Electric Birefringence in Solutions of Bis-4-Cyano-Biphenyloxyalkanes

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ELECTRIC BIREFRINGENCE IN SOLUTIONS OF BIS-4-CYANO-BIPHENYLOXYALKANES

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Abstract The electrooptical properties of 4,4'-bis-cyanobiphenyloxyalkanes in dioxane and benzene were investigated by the method of equilibrium electric birefringence. A non-monotonic dependence of the Kerr molar constant of these compounds on the length of the oxyalkane spacer was found. This dependence is due to the influence of the odd-even effect on the intramolecular orientational polar and anisotropic order. The problems are discussed of the effect of equilibrium and kinetic spacer flexibility on the value and sign of the observed birefringence and on the degree of correlation in orientations of mesogenic chain fragments in an electric field.

INTRODUCTION

It is known that the most important structural feature of thermotropic liquid-crystalline polymers is the presence in their molecules of rigid mesogenic fragments asymmetric in shape and anisotropic with respect to their physical properties. These fragments are bonded to neighboring mesogenic fragments by flexible chain parts (spacers). Although the mesogenic fragments are an active component favoring the formation of the polymer mesophase with orientational long-range order, these flexible spacers also can play an appreciable role in the ordering process in a polymer liquid crystal (LC). This role is most pronounced in strong odd-even effects observed in the thermal properties of polymer liquid crystals mesogenic in the main chain when the length of their alkyl spacers is varied.[1,2]

The starting point in the investigation of the properties of polymer LC is the study of the corresponding characteristics of their low molecular weight structural analogues, the molecules of which usually consist of the mesogenic core and two flexible (often alkyl) terminal fragments adjoining it.

It should be emphasized however, that for the low molecular weight molecules with a rigid mesogenic core the odd-even effects are much less pronounced than for polymers mesogenic in the main chain.[2]

These facts stimulated researchers to synthesize another class of low molecular weight LC the molecules of which consist of two mesogenic fragments linked by a flexible spacer (mesogenic molecules with a flexible core).[3,4] For these LC the odd-even effect manifested in the periodicity of temperature changes[3], the enthalpy and entropy of the nematic-isotropic phase transition[4], and the degree of intermolecular orientation order of the mesophases[5] is not less pronounced than that for LC polymers mesogenic in the main chain.[2]

However, it should be borne in mind that the properties of mesophases, particulary their electrooptical and dielectric properties, depend not only on intermolecular orientational order.[6] Hence, they are determined to a considerable extent by the dipole and anisotropic structure of individual molecules from which the mesophase is formed.[7] The study of this structure is usually carried out in dilute solutions.

The present paper deals with the study of electrooptical properties of 4,4'-biscyanobiphenyloxyalkanes (BCBOA) with the aim of elucidating the influence of the odd-even effect on the intramolecular polar orientational order[6] in their molecules.

PROCEDURE AND SAMPLES UNDER INVESTIGATION

The samples of BCBOA $N\equiv C$-⬡-⬡-O-$(CH_2)_n$-O-⬡-⬡-$C\equiv N$
were synthesized by the procedure developed and describ-
ed.[4] The number n of the CH_2 groups in the spacer was va-
ried from 2 to 12. All BCBOA obtained by us form nematic
mesophases, and their isotropization temperatures T_{NI} de-
termined by polarizing microscopy are listed in Table I.

TABLE I   Isotropization temperatures T_{NI} °C of BCBOA

n	2	3	4	5	6	7	8	9	10	12
T_{NI}	270	169[+]	255	186	218	182	205	176	187	171
T_{NI}^{++}	265	170[+]	250	186	221	181	201	172	184	169

+ - monotropic transition
++ - according to data.[4]

The same data are shown in Fig.I in the form of a depen-
dence of T_{NI} on the number n of methylene groups in the
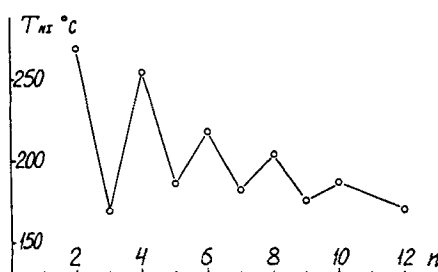spacer.

