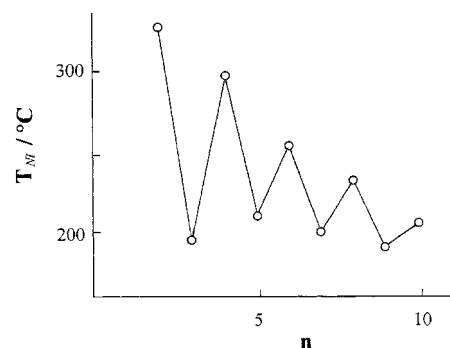


Figure 1. Isotropization temperatures T_{NI} for the BCBOAOB versus number n of methylene groups in the oxyalkane spacers.

thick by a procedure already described in detail [14–16]. For sample preparation, transparent glasses with a thin conductive coating as an electrode and thin lenses with a curvature radius R from 3 to 4 cm were used. All BCBOAOB nematics being investigated spontaneously formed planar oriented layers on glass surfaces. Their monodomain texture was achieved by previously rubbing the glasses in a predetermined direction. A mercury lamp with a green light filter (at a wavelength $\lambda = 5.46 \times 10^{-5}$ cm) was used as light source. The sample temperature was determined with the aid of a thermocouple to within 1°C . Reorientation of the nematics in an electric field was carried out by the action of sinusoidal fields in the frequency range from 10 to 500 kHz at a potential difference on the electrodes up to 700 V.

3. Results and discussion

3.1. Optical characteristics

Figure 2(a) shows the polarizing micrograph of a planar layer of the BCBOAOB nematic with $n=9$ in the absence of an electric field at a temperature $\Delta T = 21^\circ\text{C}$ ($\Delta T = T_{\text{NI}} - T$, where T is the measurement temperature) and between crossed polarizers. The figure shows a system of concentric interference rings. Analogous patterns were observed for all other BCBOAOBs. Using them, it is possible to plot the dependences of the relative retardation $\Delta\lambda/\lambda$ on layer thickness z ($z = r^2/2R$ where r is the radius of the corresponding dark ring) at a constant temperature T . Figure 3 shows the dependences of relative retardation

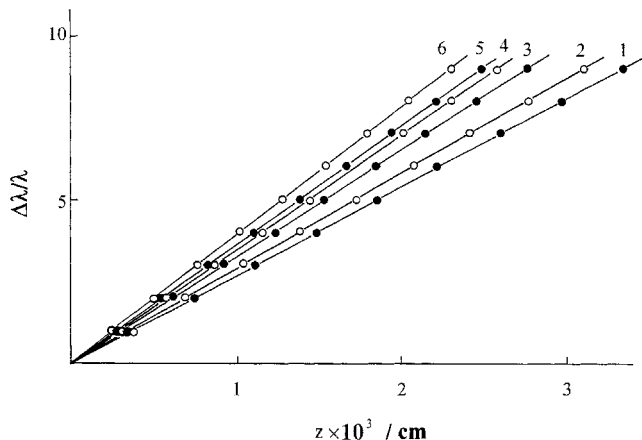


Figure 3. Relative retardation $\Delta\lambda/\lambda$ versus layer thickness z for the BCBOAOB with $n=9$ and $\Delta T/^\circ\text{C} = (1) 4.5, (2) 11, (3) 18.5, (4) 26, (5) 35.5, \text{ and } (6) 68.5$.

on layer thickness for BCBOAOB with $n=9$ at different (constant) temperatures. It can be seen that $\Delta\lambda/\lambda$ increases proportionally to z , which reflects the homogeneous nematic orientation throughout the sample region investigated. Similar results were observed for all other BCBOAOBs. It is possible to calculate the value of the birefringence Δn of the nematic ($\Delta n = n_e - n_o$, where n_e and n_o are the refractive indices of the extraordinary and ordinary beams, respectively)

$$\Delta n = (\Delta\lambda/\lambda)(\lambda/z). \quad (1)$$

The values of Δn obtained for all BCBOAOBs at different temperatures are listed in table 2. The same data are plotted in figure 4 as the dependence of Δn on ΔT for several of the BCBOAOBs.

