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Optical band gap as a physico-chemical characteristic of liquid crystal mixtures with specific interaction of component molecules

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Liquid crystal (LC) systems based on 4-*n*-pentyl-4′-cyanobiphenyl (5CB) doped with non-mesogenic salicylaldoxime (SA) and resorcinol (RES), where one could expect non-trivial behavior due to specific intermolecular interactions, were studied using differential scanning calorimetry (DSC), UV-Vis and FTIR spectroscopy. It was shown that eventual formation of supramolecular complexes led to additional temperature stabilization of the nematic phase. This effect, which we noted earlier for SA, is much more pronounced for RES. In the latter case, an increase in the nematic-to-isotropic phase transition temperature by ~15 °C was observed at RES concentration of 12 % w/w (3 : 1 molar ratio). Basing on the UV absorption data in LC state and dilute solutions, the values of optical band gap (E_g) were determined for 5CB+SA and 5CB+RES as functions of temperature and the dopant content. The concentration dependence of E_g for the 5CB+RES system shows an extremum at 3 : 1 molar ratio, which is consistent with DSC data. Possible structures of supramolecular aggregates were proposed, taking into account dipole-dipole interactions, hydrogen bonding between cyano- and OH-groups of the component molecules as well as steric factors facilitating their tightest packing.

Keywords: optical band gap, liquid crystals, pentyl cyanobiphenyl, resorcinol, nanostructurization, optical spectroscopy, differential scanning calorimetry.

Щілина оптичної смуги як фізико-хімічна характеристика рідкокристалічних сумішей зі специфічною взаємодією молекул компонентів. *П.В. Ващенко, Д.С. Софронов. Л.М. Лисецький*

Рідкокристалічні (РК) системи на основі 4-*н*-пентил-4′-ціанобіфенілу (5CB), допованого немезогенними саліцилальдоксимом (SA) та резорцинолом (RES), де можна було очікувати особливостей поведінки внаслілок специфічних міжмолекулярних взаємодій, досліджено методами диференціальної скануючої калориметрії (ДСК), а також UV-Vis та FTIR-спектроскопії. Показано, що можливе утворення надмолекулярних комплексів приводить до температурної стабілізації нематичної фази. Такий ефект, який нами раніше було відзначено для SA, є набагато більш вираженим з RES. В останньому випадку температура нематико-ізотропного фазового переходу зростає на ~15 °C при концентрації RES 12 мас. % (мольне співвідношення 3 : 1). На основі даних УФ-поглинання в РК-стані та в розведених розчинах, були встановлені значення оптичної енергетичної щілини (E_g) для 5CB+SA та 5CB+RES в залежності від температури і вмісту допанту. Концентраційна залежність E_g для системи 5CB+RES має екстремум при мольному співвідношенні 3 : 1, що узгоджується з даними термограм ДСК. Запропоновано можливі структури утворюваних міжмолекулярних агрегатів з урахуванням диполь-дипольних взаємодій, водневих зв'язків між ціано- та OH-групами молекул компонентів, а також стеричних факторів, які сприяють найщільнішому пакуванню.

1. Introduction

The fields of science that have long been well known and highly developed often set examples for development of terminology in the adjacent directions of the emerging research. In the physics of semiconductors, one of the basic notions is the energy gap (or energy band gap), often denoted as E_g, which is basically the energy difference between the highest levels of the valence band and the lowest levels of the conduction band. The E_g value represents the minimum energy needed to excite an electron from its bound state (in the valence band) to a "free" state (conduction band) where it can participate in the electrical current. If the material in question is used not as a semiconductor in an electric circuit, but for other applications that require certain optical or optico-luminescent properties, the relevant energy threshold corresponds to the state when the material starts to absorb photons, i.e., the lowest photon energy that can be absorbed to promote an electron across the band gap. In this case, E_g should better be called the "optical band gap". In most cases (indirect transitions), the exciting photons require some assistance from phonons (or involvement of other factors), so, the optical band gap is often slightly wider than the electronic band gap.

An obvious standard procedure in studying optical properties of a material is measurement of its UV-Vis and IR spectra under appropriate conditions. In this respect, an important characteristic is the absorption band edge, which marks the onset of strong absorption in the UV-Vis spectrum. Since it corresponds to the lowest energy photons that can be absorbed by the material, it suggests a way to determine its optical band gap, or E_g. As an example, one consider a detailed study on the absorption edge of zinc selenide, an important semiconductor and scintillator material [1,2].