FIGURE I   Isotropization temperature T_{NI} for BCBOA
            vs number of methylene groups n in the
            spacer.

For comparison the T_{NI} values determined previously[4] are
given in Table I. The results may be considered to be in
reasonable agreement. The values of T_{NI} exhibit a pronoun-

ced periodicity (dependence on n), thus illustration the manifestation of the odd-even effect in thermal characteristics of BCBOA.

Equilibrium electric birefringence (EB) was studied in rectangular-pulsed electric fields by a procedure described in detail.[8] A glass Kerr cell with titanium electrodes 3cm long was used. The gap between the electrodes was 0.03cm. The light source was a He-Ne laser (the light wave length λ was 6328A). A photoelectric recording scheme with modulation of the ellipticity of polarized light was used to increase sensitivity.

The solutions were prepared in nonpolar weakly conducting solvents: dioxane (DO) and benzene. The specific constants of the solvents $K = \Delta n / \rho E^2$ (where $\Delta n = n_e - n_o$ is the difference between the refractive indices of the extraordinary n_e and ordinary n_o beams, ρ is the liquid density and E is the electric field strength) are $K = 2.4 \cdot 10^{-12} g^{-1} cm^5 (300V)^{-2}$ and $K = 0.39 \cdot 10^{-12} g^{-1} cm^5 (300V)^{-2}$ for benzene and DO, respectively.

RESULTS AND DISCUSSION

Fig.2 shows the dependences of EB Δn , on the square of the strength of the rectangular-pulse electric field, E^2, for BCBOA at n=3 solutions in DO at different concentrations c. Fig.2 shows that in the range of the field strengths E used here the value of n depends linearly on E^2. Similar results were also observed for all other BCBOA both in DO and in benzene. The experimental curves make it possible to calculate the specific Kerr constant K_c of the BCBOA under investigation from the equation

$$K_c = (\Delta n_{I2} - \Delta n_I)/cE^2 \qquad (I)$$

proceeding from the difference between the EB of the solution Δn_{I2} and the solvent Δn_I at all concentrations used. It was found that in this range of c the value of K_c does not exhibit a monotonic dependence on concentra-

tion. Therefore, the value of the characteristic Kerr constant K determined by the equation

$$K = \lim_{c \to 0} K_c \qquad (2)$$

may be obtained simply by averaging K_c for each BCBOA at all c values. The values of K obtained in this way for BCBOA in DO and benzene are given in Table 2.
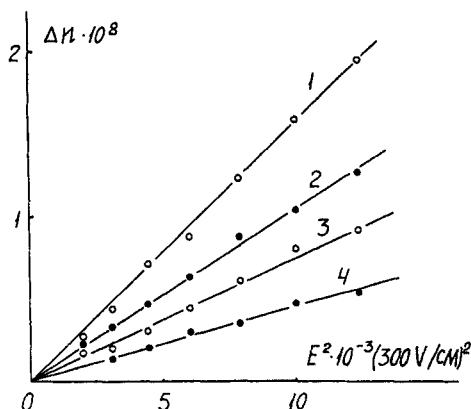

FIGURE 2   EB, Δn, vs square of electric field strength E^2 for BCBOA at n=3 in DO at different solution concentrations $c.10^2 g/cm^3$ 0.35 (I), 0.17 (2), 0.09 (3), 0 (4).

Using the values of K for BCBOA it is easy to calculate the values of the molar Kerr constant $_mK$ of the compounds being investigated from the equation

$$_mK = \frac{2}{3} M n \left[\frac{2\varepsilon + n^2}{\varepsilon (n^2 + 2)^2} \right]^2 K \qquad (3)$$

where ε and n are the dielectric permittivity and the refractive index of the solvent and M is the molecular weight of BCBOA (given in Table 2). The internal field

factor according to Onsager[9,10] is used in eq.(3). The values of $_mK$ for BCBOA in DO and benzene obtained in this way, are listed in Table 2.