Table 2 and figure 4 show that for all BCBOAOBs, Δn increases monotonically with increasing ΔT . This

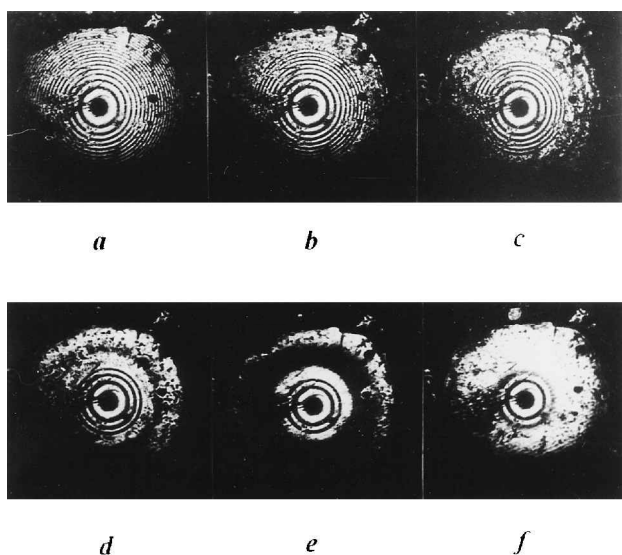


Figure 2. Polarizing micrographs of a planar/concave layer of the BCBOAOB nematic with $n=9$ and for $\Delta T = 21^\circ\text{C}$; (a) the initial planar orientation of the director, (b)–(f) the texture deformed by the electric field $\mathbf{E} \times 10^{-3}/(\text{V cm}^{-1}) = (b) 0.40, (c) 0.67, (d) 1.33, (e) 2.13, \text{ and } (f) 2.93$.

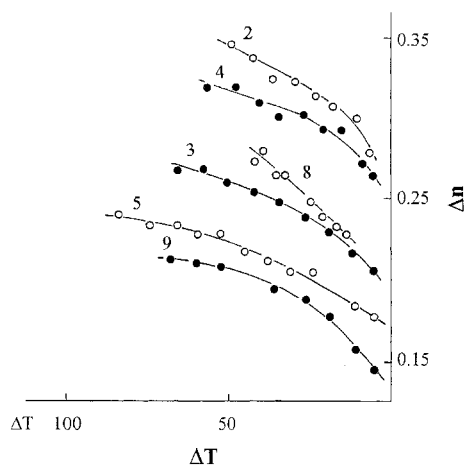


Figure 4. Birefringence Δn versus temperature for BCBOAOBs. Numbers of curves correspond to values of n .

dependence is mainly related to changes in the degree of intermolecular orientational order S with temperature. Indeed, the value of the optical anisotropy of the nematic Δn can be represented in the form of an approximate relationship [6] valid at not too great Δn values

$$\Delta n = (2\pi/3n)(n^2 + 2)N_A(\Delta\alpha/M)\rho S, \quad (2)$$

where M is the molecular mass of the nematic, ρ is its density, $\Delta\alpha$ is the polarizability anisotropy of the molecule, and n is the average refractive index of the substance. The values of $(n^2 + 2)/n$, ρ , and S in equation (2) are temperature dependent, and each of them increases with increasing ΔT . However, the temperature change in S provides the main contribution to the increase in Δn .

The data in table 2 and figure 4 show that the value of Δn for BCBOAOBs depends on both the temperature and the alkyl spacer length. Therefore, it is correct to discuss the dependence of Δn on the number n of CH_2 groups in a flexible fragment of the molecule at the same relative temperature $\tau = \Delta T/T_{\text{NI}}$ (here ΔT and T_{NI} are presented in degrees Kelvin, absolute temperature scale). Table 3 gives the anisotropies, Δn , of the BCBOAOBs being investigated. They were determined at a relative temperature $\tau = 0.04$ and, correspondingly, at the absolute temperatures of the nematics, $T = T_{\text{NI}}(1 - \tau) = 0.96 \times T_{\text{NI}}$ K. The same data are plotted in figure 5 in

Table 3. Electro-optical characteristics of BCBOAOB nematics with different numbers n of methylene groups in the spacer and at equal relative temperatures $\tau = 0.04$.

n	$\Delta T/^\circ\text{C}$	Δn	V_0/V	$(1/V_0/V^{-1})$
2	24	0.317	13.8	0.072
3	18.8	0.230	1.48	0.68
4	22.9	0.297	2.36	0.42
5	19.3	0.196	1.24	0.81
6	21.1	0.265	1.96	0.51
7	19	0.175	1.16	0.86
8	20.2	0.240	1.70	0.59
9	18.6	0.178	1.10	0.91
10	19.2	0.238	2.80	0.36

