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Orientational elasticity of nematic α,ω-bis(4-cyanobiphenyl-4′yloxy)alkanes

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The splay orientational elastic constants for the nematic phases of a series of dimeric α,ω-bis(4-cyanobiphenyl-4′-yloxy)alkanes have been determined by the method of Fréedericksz threshold transitions in a magnetic field. A dramatic odd–even effect in the dependence of the elastic constant on the spacer length of the compounds investigated was revealed. It was shown that the splay elastic constant for the nematic dimers increases with increasing length of the molecules.

1. Introduction

The recent considerable interest in the study of dimers and trimers of the 'siamese twin' type is due to the strong odd–even effect in their thermal [1] characteristics and also to marked oscillations in the degree of orientational order [2] and in the entropy and enthalpy of the isotropic liquid–liquid crystal transitions [3, 4] when the spacer length in the molecules of these compounds is varied. In our recent investigations dimeric α,ω-bis(4-cyanobiphenyl-4′yloxy)alkanes (BCBOA) and trimeric α,ω-bis(4-cyanobiphenyl-4′-yloxy)-4,4′-dialkoxybiphenyls have been studied using dilute solutions and nematic melts by methods probing the electric birefringence [5] and orientational elastic deformations in electric fields [6, 7]. A strong odd–even effect was detected for these compounds in the optical anisotropy of their nematic phases (caused by variations in the degree of long range intermolecular orientational order, S [8]) and in the electrical threshold deformational potentials (caused mainly by the conformational-dipolar changes in their intramolecular structure, i.e. the variations in intramolecular orientational-polar order [9]) as a result of change of spacer length in the molecules.

In the present work BCBOA nematic dimers were studied by measuring the orientational elastic deformations in a magnetic field with the aim of investigating the effect of the length of the flexible chain moieties on the elastic characteristics of the mesophases.

2. Experimental

The number n of CH_2 groups in the spacers of the dimers investigated ranged from 2 to 12. All the BCBOA compounds investigated exhibit thermotropic nematic mesomorphism. Their isotropization temperatures T_{NI} determined by polarizing optical microscopy are given in table 1. The T_{NI} values are close to the same data presented for these compounds previously [3]. The orientational elasticity of the BCBOA nematics was investigated using plane–concave layers up to 10^{-2} cm thick by the procedure described in detail in [10].

The curvature radius of the plane–convex lenses used was $R = 2$–3 cm. All the BCBOA nematics investigated spontaneously form films with a planar director orientation on the glass surfaces. A homogeneous texture was attained by rubbing the surfaces in a given direction. A mercury lamp with a green light filter was used as the light source (wave length $\lambda = 5.46 \times 10^{-5}$ cm). The sample temperature was determined with the aid of a thermocouple to within 1°C. The process of nematic reorientation was brought about under the influence of a magnetic field with a strength up to 6 kG.

The experimental errors are mainly caused by errors in the determination of the layer thickness corresponding to the critical boundary and may be estimated as within 5% for the elastic constant.

3. Results and discussion

Figure 1 shows polarizing microscopic textures (crossed polarizers) of the planar layer of the BCBOA nematic with $n = 10$ obtained (*a*) in the absence and

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Table 1. Isotropization temperatures and physical characteristics of the BCBOA nematics at a relative temperature $\tau = 0.057$.

n	T_{NI}/°C	$(K_{11}/\Delta\chi)$/dyne	$\Delta\chi \times 10^7$	$K_{11} \times 10^7$/dyne	$\Delta\varepsilon$
2	270	8.5	1.51	12.8	−0.38
3	169	6	1.23	7.4	2.1
4	255	7.5	1.41	10.7	0.2
5	186	7.6	1.1	8.4	1.5
6	218	9	1.3	12	1.1
7	182	7.6	1.1	8.4	3.5
8	205	10.5	1.27	13.3	3.3
9	176	11.3	0.98	11.1	4
10	187	12	1.19	14.3	5.2
12	171	14.3	1.14	16.3	6.6