TABLE 2   Electrooptical characteristics of BCBOA in DO and benzene

n	M	In DO		In benzene	
		$K.10^{10}$ $g^{-1}cm^5$ $(300V)^{-2}$	$_mK.10^{10}$ $g^{-1}cm^5$ $(300V)^{-2}$	$K.10^{10}$ $g^{-1}cm^5$ $(300V)^{-2}$	$_mK.10^{10}$ $g^{-1}cm^5$ $(300V)^{-2}$
2	416	-0.50	-6.3	-1.20	-14.0
3	430	3.26	42.4	2.6	31.1
4	444	1.48	19.9	1.07	13.3
5	458	2.66	36.8	2.23	28.6
6	472	3.6	51.3	3.4	45.0
7	486	3.82	56.1	3.53	48.1
8	500	4.3	65.1	4.24	59.3
9	514	4.6	71.3	4.5	.65.0
10	528	5.18	82.3	4.68	69.1
12	556	5.9	98.2	5.6	86.7

The data in Table 2 show that $_mK$ for BCBOA exibits a non-monotonic dependence on n. Moreover, in the course of its variation $_mK$ changes its sign from the negative at n=2 to the positive at n $\geqslant$3. These changes in $_mK$ with increasing n are clearly illustrated in Figure 3 and 4 which show the dependences of $_mK$ on n for BCBOA in DO and benzene. Although the values of $_mK$ for BCBOA in DO and benzene differ slightly, this difference is not great and, which is most important, the dependences of $_mK$ on n for BCBOA in DO and benzene are virtually indentical in shape. Hence, in further discussion of results the differences between data obtained in DO and benzene will not be taken into account. The fact that the value

of $_mK$ for BCBOA depends non-monotonically on n clearly illustrates the influence of the odd-even effect on the intramolecular polar and anisotropic order in the molecules of these compounds.
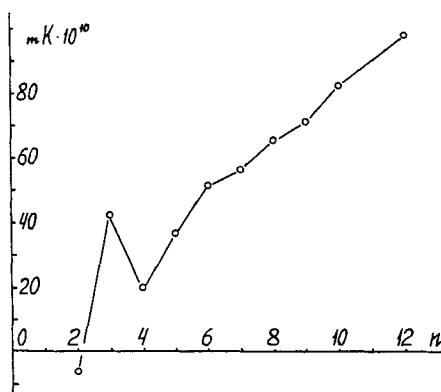

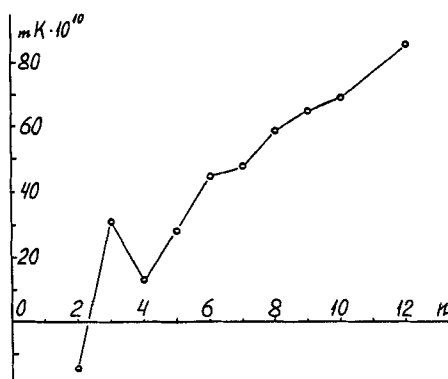FIGURE 3   Molar Kerr constant $_mK$ for BCBOA in DO vs number of methylene groups n in the spacer.

FIGURE 4   Molar Kerr constant $_mK$ for BCBOA in benzene vs number of methylene groups n in the spacer.

In fact, the transition from even n to odd n should be
accompanied by a drastic change in the angle formed by
para-aromatic axes of mesogenic cyanobiphenyl fragments
in the BCBOA molecule (in a rough approximation of the
planar trans-conformation of the oxyalkane spacer shown
in Figure 5, this angle is 0° for even n and 70° for odd
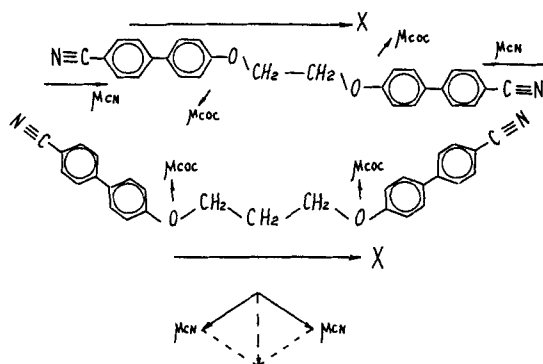n).

