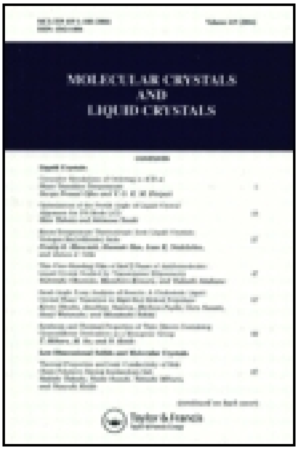

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Effect of Structure of Photoresponsive Molecules on Photochemical Phase Transition of Liquid Crystals III. Photochemical Phase Transition Behaviors of Photochromic Azobenzene Guest/Ester Host Mixtures

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Sixteen azobenzene derivatives were used as guests in an ester-type host liquid crystal (LC), 4-hexyloxyphenyl-4′-ethyl-cyclohexanecarboxylate (ECH 206), and were examined on their ability to induce the photochemical isothermal phase transition of the guest/host mixtures. Attention was focused on the effect of the mesogenic 4-cyanobiphenyl (CB) groups covalently incorporated at one end or at both ends of the azobenzene derivatives through flexible methylene spacers in order to enhance the interaction of the guest molecules with the matrix LC. Distinct odd-even effect of the methylene spacers was observed on the orientational ordering of the guests in the ECH 206 matrix, which was demonstrated by the order parameters of the mixtures evaluated by UV dichroism. The photochemical phase transition was found to occur more effectively in the mixtures with the guests of higher orientational ordering in the host.

Keywords: photochemical phase transition, azobenzene, photoisomerization, order parameter, guest/host mixture

INTRODUCTION

Use of liquid crystals (LC) as active media in display devices has become very common and has extended to full-color TV displays recently. The working principle of these display devices is mainly an electro-optic effect, thus requiring matrix arrangement of transparent electrodes. In order to improve resolution, laser-ad-

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dressed display systems have been developed, which are essentially based on the thermo-optic effects of the LCs.[1] Since the laser beam can be focused to several μ mϕ, high resolution can be expected. Although the laser beam is used in these systems for write-in processes, it is used only as a heat source, thus these systems are called heat-mode recording.[1] The heat-mode recording has in fact a number of merits, however, the photon-mode systems are superior in view of high resolution and the possibility of multiplex recording.[2] The main disadvantage of the photon-mode processes is the fading of the stored information, which is associated with the fact that the photochemical reaction has no energy threshold. When the stored information is directly read out at the wavelength of the photochromic absorption band, the stored information in the form of the photochemical products is faded by the repeated read-out processes.[2]

To prevent fade-out and to improve stability of the stored information, other methods than the direct reading of the photochemical reaction are to be developed in the photon-mode recording systems. We have been studying the photon-mode image recording processes in which a photochemical reaction occurring at a local site of the system induces phase transition isothermally, thus the photosignals are converted to the physical change of the whole system.[3-10] The merits of this way of image recording are evident. Since the photosignals are converted to the physical change of the whole system, a variety of methods other than the direct reading of the photochemical reaction can be used for non-destructive read-out of the stored information. In fact, such methods as detection of loss of birefringence[3,6-10] and change in capacitance[4] associated with the photochemical phase transition of LC systems have been successfully employed for the non-destructive read-out.

In previous studies, various photochromic azobenzene derivatives were used as guests in the 5CB host and were examined on their ability to induce the photochemical isothermal phase transition of the guest/host mixtures.[8,9] In order to enhance the interaction of the guest molecules with the matrix, the same mesogenic group, 4-cyanobiphenyl, was introduced at one end or at both ends of the azobenzene core through flexible methylene spacers and the effect of the mesogenic group on the photochemical phase transition behaviors was explored.[8,9] Although the photon-mode response of LCs has been long investigated,[11-21] very few systematic studies have so far been reported on the effect of the structure of the photochromic guest molecules on the photochemical phase transitions. In previous studies,[8,9] the photochemical phase transition behaviors of the azobenzene guests/5CB host mixtures were explored in relation to the structure of the photochromic guest molecules and it was found that the photochemical phase transition occurred more effectively in mixtures with the guests possessing the 4-cyanobiphenyl moieties that have a high affinity with the host.

In the present study, 16 azobenzene derivatives were used as guests in host LC, 4-hexyloxyphenyl-4′-ethyl-cyclohexanecarboxylate (ECH 206) which is an ester-type mesogen, and were examined on their ability to induce the photochemical phase transition of the guest/host mixtures. Particular attention was paid to the effect of the mesogenic 4-cyanobiphenyl groups covalently incorporated at one end or at both ends of the azobenzene derivatives on the photochemical phase transition behavior of the mixtures from the viewpoint of interaction between the mesogenic

4-cyanobiphenyl moieties and the host ester mesogens. The photochemical phase transition behaviors of the azobenzene/ester host mixtures were compared with those of the azobenzene/5CB mixtures.