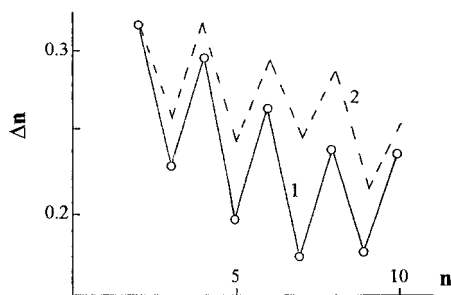


Figure 5. Birefringence Δn versus number n of CH_2 groups in the oxyalkyl chain for (1) BCBOAOBs and (2) BCBOAs at relative temperature $\tau = 0.04$.

the form of the dependence of Δn on the number n of CH_2 groups in the spacer. The curve in figure 5 demonstrates a pronounced odd-even effect in the optical characteristics of the BCBOAOB nematics investigated. These large periodical changes in Δn reflect the change in the degree of orientational order S in the mesophase with variation of alkyl chain length.

The dependence of the optical anisotropy on spacer length for the BCBOAOBs is virtually identical to the similar dependence [14] for the BCBOAs. A characteristic feature of the dependences of Δn on n for the BCBOAOBs and BCBOAs is the absence of a marked damping in the oscillations of the optical anisotropy (and, correspondingly, in the degree of intermolecular orientational order S) with increasing length of the alkyl chain fragment. This property is a specific feature of compounds whose molecules consist of several mesogenic cores joined by flexible fragments. It should be recalled that traditionally the molecules of low molecular mass liquid crystals consist of one central mesogenic core and one or two terminal alkyl chains. The odd-even effect in optical properties of these liquid crystals is relatively small and is rapidly damped and extinguished when terminal flexible parts of the molecules become longer [3, 4, 6].

Figure 5 shows that the value of the optical anisotropy Δn for BCBOAOBs in the series with either even or odd values n for the spacer has a tendency to decrease with increasing spacer length. This fact can easily be explained if it is taken into account that the main contribution to the optical anisotropy is the $\Delta\alpha$ value of the BCBOAOB molecules and this is provided by the mesogenic cores (the number of which is constant). Hence, the increase in the length of the flexible fragments in the BCBOAOB molecules leads to lower values of $\Delta\alpha/M$ in equation (2). As a result, the value of Δn decreases.

It seems of interest to compare the values of the optical anisotropies Δn of BCBOAOB and BCBOA [14] nematics. The values of Δn for BCBOAs [14] are systematically greater than those for BCBOAOBs at the same n (and the same relative temperatures τ). This fact is not fortuitous. In fact, at equal n the BCBOAOB molecule contains a 1.5 times greater number of rigid anisotropic mesogenic cores and twice as many flexible (relatively less anisotropic) fragments than the BCBOA molecule. Therefore, the value of $\Delta\alpha/M$ in equation (2) should be greater for BCBOAs than for BCBOAOBs, which leads (at close S values) to a greater value of Δn for BCBOAs than for BCBOAOBs.

3.2. Elastic deformations and electro-optical characteristics

The results obtained for BCBOAOBs by the method of elastic deformations in electric fields are illustrated in

figures 2(b) to 2(f). These figures show the polarizing micrographs of an initially planar layer of the BCBOAOB nematic with $n = 9$, which was deformed by electric fields of different strengths E . This deformation is the splay elastic deformation through which the system of interference rings is distorted in the region of layer thickness $z \geq z_0$ (z_0 is the layer thickness corresponding to the critical boundary). The reorientation characteristics of the BCBOAOB molecules in the electric field show that the sign of the dielectric anisotropy $\Delta\epsilon$ of this nematic is positive. Similar results were obtained for all the other BCBOAOBs. By using these patterns and measuring the radius r_0 of the critical boundary, it is possible to calculate the value of the threshold potential V_0 of a BCBOAOB

$$V_0 = z_0 E, \quad z_0 = r_0^2 / 2R. \quad (3)$$

The values of V_0 for BCBOAOBs determined at different temperatures are listed in table 2. The same data are illustrated in figure 6 by the dependences of V_0 on ΔT for the same BCBOAOBs.