FIGURE 5   Conformation of BCBOA molecules at n=2
            and n=3 in the case of a planar trans-
            -form of the oxyalkane spacer.

The value of the observed EB in BCBOA solutions is main-
ly determined by the dipole moment formed by two cyan
groups rigidly bonded to mesogenic fragments and by the
optical anisotropy of biphenyl moieties of the molecule.
These abrupt variations in the angle should gratly change
the value of optical anisotropy of BCBOA molecules and
that of its dipole moment μ and its orientation with re-
spect to the main axes of the tensor of optical (and di-
electric) polarizability. This, in turn, results in a
drastic change in $_m K$ with the variation in n.
        In order to evaluate quantitatively the $_m K$ value of
BCBOA it is possible to use the well-known equation of

the Kerr molar constant $_mK$, for molecules exhibiting the symmetry of optical and dielectric properties[II]

$$_mK = B \left(\gamma_x - \gamma_y \right) \left[\delta_x - \delta_y + \frac{\mu^2}{kT} \frac{3\cos^2\theta - I}{2} \right] \qquad (4)$$

where $\gamma_x - \gamma_y$ and $\delta_x - \delta_y$ are the optical and dielectric anisotropies of the molecule, μ is its dipole moment, θ is the slope of the dipole moment with respect to the symmetry axis (axis X) of the molecule and $B = 4\pi N_A/405kT$. In this case it is reasonable to choose as axis X the axis of the greatest polarizability of the molecule (Figure 5). Taking into account the fact that the contribution provided the oxyalkane spacer to the optical anisotropy of BCBOA does not exceed IO% of that of the two biphenyl fragments even at n= IO, it is possible to assume for BCBOA with even n in Eq.(4) that $\gamma_x - \gamma_y = \delta_x - \delta_y = 2 \Delta b$ (where $\Delta b = I50.I0^{-25} cm^3$ is the optical anisotropy of biphenyl fragment[I2]) and $\mu = 0$. The evaluation of $_mK$ in this way gives $_mK = 2.I0^{-IO} g^{-I} cm^5 (300 V)^{-2}$. This value is relatively small and positive in sign because at even n for BCBOA molecules with an oxyalkane spacer in trans-conformation the dipole moment is equal to zero. A similar evaluation of K (using Eq.(4)) choosing a planar trans-conformation of the oxyalkane spacer (Figure 5) can also be carried out at odd n. In this case the BCBOA molecule exhibits a considerable dipole moment caused by the presence of CN and COC groups in the chain ($\mu_{CN} = 4D$ and $\mu_{COC} = I.25D$). In this case it is also reasonable to choose the axis of the highest polarizability of the molecule which coincides with the direction of the growth of the planar trans-chain of the oxyalkane spacer. Then the total dipole moment equal to $\mu = 2 \mu_{CN} \cos 55° - 2 \mu_{COC} \approx 2D$ is normal to the X axis (i.e. in Eq.(4) $\theta = 90°$). If owing to the above considerations the contribution of the oxyalkane spacer to the optical ani-

sotropy of BCBOA is neglected, it may be assumed in Eq.
(4) that $\gamma_x - \gamma_y = \delta_x - \delta_y = 2\Delta b(3\cos^2 35° - I)/2$ the
value of $_mK$ for BCBOA evaluated at odd n on the basis of
the above considerations is close to $-I.2.IO^{-IO}g^{-I}cm^5$
$(300V)^{-2}$. This is a relatively small value, and its nega-
tive sign is due to the fact in the case of a planar
trans-conformation of the spacer the dipole moment in
the BCBOA molecule at odd n is normal to the axis of the
greatest polarizability of the molecule. It can be easi-
ly seen that the experimentally determined $_mK$ values do
not agree with the above estimation both in the absolute
value and in sign. The essential differences between the
experimental and theoretical values of $_mK$ for BCBOA may
be caused by at least two reasons which were not taken
into account in the above estimation: first, the devia-
tion of oxyalkane spacer conformation from the planar
trans-form (equilibrium chain flexibility) and second,
possible manifestation of kinetic flexibility of BCBOA
molecule, which leads to a more independent orientation
in the electric field of strongly polar mesogenic frag-
ments contained in its molecule.