EXPERIMENTAL

In Figure 1 are shown the structures of the photochromic azobenzene guests and their abbreviations used in this study. The azobenzene guest molecules are classified into three groups as described in the previous paper:[8,9] $AB(nCB)_2$ in which 4-cyanobiphenyl moieties are attached to both sides of azobenzene at the para positions through various lengths of methylene spacers, 1ABnCB where the 4-cyanobiphenyl moiety is attached to one side of the azobenzene, and nABm or k,lABm which possess alkoxy substituents at both para positions of azobenzene or at various positions of the azobenzene phenyl rings. Synthesis and their thermotropic properties are described in full detail in the previous paper.[8]

4-Hexyloxyphenyl-4′-ethyl-cyclohexanecarboxylate (ECH 206) was used as a host LC throughout this work, which was purchased from Fuji Pigment Co., Ltd. and used without further purification.

Liquid crystalline behavior and phase transition behavior were examined on an Olympus model BHSP polarizing microscope equipped with a Mettler hot stage model FP-80 and FP-82. The thermodynamic properties of the host/guest mixtures were determined with a differential scanning calorimeter (SEIKO I&E SSC-5000) at a heating rate of 5°C/min. At least four scans were performed for each sample to check reproducibility.

Polarized absorption spectra were recorded with a Hitachi UV-200 spectrophotometer with the aid of a polarizer. Oriented samples of the host/guest LC mixtures for the polarized absorption spectroscopy were prepared by injecting the mixture (isotropic) into an LC cell with parallel homogeneous orientation (EHC Inc.; cell gap, 9 μm) and by cooling gradually to an appropriate temperature.

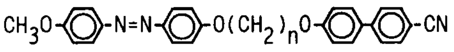
Photochemically induced isothermal phase transition behaviors of the host/guest mixtures were investigated by means of an apparatus already reported.[6,9] With this apparatus, the photochemical phase transition behavior of the guest/host mixtures as well as the photoisomerization behavior of the guest photochromic molecules could be followed simultaneously. The sample was placed in a thermostated block and irradiated with a monochromatic light from a JASCO CRM-FA irradiator. Photochemical phase transition behavior was observed by monitoring the intensity of the linearly polarized light at 633 nm from a He-Ne laser transmitted through a pair of crossed polarizers with a photodiode.

RESULTS AND DISCUSSION

Order parameters determined by UV dichroism

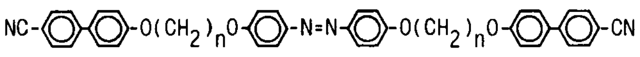
For a uniaxially symmetrical system, the dichroic ratio, R (Equation 1), is related to the order parameter, S, by Equation 2 when the transition moment of the

1ABnCB

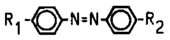


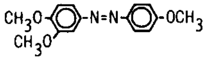
n	
3	1AB3CB
4	1AB4CB
5	1AB5CB
6	1AB6CB
8	1AB8CB

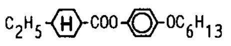
AB(nCB)$_2$



n	
3	AB(3CB)$_2$
4	AB(4CB)$_2$
5	AB(5CB)$_2$
6	AB(6CB)$_2$



R_1	R_2	
CH_3O	CH_3O	1AB1
	C_3H_7O	1AB3
	$C_8H_{17}O$	1AB8
	$C_{12}H_{25}O$	1AB12
C_3H_7O	C_3H_7O	3AB3
$C_8H_{17}O$	$C_8H_{17}O$	8AB8
		1,1AB1



ECH206

FIGURE 1 Structure of photochromic azobenzene guests and a host LC used in this study and their abbreviations.

chromophore is oriented parallel to the long axis of the molecule,[22]

$$R = \frac{A_{\parallel}}{A_{\perp}} \tag{1}$$

$$S = \frac{R - 1}{R + 2} \tag{2}$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances measured by the polarized light with parallel and perpendicular orientation to the optical axis of the molecule, respectively.

Figure 2 shows the polarized absorption spectra of a 1AB3/ECH206 mixture measured at 43°C, which corresponds to the reduced temperature T_{red} ($= T/T_{NI}$) of 0.99. These spectra have been corrected for the absorption or scattering due to ECH206 alone. A peak with maximum at 360 nm is due to the $\pi - \pi^*$ transition of the azobenzene moiety. We used this peak for the determination of the order parameters. It must be mentioned here that the order parameters determined in this study are concerned with the azobenzene chromophores since the transition moments used in the determination of the order parameters are only connected with the azobenzene moieties.