(*b*) in the presence of a magnetic field (applied normal to the layer plane) at $\Delta T = 30$°C ($\Delta T = T_{NI} - T$, where T is the measurement temperature). The resulting deformation is the splay deformation whereby the system of interference rings is distorted in the range of layer thicknesses $z \geqslant z_c$. Similar results were obtained for all the other BCBOA compounds. Using these patterns and measuring the radius r_c of the critical boundary, it is possible to calculate z_c

$$z_c = r_c^2/2R \tag{1}$$

where z_c is the layer thickness corresponding to the critical boundary and R is the radius of the lens curvature. The values of z_c make it possible to calculate the ratio of the splay elastic constant K_{11} to the diamagnetic anisotropy of unit volume of the nematic $\Delta\chi$ using the well known, classical Fréedericksz equation

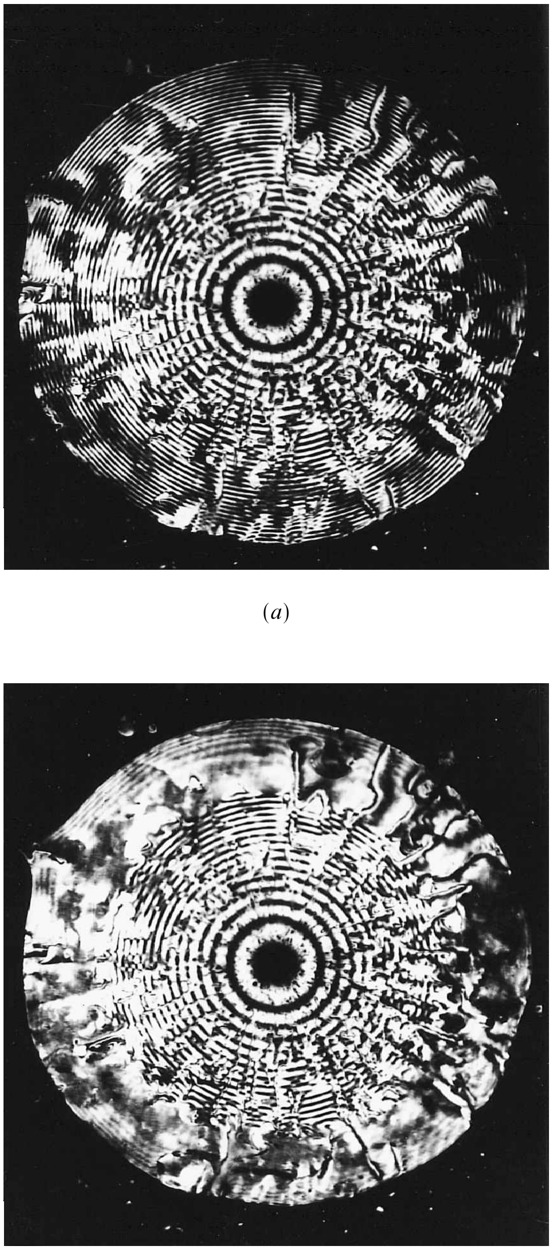
$$z_c\mathbf{H} = \pi(K_{11}/\Delta\chi)^{1/2} \tag{2}$$

where $\mathbf{H}$ is the magnetic field strength. In equation (2) all data should be presented in cgs units and correspondingly the values of K_{11} are obtained in dynes (as traditionally presented in the vast majority of papers connected with investigations of the orientational elasticity of liquid crystals).