There are many materials that do not fall directly under definition of semiconductors, but the absorption band edge is a very important characteristic of theirs, largely determining their application fields [3–5]. In this respect, we can also consider liquid crystals (LC). In the orientationally ordered nematic phase (N), standard basic substances for electrooptical cells 5CB (4-pentyl-4′-cyanobiphenyl) [6] and its homologues show the absorption edge at about ~310-330 nm, for azomethines, whereas azo- and azoxy nematics it is noticeably higher (350-400 nm, and even more in the presence of *cis*-isomers), while for non-aromatic cyclohexanecarboxylic acids, 4-alkyl-cyclohexylcyclohexanes or cholesterol esters, the absorption edge is clearly UV-shifted towards 250-300 nm [7]. From the viewpoint of organic and physical chemistry, this can be easily explained by the presence or absence of double bonds and π-electrons, which determines the absorption spectra of these compounds. Still, some physicists involved in the LC science would prefer a generalized description involving the terms conventional for solid-state and semiconductor physics, so, they carried out a number of studies of LC systems analyzing the emergent energy gap / optical band gap values E_g.

The pioneers of this approach should probably be noted as Mishra, Dhar and Dabrowski [8–10], who started to systematically apply the E_g approach to cyanobiphenyl LC doped with various nanoparticles (gold, silver, barium titanate, carbon nanotubes, *etc.*). In parallel, this approach was used for other LC types, *e.g.*, discotic [11]. In further developments, E_g-related studies were used to characterize the enhancement of the nematic phase stability by introduction of copper oxide nanoparticles [12].

Alongside the liquid crystals, one can note other examples of materials that are also far from classical semiconductors but still subject to the E_g approach. Thus, powder mixtures of zinc oxide with other oxide components were considered in [13].

The main feature of these works was the use of an equation that is ascribed to early papers by Tauc [14,15]. It is generally written as

$$ah\nu = (h\nu - E_g)^n \qquad (1)$$

where E_g is the optical band gap energy corresponding to the specific transition in the sample, $h\nu$ is the energy of a photon of incident light wavelength in the units of energy, and a is the absorption coefficient, generally taken as $a = 2.303\ A/d$ (where d and A are the thickness of the cell and absorbance, respectively). The absorbance is often considered equal to the standard optical density $D = -\ln(I/I_0)$, though it is correct only if scattering and other reflection factors can be neglected. In the original paper [15], the value of the exponent n was vaguely assumed to be 2 or 3; later, *e.g.*, in [8–12], this exponent was considered as dependent upon the type of transition, *i.e.*, taking values 1/2, 2, 3/2 or 3 for the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. However, up to date there

has been no truly rigorous and convincing proof or/derivation of the expression (1).

The magic of E_g approach was so strong for some researches in the field of liquid crystals that they even attempted to explain the selective reflection of cholesterol esters using these notions [16] (which could be much more naturally explained by the Bragg diffraction on the helical pitch). On the other hand, the E_g approach was successfully used in an interesting study on LC mixtures of alkylcyanobiphenyls and 4-pentylbenzoic acid, where formation of hydrogen bonds between the component molecules lead to enhancement of LC ordering [17]. In that paper, E_g values for the mixtures studied were determined from UV spectra taken in diluted solutions under standard physico-chemical conditions.

As a non-trivial link between semiconductor physics and quantum organic chemistry, the concept of E_g is closely related to the energy levels of electrons of organic molecules forming the material in condensed phase. It reflects the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which, for isolated molecules, can be calculated by conventional methods of quantum chemistry.

In this paper, we will analyze two sets of experimental data obtained for nematic LC mixtures. The first set is related to mixtures of 4-pentyl-4′-cyanobiphenyl (5CB) and salicylaldoxime (SA) – the corresponding DSC, spectroscopy and other data were recently published in our previous paper [18].The main peculiar feature of the 5CB+SA mixture is a non-trivial increase in the nematic to isotropic transition temperature (T_i) up to ~3% of the SA dopant, with the nematic phase persisting up to ~30%. Such behavior could be ascribed to specific interactions between cyanobiphenyl and azomethine molecules [19,20], with SA being a representative of that chemical class. Also, SA is of interest as a component of so-called "deep eutectics" used as solvents for extraction of metal species [21].