Figure 3 shows the order parameters determined at $T_{red} = 0.99$ for 1ABn/ECH206 mixtures as a function of the methylene spacer length *n*. In a series of the 1ABn/ECH206 mixtures the *S* values were nearly the same, giving the values of 0.35 – 0.4, although a clear tendency was observed: the *S* value increased rather monotonically with the alkyl chain length. This indicates that 1ABn with higher values of *n* is aligned in the host ECH206 with more ordered orientation.

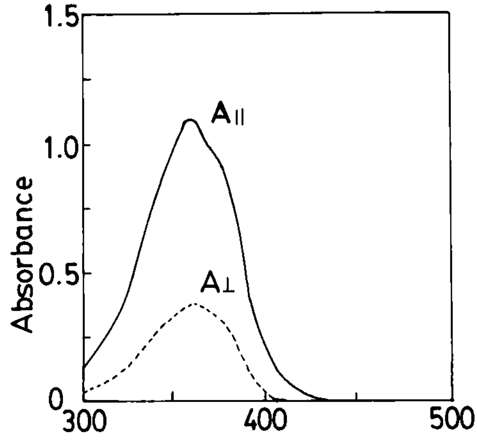


FIGURE 2 Polarized absorption spectra of 1AB3/ECH206 mixture at 32°C. $A_{\parallel}$, polarized parallel to the optical axis; $A_{\perp}$, polarized perpendicular to the optical axis. The concentration of the guest was 1 mol%. The spectra were corrected for the absorption or scattering due to ECH206 alone.

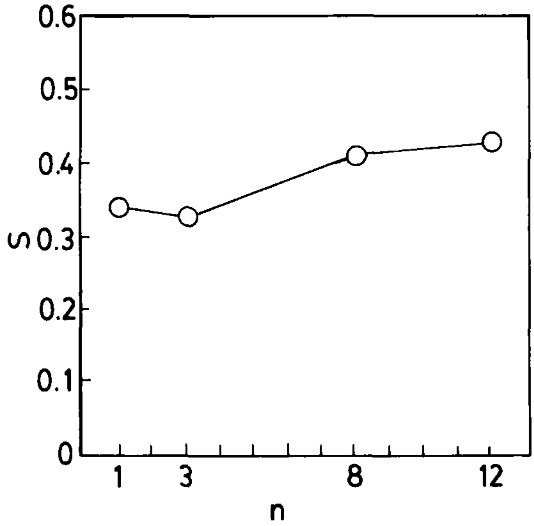


FIGURE 3 Order parameters of the 1ABn/ECH206 mixtures as a function of the number of methylene units in the spacer chains. The order parameters were determined at T_{red} = 0.99 and the concentration of the azo guest was 1 mol %.

Figure 4 shows the order parameters determined at T_{red} = 0.99 for $AB(nCB)_2$/ECH206 and 1ABnCB/ECH206 mixtures as a function of the methylene spacer length *n*. In a series of the $AB(nCB)_2$/ECH206 mixtures the azobenzene chromophores with an even number of methylene spacers gave high values of *S* and those with an odd number showed rather low values of *S*. Thus, a distinct odd-even effect

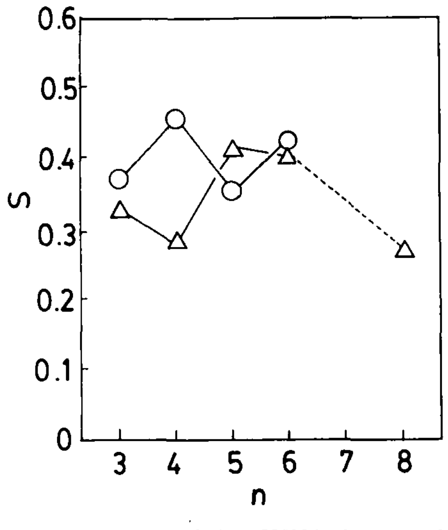


FIGURE 4 Order parameters of the $AB(nCB)_2$/ECH206 mixtures and the 1ABnCB/ECH206 mixtures as a function of the number of methylene units in the spacer chains. (○), $AB(nCB)_2$/ECH206 mixtures; (△), 1ABnCB/ECH206 mixtures. The order parameters were determined at T_{red} = 0.99 and the concentration of the azo guest was 1 mol %.

on the order parameters has been observed for the azobenzene guests with cyanobiphenyl moieties at both ends of the azobenzene core via methylene spacers. This is well explicable in terms of the spatial orientation adopted by the two cyanobiphenyl mesogens and the central azobenzene chromophore in a single molecule as evidenced by CPK molecular models. In AB(nCB)$_2$ with an even number of n, all mesogens can be aligned parallel to each other, thus a rod-like shape of the molecule, essential for high orientational ordering of the guest in the nematic host, can be easily obtained. It is, therefore, quite reasonable that the order parameter in these mixtures is high. On the other hand, in AB(nCB)$_2$ with an odd number of n, the two cyanobiphenyl mesogens and the central azobenzene chromophore are not aligned parallel, thereby the molecular shape of these molecules is entirely different from the rods, giving a less ordered orientation in the nematic host. The same tendency was observed for a series of the AB(nCB)$_2$/5CB mixtures.[9]