The values of $K_{11}/\Delta\chi$ for all the BCBOA compounds at different temperatures are given in table 2. The temperature dependences of $K_{11}/\Delta\chi$ for some of the BCBOA compounds are shown in figure 2. As can be seen from table 2 and figure 2, the $K_{11}/\Delta\chi$ ratios for all the BCBOA decrease with increasing temperature. This fact indicates that the orientational elastic constant K_{11} decreases with temperature more rapidly than $\Delta\chi$ (and, correspondingly, than S [8]). This behaviour is typical for low molecular mass and polymeric nematics. It must be pointed out that the $K_{11}/\Delta\chi$ ratio for the BCBOA depends not only on temperature, but also on the number n of CH_2 groups in the spacer. Also one must remember that the temperature ranges of the nematic mesophases for the compounds under investigation are wide and that this is their specific feature. It is necessary therefore to discuss this ratio at the same relative temperature $\tau = \Delta T/T_{NI}$ (ΔT and T_{NI} are presented in units of Kelvin's absolute temperature scale), just as we have done previously in discussing the optical and electro-optical properties of BCBOA nematics [6].

Table 1 lists the values of $K_{11}/\Delta\chi$ for the BCBOA nematics at the same relative temperature $\tau = 0.057$. The same data are illustrated in figure 3 in the form of the dependence of $K_{11}/\Delta\chi$ on the number n of CH_2 groups in the spacer. Table 1 and figure 3 show that the $K_{11}/\Delta\chi$ ratios have a general increasing trend with increasing n with some deviations (they are particularly noticeable for the BCBOA with $n = 2$ and 7). The increase in $K_{11}/\Delta\chi$ with increasing n may be due both to a decrease in $\Delta\chi$ with the decreasing fraction of aromatic moiety in the BCBOA molecules and to the increase in the orientational elastic constant with increasing length of the molecule.

To discuss the dependence of the orientational elastic constant K_{11} on spacer length, it is necessary to know the values of the diamagnetic anisotropy $\Delta\chi$ of the BCBOA nematics; these are not however known, but values can be determined relatively precisely on the basis of the mass fraction of aromatic moiety in the molecule. For this purpose it is possible to use the data in [11] where experimental values of molar anisotropies $\Delta\chi_m$ are quoted for a number of nematic liquid crystals. The values of $\Delta\chi$ for unit volume of the nematics were calculated from the known values of their molecular masses and by assuming their densities to be $\rho = 1$ g cm^{-3}. In the following discussion we will be interested only in values of $\Delta\chi$ for the BCBOA nematics at the same relative temperature $\tau = 0.057$. Therefore, the values of $\Delta\chi$ obtained at the same relative temperature for the nematics investigated in [11] will be used. Figure 4 shows the dependence of $\Delta\chi$ on the mass fraction W of the aromatic moiety in the molecule for a number of



(*a*)

(*b*)

Figure 1. Polarizing microscopic textures (crossed polarizers) of a planar layer of the BCBOA nematic with $n=10$ obtained (*a*) in the absence and (*b*) in the presence of a magnetic field $\mathbf{H}=5$ kG at $\Delta T=30°$C.

Table 2. The values of $K_{11}/\Delta\chi$ at different temperatures ΔT of the nematic dimers.

n	$\Delta T/°$C	$(K_{11}/\Delta\chi)$/dyne
2	21	7.6
	22	8
	23	8
	28	8.6
	36	8.9
	43	8.6
	50	9.3
	58	8.6
	64	8.9
	70	8.9
	90	8.6
	109	9.9
3	3	4.6
	7	5.3
	12	5.5
	16	5.8
	20	6
	24	6
	26	6
4	18	7
	33	7.4
	39	7.7
	58	7.9
	75	7.9
	83	7.9
	93	8.3
	101	8.9
	109	9
	122	9.6
5	15	6.5
	23	6.7
	29	7.5
	34	7.8
	39	8.6
	45	10.2
	52	10.2
	71	11.3
	75	10.6
	79	10.6
	82	10.6
	91	10.6
6	10	7.9
	12	8.6
	18	8.8
	26	8.8
	27	9.1
	48	9
	52	9.3
	59	9.3
	66	9.8
	74	10.4

the nematics investigated in [11] at the same relative temperature $\tau=0.057$. The points in figure 4 may be approximated by a straight line which is also shown in this figure. If this dependence is extrapolated to $W=1$ (i.e. to a molecule consisting only of benzene rings), then the value of $\Delta\chi$ obtained will be smaller by a factor of two than that for crystalline benzene with respect to the axis lying in the plane of the phenyl ring [12, 13]. This result means that at the predetermined relative temperature τ the degree of orientational order S of the nematics investigated in [11] is close to 0.5.