It can be seen from table 2 and figure 6 that for most BCBOAOBs (except BCBOAOB with $n = 2$) the value of V_0 decreases with increasing sample temperature. This fact implies that the splay elastic constant K_1 of these nematics decreases with increasing temperature more drastically than does their dielectric anisotropy $\Delta\epsilon$. This relationship is typical of low molecular weight unassociated nematics. It can also be seen from table 2 and figure 6 that, at constant temperature, V_0 depends non-monotonically on the length of the alkyl spacers in the BCBOAOB molecules. Let us apply the expression relating the values of V_0 and $\Delta\epsilon$ for nematics:

$$V_0 = 2\pi^{3/2} (K_1 / |\Delta\epsilon|)^{1/2}. \quad (4)$$

Periodical changes in V_0 with the variation of spacer length in the BCBOAOB molecule can be related to oscillations of the values of both $\Delta\epsilon$ and K_1 . However,

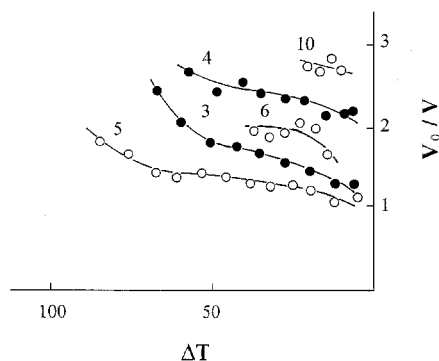


Figure 6. Threshold potential V_0 versus temperature ΔT for BCBOAOBs. Numbers of curves correspond to values of n .

taking into account the fact that the change in the number of CH_2 groups in the flexible fragment of the BCBOAOB chain from an even to an odd number should strongly change the dipolar geometry of the molecule, and also bearing in mind the results in [14], it is reasonable to explain the oscillations of the value of V_0 mainly on the basis of the non-monotonic dependence of $\Delta\epsilon$ on n .

Just as in discussing the optical characteristics of BCBOAOBs, the values of V_0 for nematics with different n values should be compared at the same temperature τ . The values of V_0 obtained in this way are given in table 3. The same table lists the values of $1/V_0$ which characterize, at least qualitatively (in accordance with equation (4)) the corresponding changes in $\Delta\epsilon$. The same data for the BCBOAOBs are plotted in figure 7 as the dependence of $1/V_0$ on n (curve 1).

Curve 1 in figure 7 clearly illustrates the periodicity of changes in $1/V_0$ (and hence in $\Delta\epsilon$) when n is varied. It is of interest to compare this dependence with the dependence of Δn (determined by changes in the degree of intermolecular orientational order S) on n . Both these dependences are markedly non-monotonic when n is varied. However, they exhibit considerable differences: the maxima in the values of Δn (and, hence, in those of S) fall on even n , whereas those of $1/V_0$ (and those of $\Delta\epsilon$) fall on odd n values. Moreover, the increase in n (for both even and odd homologous series) is accompanied on the average by an increase in $1/V_0$ (and in $\Delta\epsilon$) and a decrease in Δn .

These differences require additional discussion. The oscillations in the values of Δn when n is varied depend mainly on the change in S (see equation (2)). However, the dielectric anisotropy of the nematic, $\Delta\epsilon$, not only depends on S but also to a considerable extent is

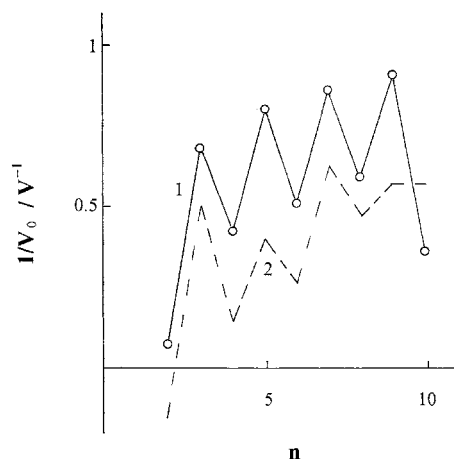


Figure 7. Inverse value $1/V_0$ of the threshold potential V_0 for (1) BCBOAOB and (2) BCBOA nematics versus number n of CH_2 groups in the oxyalkyl chain.

determined by the dipolar architecture of the molecules. For a molecular model with axial symmetry of the dielectric polarizability, the value of $\Delta\epsilon$ can be expressed in the form of an approximate relationship [17]

$$\Delta\epsilon = 4\pi N_A P Q X S, \quad (5)$$

where P and Q are the internal field multipliers. The function X characterizing the dipolar anisotropic structure of molecules and their intramolecular orientational polar order [14, 18, 19] is given by

$$X = \Delta\delta + (\mu^2/2kT)(3 \cos^2 \theta - 1), \quad (6)$$

where $\Delta\delta$ is the anisotropy of the electric polarizability

of the molecule and μ is its dipole moment forming an angle θ with the axis of symmetry of the molecule.