In contrast to the behavior of the AB(nCB)$_2$/ECH206 mixtures, the 1ABnCB/ECH206 mixtures showed quite a different behavior. Namely, 1ABnCB, with an even number of methylene spacers, gave rather low values of S and those with an odd number showed high values of S. Thus, the apparently opposite odd-even effect on the order parameter has been observed in view of the spatial orientation adopted by the cyanobiphenyl and azobenzene moieties. With the aid of the CPK molecular models, we can visualize the relative orientation of the relevant two mesogenic groups. In 1ABnCB with an even number of n, the two mesogenic groups can be aligned rather parallel, thereby the whole molecule can take a rod-like shape. On the other hand, in 1ABnCB with an odd number of n, the two mesogenic groups are not aligned parallel, giving a molecular shape different from the rod. This opposite odd-even effect on the order parameter as seen in the 1ABnCB/ECH206 was not observed in the 1ABnCB/5CB mixtures.[9]

The formation of the LC state has been treated theoretically by many workers.[23–26] In the early stage of the theoretical development, the excluded volume effect was only considered to be responsible for the appearance of the nematic phase,[23,25] and later the anisotropic dispersion forces were shown to be the origin of the existence of the nematic phase.[24,26] It is well known that dipole-dipole interaction plays a significant role in the intermolecular interaction,[26,27] so that it does not seem to be unreasonable to involve the dipole-dipole interaction when we consider the orientation of mesogens in the LC phases, particularly in such cases where the mesogens concerned possess relatively strong permanent dipoles as in the case of the present guest/host mixtures. In fact, such dipole-dipole interaction was taken into account in the theoretical treatment of the smectic C phase formation.[28] It is reasonable to assume that the 4-cyanobiphenyl moiety possesses a dipole along its long molecular axis and ECH206 has a dipole along the direction of the C=O group. If the dipole-dipole interaction operates between the azobenzene guest having the 4-cyanobiphenyl moiety and the host ECH206, it would act in such a way that the overall potentials would be minimized; namely, the relevant two dipoles would be aligned rather parallel in the mixtures. Because of the non-parallel configuration of the dipole and the molecular long axis in ECH206, this consideration will lead to non-parallel alignment of the 4-cyanobiphenyl part in the guest and the molecular axis of the host mesogens. As mentioned above, the

4-cyanobiphenyl moiety and the azobenzene part are aligned parallel in 1ABnCB with an even number of *n*, thereby the orientation of the 4-cyanobiphenyl moiety is expected to affect the orientation of the azobenzene moiety in such a way that the direction of the long axis of the azobenzene moiety would be tilted with respect to the director of the host, leading to a low value of the order parameter, particularly when the methylene spacer is short, as $n = 4$. In contrast, in 1ABnCB with an odd number of *n*, the 4-cyanobiphenyl moiety and the azobenzene moiety are not aligned parallel, being tilted to the same direction with respect to the major extension axis of the molecule, thus it is possible for the azobenzene moiety to be aligned rather parallel to the director of the nematic host when the 4-cyanobiphenyl moiety is oriented across the long axis of the host. This may be the origin of the apparently opposite odd-even effect observed in the 1ABnCB/ECH206 mixtures.

On the other hand, in AB(nCB)$_2$ the two 4-cyanobiphenyl moieties are attached in the opposite way at the ends of a single molecule, so that the overall dipole seems to be weakened, resulting in the very weak dipole-dipole interaction between the guest and the host. It seems reasonable, therefore, that the AB(nCB)$_2$/ECH206 mixtures exhibited the ordinary odd-even effect for the orientational ordering of the relevant mesogenic moieties.

Photochemical phase transition behaviors of the guest/host mixtures

In Figure 5 is shown a typical example of the photochemical phase transition behavior of the present guest/host mixtures, in which a 1AB12/ECH206 mixture containing 1 mol% of the guest molecules was irradiated at 360 nm at $T_{red} = 0.99$. Transmittance of the linearly polarized light (633 nm) through the crossed polarizers