The other set involves our preliminary DSC and spectroscopy results of the LC mixtures of 5CB and resorcinol (1,3-dihydroxybenzene). In 5CB+resorcinol mixtures, one could expect formation of hydrogen bonds between cyano and hydroxy groups, suggesting eventual formation of hydrogen-bonded liquid crystal structures, such as observed in [22-24]. In both cases, we observed enhancement of the nematic phase thermal stability due to specific intermolecular interactions.

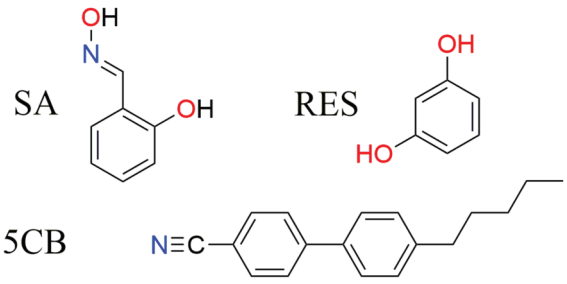

Fig. 1. Chemical structure of 4-pentyl-4′-cyanobiphenyl (5CB), salicylaldoxime (SA) and resorcinol (RES).

2. Materials and methods

4-*n*-pentyl-4′-cyanobiphenyl (5CB), 99.5 % purity, was obtained from State Plant for Chemical Reagents STC "Institute for Single Crystals", NAS of Ukraine. Chemically pure salycilaldoxime (SA) manufactured by "Thermo Fisher Scientific" and resorcinol (RES) manufactured by "Sumitomo Chemical" were also explored. Chemical structures of the compounds are presented in Fig. 1. LC mixtures and solutions were prepared using Mettler XP 26 microbalances (Mettler-Toledo), with accuracy of weighting 0.002 mg. SA content in LC mixtures was up to 36 % w/w, RES content was up to 30 % w/w.

Spectroscopic measurements were performed using a Shimadzu UV-2450 spectrophotometer (Shimadzu, Japan). Original UV-Vis spectra were obtained in a wavelength range of 190 – 800 nm. LC mixtures were investigated in two forms, whether condensed or solved in iso-octanol. The thin films were prepared in a sandwich-type cell of two 20 × 20 mm leucosapphire plates with 20 μm polyethylene terephthalate spacers. The cell with a sample was placed in a home-made thermocontrolled sample holder equipped with a Termex M 01 flowing-water thermostat which allowed us to obtain UV-Vis spectra within a temperature range of 15 – 90 °C. Before each measurement, a sample was incubated at a selected temperature for at least 10 minutes. Spectra of dissolved LC mixtures (10 mM in iso-octanol) were obtained in the same way, but solely at room temperature to prevent solvent evaporation during prolonged measurements.

Obtaining E_g values was performed by means of Tauc plots [14,15], i.e. $(ahv)^{1/2}$ *vs.* hv dependences. According to Eq. 1 (see Introduction), extrapolation of specrum edge to $(ahv)^{1/2} = 0$ directly gives E_g for a system under consideration. Experimental errors of E_g val-

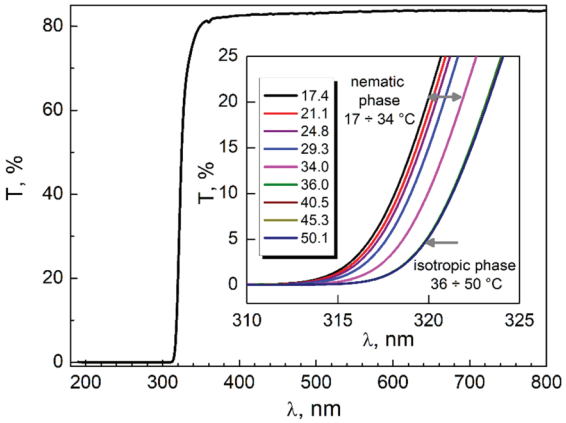

Fig. 2. General shape of 5CB UV-Vis spectra, 20 μm layer. Inset: changes of the spectra edges in nematic and isotropic phases. The sample temperatures (in °C) are listed in the legend.

ues were calculated as the standard deviation of the data set obtained in the isotropic phase. It typically was *ca.* 10^{-4} eV. Processing of original spectroscopic data was performed using LibreOffice Calc software.