Let us consider the value and sign of $_mK$ for BCBOA
at n=2. In this case the experimental value of $_mK$ is ne-
gative and the calculated value is positive. The mani-
festation of kinetic flexibility in BCBOA molecules sho-
uld lead to an increase in positive EB. At the same time
for BCBOA at n=2 the experimental value of $_mK$ is nega-
tive and the calculated value is positive. This fact in-
dicates that the main role in the EB phenomenon for
BCBOA at n=2 is not played by kinetic chain flexibility
but by its equilibrium flexibility expressed in the de-
viation of the shape of the oxyalkane spacer from the
planar trans-conformation. This fact is not unexpected.
It is well known[13] that, under equilibrium conditions
gauche-isomers in the polyoxymethylene molecule have a
considerable statistical weight. In our case as a result

of the deviation of the spacer shape from the trans-con-
formation, for instance at the oxygen atom, amesogenic
fragments leave the same plane and, hence, non-compensa-
ted dipole moment should appear. This dipole will be di-
rected at a considerable angle to the direction of the
greatest polarizability of the molecule. As a result of
this conformational change in a BCBOA molecules at n=2,
negative EB in solution appears.

The experimentally observed $_mK$ value for BCBOA at
n=3 (and at all odd n) is positive in contrast to what
might be expected for the planar trans-configuration of
the spacer. This difference may probably be caused by
the two above reasons. However, in this case it is not
possible to decide which of the two should be preferred
because both the manifestation of kinetic flexibility
and the deviation of the spacer shape from the planar
trans-shape caused by equilibrium flexibility may lead
to an increase in positive EB in BCBOA solutions with
odd n.

Although the experimental value of $_mK$ for BCBOA at
n=4 is much lower than that at n=3 and n=5, it is alrea-
dy positive. This fact indicates that the kinetic flexi-
bility of the spacer plays a considerable role in the EB
phenomenon for BCBOA at n=4.

At $n \geqslant 4$ the dependence of $_mK$ for BCBOA on n increa-
ses monotonically. This behavior of $_mK$ shows that the
equilibrium orientational correlation between the meso-
genic fragments of BCBOA becomes weaker and, correspond-
ingly, the intramolecular orientational polar and aniso-
tropic order decreases with increasing n. It also indi-
cates that the role of the deformational factor in the
observed EB increases. However, it can be observed that
the dependence of $_mK$ on n has a tendency to saturation.

In order to answer the question of the possible li-
miting $_mK$ value for BCBOA at $n \rightarrow \infty$, EB was investigated
in solutions of 4,4-cyanobiphenyloxyalkanes (CBOA)

$N \equiv C$-⬡-⬡-O-$(CH_2)_k$-CH_3. In fact, the value of $_mK$ for BCBOA at $n\to\infty$, i.e. in the absence of mutual correlation in orientations of mesogenic fragments, should be twice as large as that for CBOA at $k\to\infty$. The values of K and $_mK$ for CBOA are listed in Table 3.

TABLE 3   The values of K and $_mK$ for CBOA in DO and benzene

k	M	In DO		In benzene	
		$K \cdot 10^{10}$ $g^{-1}cm^5$ $(300V)^{-2}$	$_mK \cdot 10^{10}$ $g^{-1}cm^5$ $(300V)^{-2}$	$K \cdot 10^{10}$ $g^{-1}cm^5$ $(300V)^{-2}$	$_mK \cdot 10^{10}$ $g^{-1}cm^5$ $(300V)^{-2}$
0	209	9.45	59.6	10.3	60
4	265	8.60	68.8	9.37	69.5
9	335	7.3	74	7.31	68.6

If the data in Table 2 and Table 3 are compared, it can be seen that the values of $_mK$ for BCBOA (even at n=I2) are much lower than 2_mK for CBOA (at k=4 or k=9). This fact shows unequivocally that although intramolecular correlation in the orientations of BCBOA mesogenic fragments in the electric field becomes much weaker with increasing n, it is still relatively high at n=I2.

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