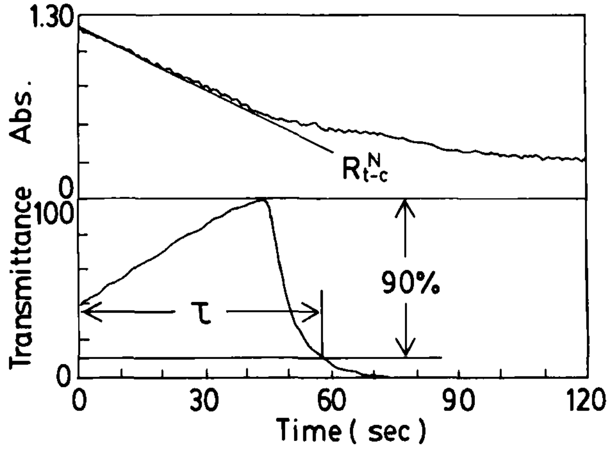


FIGURE 5 Photochemically induced isothermal phase transition behavior of ECH206 doped with 1 mol% of 1AB12 (lower part) and the photoisomerization behavior of the photochromic dopant (upper part). Change in absorbance of 1AB12 in ECH206 at 360 nm is plotted as a function of irradiation time in the upper part and the transmittance between a pair of the crossed polarizers is plotted in the lower part of the figure as a function of the irradiation time ($\lambda_{ex} = 360$ nm). Irradiation was performed at $T_{red} = 0.99$.

between which the sample was placed, I_t, was measured as a function of the irradiation time. At the same time, the change in absorbance of the azobenzene chromophore at the irradiation wavelength (360 nm) was followed *in situ* and is shown in the upper part of Figure 5. It is clear that photoirradiation at 360 nm brought about trans → cis isomerization of 1AB12 doped in ECH206 as evidenced by a decrease in absorbance at 360 nm, and the trans → cis photoisomerization of the dopant induced nematic (N) → isotropic (I) phase transition of the host LC as demonstrated by a complete loss of birefringence ($I_t = 0$). Isothermal phase transition of the host LC can be induced in this way by photochemical reaction of the incorporated photoresponsive molecules.

In order to discuss the photochemical phase transition behavior quantitatively, we defined the response time, τ, as the time required to reduce the transmittance, I_t, to 10% of the maximum value (lower part of Figure 5). Furthermore, since we realized that the rate of the trans → cis photoisomerization of the azobenzene guests was strongly dependent on the structure of the guest molecules, we determined the isomerization rate from the initial slope of the time-course of the absorbance change and termed it as R_{t-c} (upper part of Figure 5).

The effect of temperature on the photochemical phase transition behaviors of the guest/host mixtures must be mentioned here. The rate of the phase transition, evaluated by the reciprocal of the response time (τ^{-1}, Figure 5), was strongly dependent on the temperature and decreased with decreasing temperature. The rate of the isothermal phase transition is closely related to the lowering of the phase transition temperature brought about by accumulation of the cis-form of the azobenzene chromophores.[9] Namely, T_{NI} of the guest/host mixture decreases as the concentration of the cis-form increases and when T_{NI} of the system is lowered below the irradiation temperature, the isothermal phase transition is induced. Thus, when the irradiation temperature is close to T_{NI} of the initial state, the amount of the cis-form required to lower T_{NI} below the irradiation temperature is rather small and the phase transition is induced rapidly. On the other hand, when the irradiation temperature is low, a large amount of the cis-form is necessary to lower T_{NI} of the system below the irradiation temperature, thus the rate of the phase transition is expected to be low. In the following, therefore, all the photochemical phase transition behaviors were evaluated at $T_{red} = 0.99$.

In Figure 6, 7 and 8, the rates of the trans → cis photoisomerization of the photochromic azobenzene derivatives in two different phases of the host LC are plotted as a function of the number of methylene chains in the flexible spacers: *N* ($T_{red} = 0.99$, ○); and *I* ($T_{red} = 1.02$, Δ) phases. The concentration of the dopant was 1 mol% in ECH206.

Figure 6 shows the rates of photoisomerization (R_{t-c}) of a series of the 1ABn/ECH206 mixtures. It is clearly seen that the rate of the photoisomerization was higher in the *I* phase than in the *N* phase of the host, and this tendency was observed in the 1ABnCB/ECH206 and $AB(nCB)_2$/ECH206 mixtures as well as those of the 5CB host.[9] Of note is the fact that the values of R_{t-c} of the azobenzene guests in the ECH206 host were slightly lower than those in the 5CB host,[9] although ECH206 was expected to show lower viscosity than 5CB. The rates of the photoisomerization were not significantly affected by the number of methylene chains in the *N* phase.