Differential scanning calorimetry (DSC) measurements were carried out by means of a DSC 1 microcalorimeter (Mettler Toledo). LC mixtures or individual compounds (10 – 15 mg) were placed into standard 40 μm aluminum crucibles with lids, without further sealing. Then the samples were subjected to heating-cooling scans at 2 K/min scanning rate. The temperature range was selected to overlap all the phase transitions examined with margins of *ca.* 10 °C. The original DSC data were further processed with an original software Mettler Star^e 11.0. The phase transition temperatures were determined with accuracy of 0.1 °C.

3. Results and discussion

First, 5CB matrix without dopants was examined using UV-Vis technique. Fig. 2 represents original spectra obtained for thin layer of 5CB over the temperature range encompassing both nematic and isotropic phases (15-50 °C). As one can see from the general shape of the spectra, it does not contain any characteristic features within the entire wavelength range. However, the spectrum edge appeared to be changed significantly depending on temperature (see the inset in Fig. 2). Indeed, a pronounced red-shift of the edge takes place below 34 °C whereas no changes are observed in the spectra above this temperature. Taking into account that the temperature of nematic-to-isotropic phase transition of 5CB is *ca.* 35 °C [6], one can firmly attribute the former temperature range to the nematic phase and the latter one to the isotropic phase. So, the UV spectrum edge of 5CB is strongly affected by its phase state.

Based on the original spectroscopy data, Tauc plots obtained for 5CB under different temperatures (Fig. 3, a) were revealed the changes in E_g values depending on temperature and phase state of the LC system. In the same way, E_g values were obtained for 5CB, SA and their mixtures dissolved in iso-octanol (Fig. 3, b). To summarize, all E_g values obtained for these systems in various experimental conditions are collected in Table 1.

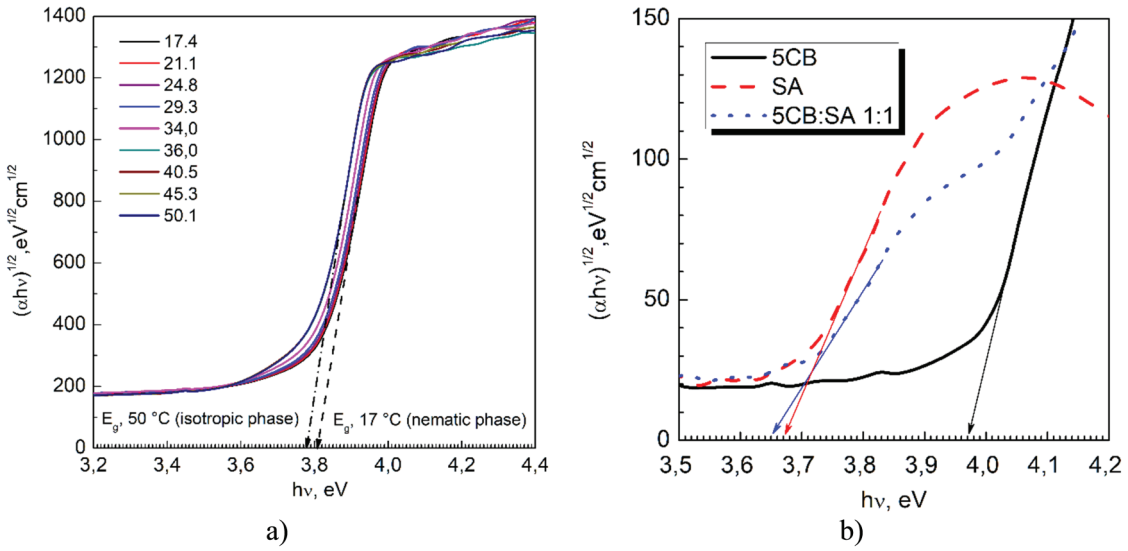

Fig. 3. Determining E_g values from spectroscopy data in various experimental conditions. Tauc plots for 5CB, 20 μm layer (a) and 10 mM iso-octanol solutions of 5CB, SA and their mixture 1 : 1 mol/mol (b). Arrows point to the corresponding E_g values.

Table 1. E_g values obtained experimentally (exp) or calculated (calc) for 5CB, SA and their mixture 1 : 1 mol/mol in various conditions.