The results obtained in this work show that the odd-even effect observed in the dielectric characteristics of BCBOAOB nematics is determined by oscillations of the function X with the variation in n . In order to explain this fact (at least qualitatively), let us consider figure 8 which shows the conformations of BCBOAOB molecules with (a) $n=2$ and (b), (c) $n=3$ in the approximation of a planar *trans*-conformation of the oxyalkyl fragment. It follows from figure 8 (a, b) that the conformations of the BCBOAOB molecules represented here are such that for both odd and even n , all dipoles in the

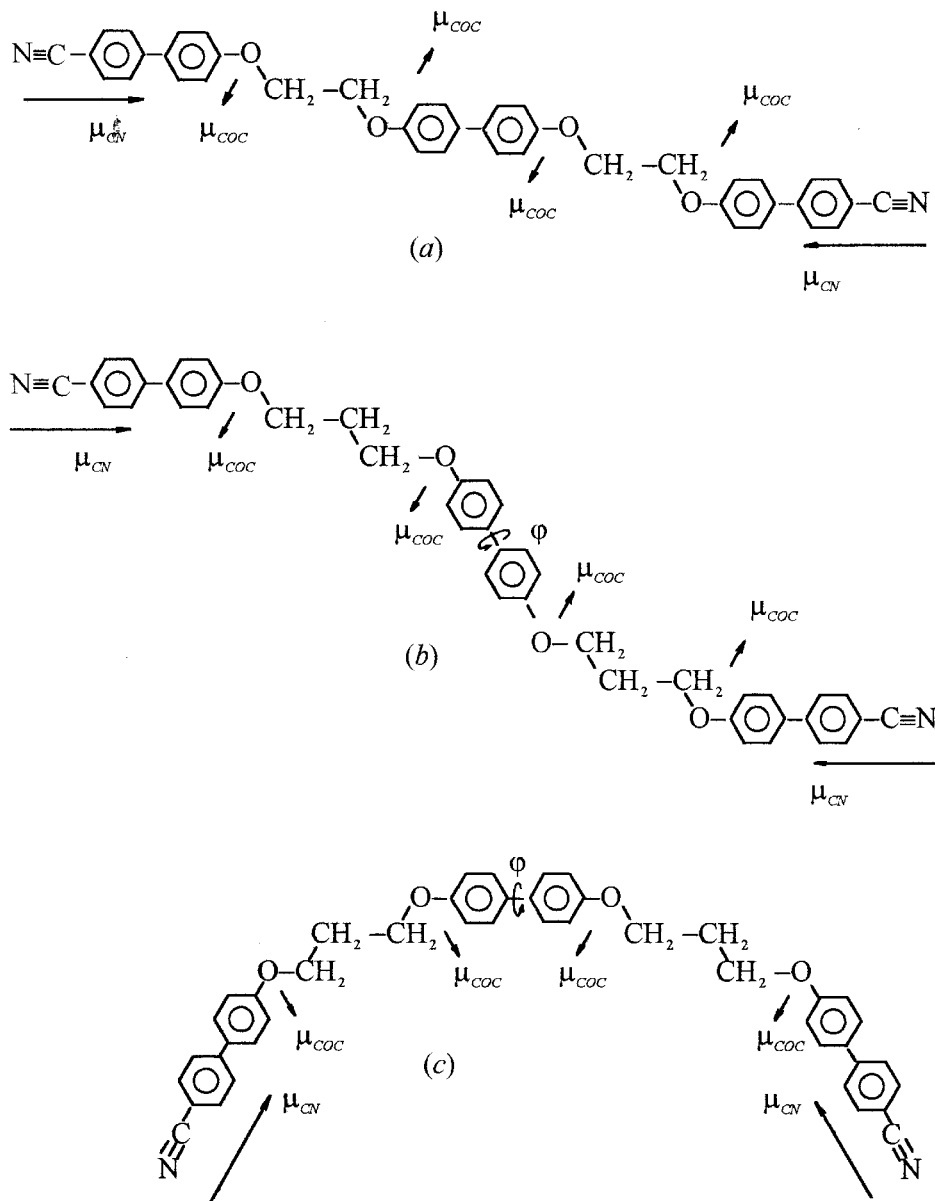


Figure 8. Conformations of BCBOAOB molecules with $n=(a)$ 2 and (b), (c) 3 in the case of a planar *trans*-conformation of the oxyalkyl fragment. Angle $\phi=(b)$ 0° and (c) 180° .