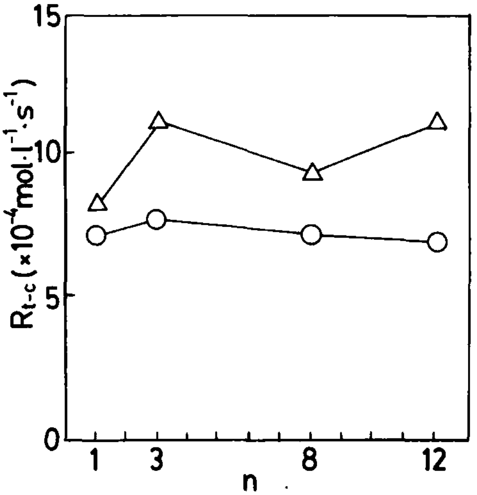


FIGURE 6 Rates of photoisomerization of 1ABn doped in ECH206 in the nematic (○, T_{red} = 0.99) and isotropic phases (△, T_{red} = 1.02) as a function of the number of methylene units in the spacer chains. The concentration of the dopant was 1 mol % in the mixtures and photoirradiation was performed at 360 nm.

In a series of 1ABnCB/ECH206 mixtures, the rates of photoisomerization were affected in the *N* phase by the spacer length *n* and the 1ABnCB with *n* = 5 exhibited the lowest rate of the photoisomerization, as shown in Figure 7. A correlation seems to exist between R_{t-c} and *S* of the 1ABnCB/ECH206 mixtures. Namely, the *S* value of the 1AB5CB/ECH206 was highest and this mixture gave the lowest

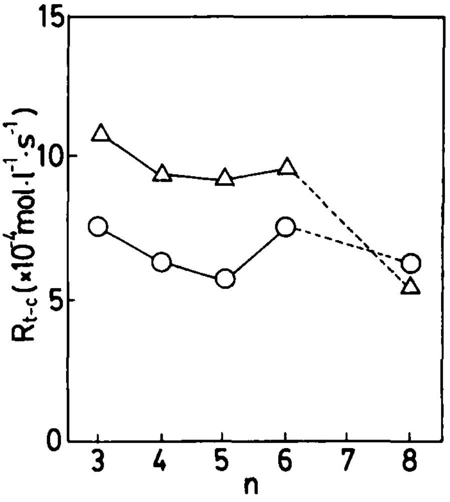


FIGURE 7 Rates of photoisomerization of 1ABnCB doped in ECH206 in the nematic (○, T_{red} = 0.99) and isotropic phases (△, T_{red} = 1.02) as a function of the number of methylene units in the spacer chains. The concentration of the dopant was 1 mol % in the mixtures and photoirradiation was performed at 360 nm.

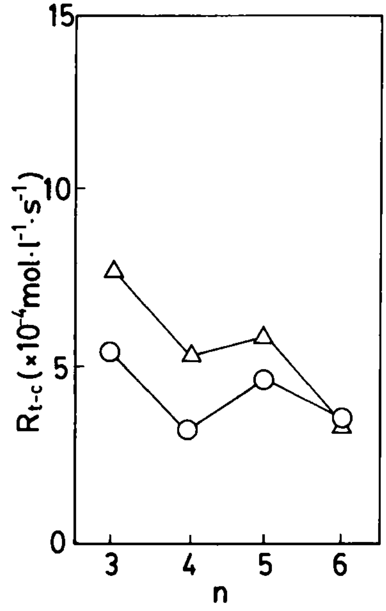


FIGURE 8 Rates of photoisomerization of AB(nCB)$_2$ doped in ECH206 in the nematic (○, T_{red} = 0.99) and isotropic phases (△, T_{red} = 1.02) as a function of the number of methylene units in the spacer chains. The concentration of the dopant was 1 mol % in the mixtures and photoirradiation was performed at 360 nm.

value of R_{t-c}. This may apparently be a consequence of a close-packing of the azobenzene part of the guest molecules in the host, since when the order parameter of the azobenzene chromophore is high, packing in the vicinity of the azobenzene moiety is expected to be high. The photoisomerization of the azobenzene part requires some free volume in the host medium regardless of the isomerization mechanism,[29] so that in a mixture of the azobenzene guest and a host with a high value of the order parameter the photoisomerization is expected to be more restricted due to less free volume available. This concept is further supported by the fact that a distinct relation was observed in a series of the AB(nCB)$_2$/ECH206 mixtures between R_{t-c} and S as shown in Figure 8: the AB(nCB)$_2$/ECH206 mixtures with an even number of n showed high values of S and low values of R_{t-c}, whereas those with an odd number of n exhibited low values of S and a high value of R_{t-c}.