Table 2. (*continued*).

n	$\Delta T/°C$	$(K_{11}/\Delta\chi)$/dyne
7	7	6
	10	7.4
	14	7
	20	7.5
	29	7.5
	44	8
	50	9.3
	57	9.9
	64	10.3
	69	10.3
	75	10.6
8	8	8.6
	22	10.4
	28	10.4
	36	10.8
	44	11.1
	51	11.1
	60	11.1
	66	11.1
	73	11.9
9	16	10.8
	24	11.3
	30	10.8
	45	12.1
	52	12.1
	60	12.9
	67	12.9
	76	12.9
10	14	11.3
	20	12.5
	22	12.4
	37	12.4
	43	13.8
	50	13.3
	52	13.2
	63	14.3
	65	14
12	5	9.8
	11	11.6
	15	11.6
	16	12.8
	27	14.6
	30	14.6
	35	14.6
	42	15.3
	48	15.7

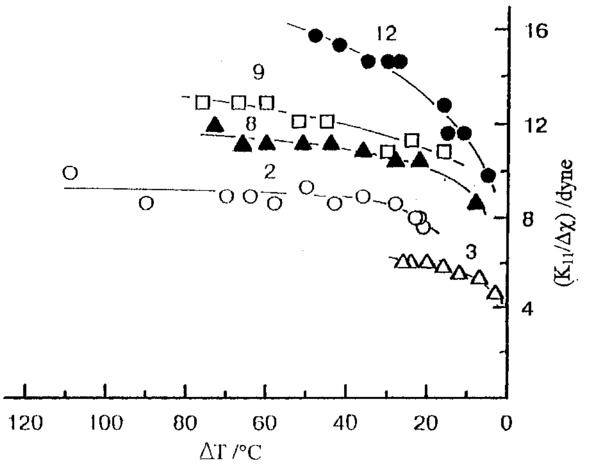


Figure 2. The temperature dependences of $K_{11}/\Delta\chi$ for some BCBOA. The numbers on the curves correspond to the numbers n of CH_2 groups in the BCBOA spacers.

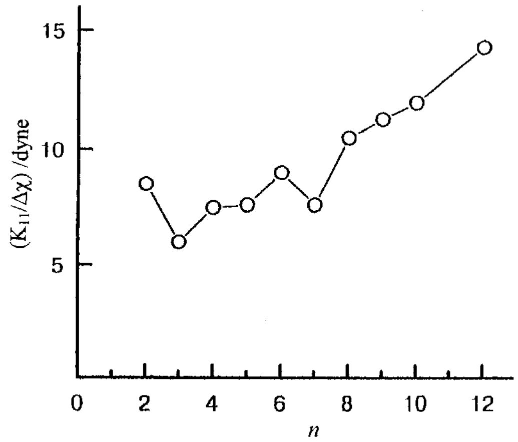


Figure 3. The dependence of $K_{11}/\Delta\chi$ on the number n of CH_2 groups in the spacer for BCBOA nematics at the same relative temperature $\tau = 0.057$.