molecules are compensated. Therefore, bearing in mind the approximations used for these conformations of the molecules, the value of X should change only slightly with variation in n . In this case, it is difficult to expect a strong odd–even effect in the dielectric properties of BCBOAOB nematics. This conclusion contradicts the experimental data. However, in the nematic phase of BCBOAOBs with odd n , molecules can exist in the conformation which is close to that shown in figure 8(c) (this conformation is obtained from the conformation shown in figure 8(b) by rotation of one half of the molecule about the central *para*-aromatic axis through an angle $0 \leq \varphi \leq 180^\circ$). The peculiar feature of this conformation is the large non-compensated molecular dipole leading to a change in the value of $\Delta\varepsilon$ of a BCBOAOB when even n is replaced by odd n .

The general tendency (in the series of both odd and even BCBOAOB homologues) to increasing $1/V_0$ and $\Delta\varepsilon$ with increasing n is due to an increase in the distance between strongly polar cyano groups. This increase leads to a weakening of the correlation in the orientation of mesogenic polar fragments of BCBOAOB molecules in an electric field (a manifestation of equilibrium and kinetic flexibility), which causes an increase in $\Delta\varepsilon$. In other words, the general tendency to increasing $\Delta\varepsilon$ with increasing n results from the fact that, in this case, the intramolecular orientational polar order of BCBOAOBs becomes less perfect. However, it is still sufficiently great for the manifestation of the strong odd–even effect in dielectric characteristics of BCBOAOB nematics even at high n .

The values of the threshold potential V_0 for BCBOAOBs with $n = 10$ seem excessively high. This is possibly caused by the existence of fluctuating nuclei of smectic phase in the nematic. Their existence can lead to an increase in the value of the elastic constant K_1 of the nematic [20] or to a decrease in the positive dielectric anisotropy $\Delta\varepsilon$ [21]. These two possibilities should lead to an increase in the observed value of V_0 . These fluctuations can also probably explain the increase in V_0 for some BCBOAOBs at high ΔT (table 2 and figure 6).

It is of interest to compare the results of the electro-optic investigations of BCBOAOB and BCBOA nematics. For comparison, figure 7 (curve 2) shows the dependence of $1/V_0$ on n for BCBOAs. It can be seen that the shapes of curves 1 and 2 are largely identical: both dependences exhibit considerable oscillations combined with a general tendency to increase with increasing n . For both dimers and trimers, the maxima in the values of $1/V_0$ (and, hence, those of $\Delta\varepsilon$) are observed at odd n and the minima at even n . However, the dependence of $\Delta\varepsilon$ on n for dimers is accompanied by a change in sign at $n = 2$, which is not observed for trimers. This fact is

not fortuitous. In fact, the main reason for variations (oscillations superimposed on a general increase), in $1/V_0$ and in $\Delta\varepsilon$ is the change in the function X characterizing the intramolecular orientational polar order. For both dimers and trimers this order decreases with increasing spacer length, i.e. with increasing distance between strongly polar cyano groups. For the same number of CH_2 groups in the spacers, in trimers the length of flexible fragments between cyano groups is twice as large as that in dimers. This is the explanation of the difference in the signs of $\Delta\varepsilon$ for dimers and trimers at $n = 2$. The same fact probably accounts for the higher $1/V_0$ values for trimers than for dimers at the same n .

4. Conclusions

It has been shown that the electro-optical properties of nematic mesophases of dimers and trimers exhibit a strong odd–even effect when the number n of CH_2 groups in the spacers is varied. The maxima in the values of the optical anisotropy Δn determined by intermolecular orientational order are observed at even n . Oscillations in the dependence of Δn on n for dimers and trimers investigated are not damped with increasing n , a characteristic feature of compounds whose molecules consist of two or more mesogenic cores joined by flexible spacers.

The maxima in the values of the dielectric anisotropy $\Delta\varepsilon$, mainly determined by intramolecular orientational polar order, are observed at odd n . The general shape of the dependences of $1/V_0$ on n for dimers and trimers is largely identical, but for dimers this dependence is accompanied by a change in the sign of $\Delta\varepsilon$, which is not observed for trimers. This is caused by a greater separation of strongly polar CN groups in trimer molecules than that in dimers. As a result, their orientational correlation in the electric field is weakened. This weakening of correlation with increasing length of spacer also leads to an increase in $1/V_0$ for dimers and trimers in the series with both odd and even n .

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