The corrected rates of the photochemical $N \rightarrow I$ phase transition of the guest/host mixtures are shown as a function of the number of methylene chains in Figure 9 for a series of the 1ABn/ECH206 mixtures, in Figure 10 for a series of the 1ABnCB/ECH206 mixtures and in Figure 11 for a series of the AB(nCB)$_2$/ECH206 mixtures. In all cases, the photoirradiation was performed at T_{red} = 0.99 at 360 nm for the mixtures containing 1 mol% of the dopant and the rate of the phase transition was evaluated by the reciprocal of the response time, τ^{-1}, as shown in Figure 5. However, the rate of the photoisomerization was different from mixtures to mixtures, as described above; thus, for the quantitative evaluation of the efficiency of the azobenzene guests to induce the photochemical phase transition of

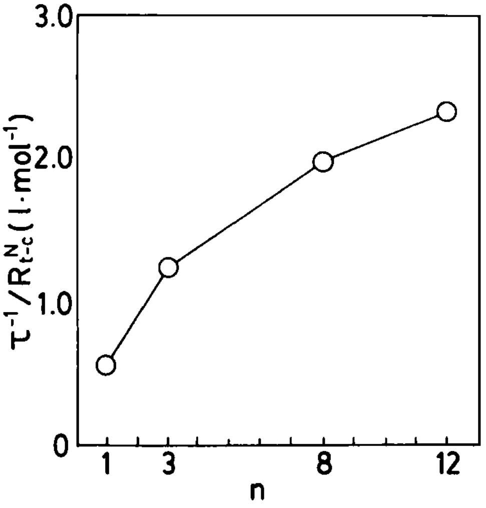


FIGURE 9 Corrected rates of the photochemical phase transition (τ^{-1}/R^{N}_{t-c})of the 1ABn/ECH206 mixtures as a function of the number of methylene units in the spacer chains. The concentration of the dopant was 1 mol % in the mixtures and photoirradiation was performed at 360 nm at T_{red} = 0.99.

the guest/host mixtures, the apparent rate (τ^{-1}) should be divided by the rate of the photoisomerization of the guest molecule (R_{t-c}) measured in the N phase at T_{red} = 0.99 (R^{N}_{t-c}). In Figures 9–11 are shown the corrected rates of the photochemical phase transition thus calculated (τ^{-1}/R^{N}_{t-c}).

In the 1ABn/ECH206 mixtures, the rate of the photochemical phase transition was found to increase by increasing the number of methylene chains (Figure 9).

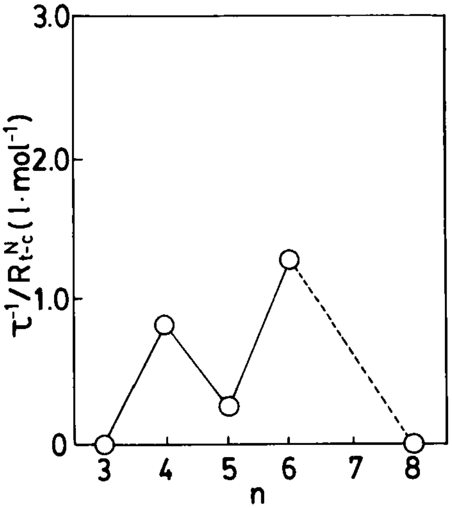


FIGURE 10 Corrected rates of the photochemical phase transition (τ^{-1}/R^{N}_{t-c}) of the 1ABnCB/ECH206 mixtures as a function of the number of methylene units in the spacer chains. The concentration of the dopant was 1 mol % in the mixtures and photoirradiation was performed at 360 nm at T_{red} = 0.99.

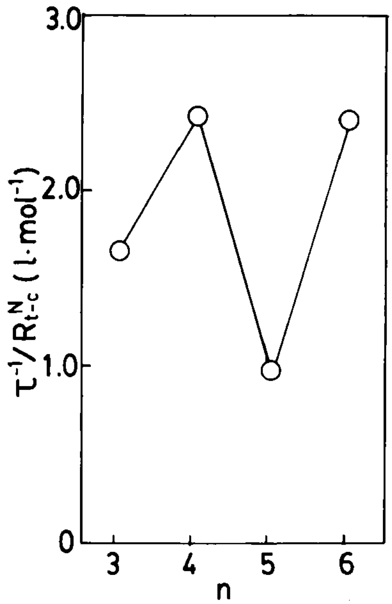


FIGURE 11 Corrected rates of the photochemical phase transition (τ^{-1}/R^N_{t-c}) of the AB(nCB)$_2$/ECH206 mixtures as a function of the number of methylene units in the spacer chains. The concentration of the dopant was 1 mol % in the mixtures and photoirradiation was performed at 360 nm at T_{red} = 0.99.

This may result from the increasing *S* value of the 1ABn/ECH206 mixtures with the methylene spacer *n*. Dopants in closely-packed matrices are expected to be restricted in the photoisomerization, but owing to the strong interaction, the influence of the isomerization on the matrix, once occurred, is assumed to be significant. This interpretation seems to be rationalized most clearly for the photochemical phase transition behaviors of the AB(nCB)$_2$/ECH206 mixtures (Figure 11). The most distinct odd-even effect was observed for the order parameters, the rates of the photoisomerization and the rates of the photochemical phase transition in the AB(nCB)$_2$/ECH206 mixtures.