To calculate the values of $\Delta\chi$ for the BCBOA nematics studied here, it is necessary first to calculate the values of W and second to take into account the fact that for the nematics of the dimer series the values of S (and, hence, of $\Delta\chi$) experience strong odd–even oscillations. It is not difficult to take into account this latter fact because the values of S for the BCBOA at $\tau = 0.057$ have been determined previously [6] from data on the optical anisotropy of these compounds in the crystalline phase. It should be borne in mind that the values of S obtained by us were in good agreement with the corresponding values measured at the isotropization temperature by NMR spectroscopy [2]. Therefore, the $\Delta\chi$ values for the BCBOA can be calculated from the tangent of the slope of the linear dependence in figure 4 and the value of S at $\tau = 0.057$ according to the equation

$$\Delta\chi = (1.76 \times 10^{-7} W S)/0.5. \qquad (3)$$

Using the values of $\Delta\chi$ determined in this way, it is easy to calculate the orientational elastic constants K_{11} of the BCBOA nematics; these are listed in table 1. The same data are plotted in figure 5 in the form of the dependence of K_{11} on the number n of CH_2 groups in the spacer. It can be seen from table 1 and figure 5 that the dependence of K_{11} on n exhibits a pronounced

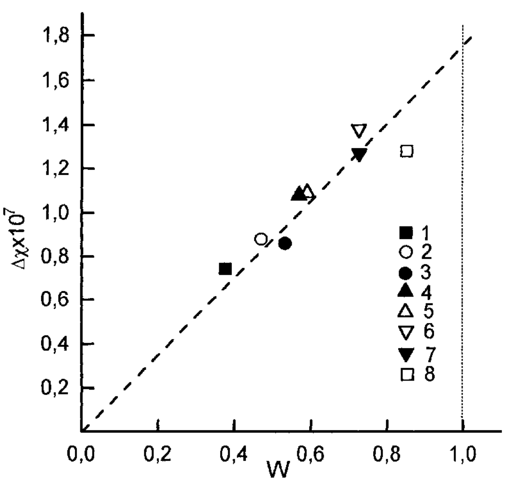


Figure 4. The dependence of $\Delta\chi$ on the mass fraction W of the aromatic moiety in the molecule for a number of nematics at the same relative temperature $\tau = 0.057$: (1) *p*-methoxycinnamic acid, (2) *p*-acetoxybenzalazine, (3) *p*-azoxyphenetole, (4) anisaldazine, (5) *p*-azoxyanisole, (6) *di*anisalbenzidine, (7) anisal-*p*-aminoazobenzene, (8) *di*benzalbenzidine.

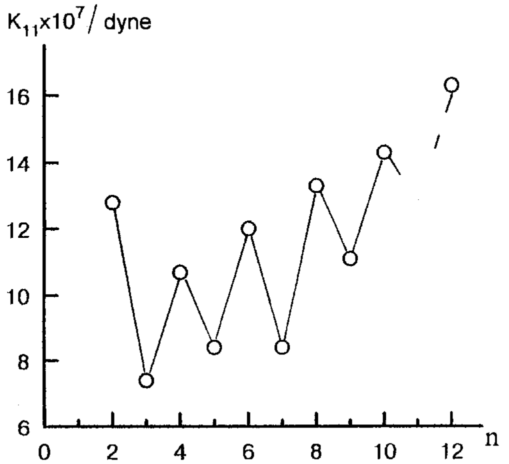


Figure 5. The dependence of K_{11} on the number n of CH_2 groups in the spacer for the BCBOA nematics at the same relative temperature $\tau = 0.057$.

odd–even effect, the maxima in the K_{11} values corresponding to even n and the minima to odd n. An analogues result was obtained previously for two dimeric esters with 9 and 10 CH_2 groups in their spacers [14].

Note that the oscillations in the K_{11} values are almost completely determined by the effect of the oscillations in $\Delta\chi$ on S when n is varied (the $K_{11}/\Delta\chi$ ratio does not exhibit the odd–even effect with the exception of $n = 2$ and 7).

According to the Saupe molecular theory [15], the elastic constants of nematics should be proportional to S^2 values. The experimental data obtained in this work show that this prediction does not apply for the dimers under investigation and so this theory cannot be directly applied for discussion of the elastic properties of these compounds.