Comparison of the rate of photochemical phase transition with the order parameter of the guest/host mixture

Figure 12 shows the corrected rates of the photochemical phase transition of the guest/host mixtures as a function of the order parameters of the mixtures. Both the rates and the order parameters were evaluated at T_{red} = 0.99. It is seen that 1,1AB1 which possesses more than one substituent in phenyl rings of the azobenzene core could not induce the phase transition of the host photochemically. This molecule was found to be photoisomerized in ECH206 at a similar rate to that of 1AB1. Because of multiple substitution at the azobenzene core with rather short alkoxy groups (OCH_3), the shape of this molecule is considered as a cylinder with a small ratio of length to diameter. Thus, orientational ordering in the LC matrix is small as demonstrated by the low value of *S* for this molecule. Furthermore,

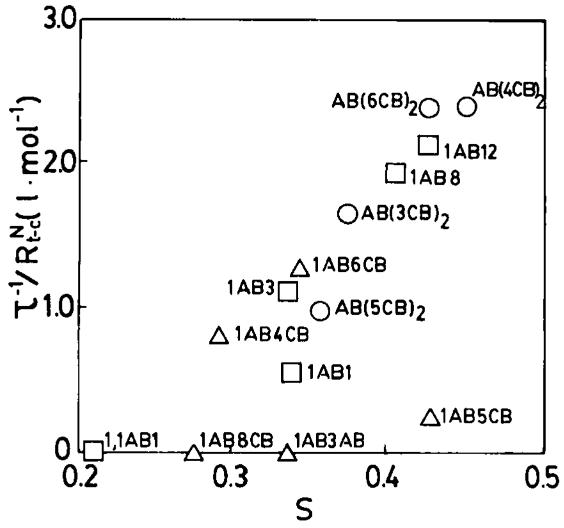


FIGURE 12 Corrected rates of the photochemical phase transition of the guest/host mixtures as a function of the order parameters of the mixtures. The rates of the photochemical phase transition and the order parameters of the mixtures were evaluated at $T_{red} = 0.99$.

change in the molecular shape on photoisomerization to the cis form is expectedly small, since the cis form takes a rather spherical form. As a result, perturbation imposed on the matrix in the form of the trans → cis isomerization acts least effectively, leading to non-occurrence of the photochemical phase transition of the host.

In a series of the azobenzene guests/ECH206 host mixtures examined in the present study, there seems to be a good correlation between the order parameters and the corrected rates of the photochemical phase transition. The photochemical phase transition took place more effectively in those mixtures that exhibited a higher value of the order parameter. This correlation seems to be explicable in terms of the strong interaction of the guest with the host in such mixtures where the photoisomerization of the azobenzene guests is expected to act effectively as the perturbation to the matrix.

As a final remark, it is worth mentioning here that the corrected rates of the photochemical phase transition of the azobenzene guest/ECH206 mixtures were lower by approximately two order of magnitude than those of the same azobenzene/5CB mixtures,[9] although the rates of the photoisomerization of the azobenzene guests were nearly the same in both host LCs (Figure 13). This result demonstrates that the incorporation of the 4-cyanobiphenyl moieties in the photochromic guest molecules is not always effective to induce the photochemical phase transition of the guest/host mixtures and in the molecular design of the highly efficient photochromic guest molecules such factors as affinity of the incorporated mesogenic groups with the host mesogens are to be considered.

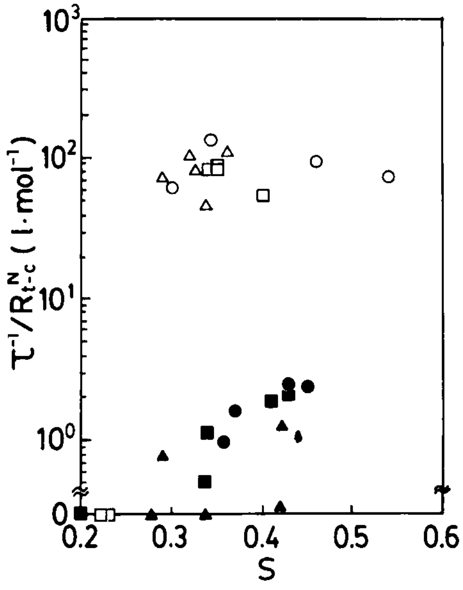


FIGURE 13 Comparison in the corrected rates of the photochemical phase transition of the azo guest/host mixtures as a function of the order parameters of the mixtures between the azo guest/ECH206 and the azo guest/5CB mixtures. The azo guest/ECH206 mixtures: (●), AB(nCB)$_2$; (▲), 1ABnCB; (■), mABn or k,lABm. The azo guest/5CB mixtures: (○), AB(nCB)$_2$; (△), 1ABnCB; (□), mABn or k,lABm. The data for the azo guest/5CB mixtures were taken from Reference 9.

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