The analysis of the dependence in figure 5 also suggests that the value of K_{11} in the series of both odd and even n members tends to increase with increasing n. In other words, for BCBOA nematics the value of K_{11} increases with the length of the molecules, which agrees qualitatively with the predictions of theories of orientational elasticity [16].

Using the values of K_{11} it is possible to calculate from values obtained previously [6] for the threshold potential in an electric field V_0 the dielectric anisotropy of the BCBOA nematics according to the equation

$$\Delta\varepsilon = (4\pi^3 K_{11})/V_0^2. \tag{4}$$

The values of $\Delta\varepsilon$ obtained by this procedure are given in table 1. The same data are illustrated in figure 6 in the form of the dependence of $\Delta\varepsilon$ on the number n of methylene groups in the spacer. It can be seen from table 1 and figure 6 that this dependence exhibits a strong odd–even effect and at $n = 2$ the sign is changed. These facts are due to the changes in the intramolecular dipolar structure of the compounds under investigation with variation in the spacer length, and are discussed in detail in our previous papers [5–7].

The comparison of the dependence of $\Delta\varepsilon$ on n for nematics with the dependence of the molar Kerr constant ${}_{\mathrm{m}}K$ on n for dilute BCBOA solutions (broken curve in figure 6) confirms our previous conclusion [6] that intramolecular orientational-polar order in these compounds increases in the mesophase owing to the existence of the nematic potential. The general tendency to increasing $\Delta\varepsilon$ with increasing n is due to the weakening of the correlation in the orientations of the strongly

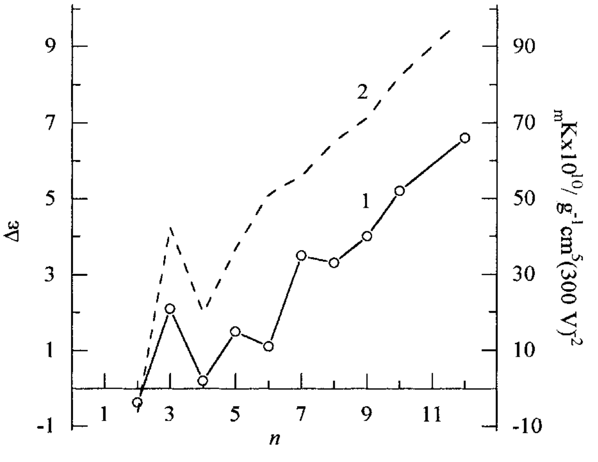


Figure 6. The dependences of (1) $\Delta\varepsilon$ on the number n of methylene groups in the spacer for the BCBOA nematics, and (2) the molar Kerr constant ${}_{\mathrm{m}}K$ on n for dilute BCBOA solutions (broken curve).

polar cyanobiphenyl groups in the electric field with increasing spacer length. At the same time it should be pointed out that the $\Delta\varepsilon$ values for all the BCBOA compounds investigated are much lower than the dielectric anisotropies of 4-alkoxy-4′-cyanobiphenyls (cyanobiphenyloxyalkanes) ($\Delta\varepsilon \approx 11$–15 [17, 18]) at a close relative temperature. This fact indicates that the orientational correlation of the mesogenic BCBOA fragments is rather strong even at $n = 12$.

4. Conclusions

It has been shown that the splay orientational elastic constants of a series of BCBOA nematics exhibit a strong odd–even effect when the length of the oxyalkane spacer is varied. The oscillations in the dependence of K_{11} on n are mostly determined by the odd–even effect in the dependence of the degree of intermolecular orientational order on n in the nematics investigated. An increase in the orientational elastic constant K_{11} with increasing elongation of the molecule is detected in the series of both even and odd BCBOA homologues. Based on experimental data, the dielectric anisotropy of the BCBOA nematics is calculated and the previous conclusion [6] that intramolecular orientational-polar order of the compounds investigated increases in the mesophase owing to the existence of the nematic potential is confirmed.

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