Compounds	*Conditions*	E_g, *eV*
5CB	HOMO-LUMO gap, vacuum (calc)	4.89 [18]
	Iso-octanol solution 10 mM (exp)	3.97
	Nematic phase, 20 μm layer (exp)	3.81
	Isotropic phase, 20 μm layer (exp)	3.78
SA	HOMO-LUMO gap, vacuum (calc)	4.95 [18]
	Iso-octanol solution 10 mM (exp)	3.67
	Isotropic phase, 20 μm layer (exp)	3.39
5CB : SA 1 : 1 mol/mol	Iso-octanol solution 10 mM (exp)	3.65
	Iso-octanol solution 10 mM, additive (calc)	3.82
	Isotropic phase, 20 μm layer (exp)	3.61
	Isotropic phase, 20 μm layer, additive (calc)	3.58

Table 1 contains both experimental and calculated E_g values obtained for 5CB, SA and their equimolar mixture. Note that the highest values were obtained for an isolated molecule in the vacuum, i.e. in the case when intermolecular interactions are excluded. Then, a significant difference in E_g values was observed between dissolved and undissolved substances, which is naturally related to the solvatochromic effect. Besides, there is a minor but reliable distinction between nematic and isotropic phases. Additionally, calculated additive E_g values in the 5CB+SA mixture (both dissolved and undissolved) differ from the experimental ones, indicating specific interactions between the components. So, the collected data clearly demonstrate significant impact of phase state and intermolecular interactions on E_g value.

As it was shown in our previous work [18], 5CB+SA system exhibits non-trivial thermodynamic behavior due to interplay of both steric factors and formation of weak intermolecular complexes. In order to pick up some additional information, we have examined the system with 5CB : SA molar ratio 2 : 1 (judging from the molecular structures depicted in Fig. 1, this ratio is stoichiometric). The resulting temperature dependences are presented in Fig. 4. The reduced temperature T/T_i was used (where T is the absolute temperature applicated in the experiment and T_i is the absolute temperature of nematic-to-isotropic phase transition of a given system) for accounting significant altering of LC phase transitions under dopants introduction. Surprisingly, no difference was found in nematic and isotropic phase for the mixture, as distinct from 5CB itself and other related systems (see below). In view of the above considerations, this finding may be explained by unchanged local surroundings of SA molecules

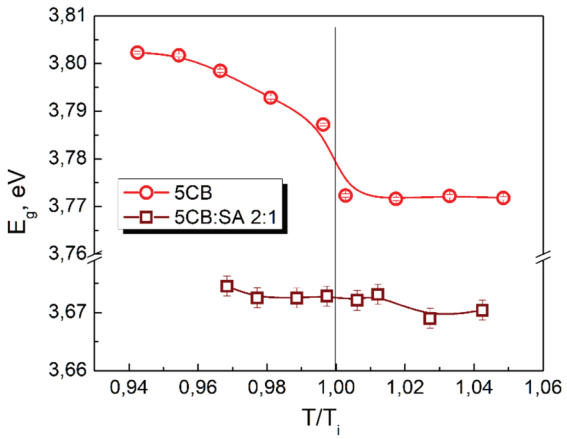

Fig. 4. Dependences of E_g values on the reduced temperature T/T_i for 5CB matrix and mixture 5CB : SA 2 : 1 mol/mol. The vertical solid line marks N → I transition. Error bars correspond to standard deviation of E_g values calculated for data obtained in the isotropic phase.

despite of the macroscopic phase state of the system. Taken together, the data of Table 1 and Fig. 4 demonstrate that E_g value provides useful additional information for deciphering the features of complex nanostructured systems.

Moving to another considered system, 5CB+RES, it should be emphasized that the impact of specific intermolecular interactions seems to be pivotal in this case. Indeed, our FTIR data (Fig. 5) clearly indicate essential changes in both the valent vibration band νOH of RES (3400 cm^{-1}) and the valent vibration band νCN of 5CB (2220 cm^{-1}) in the mixtures. One can see a bathochromic shift of the νOH band increased with RES concentration (Fig. 5, a). Simultaneously, appearance of a high-frequency shoulder of the νCN band is registered (Fig. 5, c), which can be directly attributed to involving the cyano groups in hydrogen bond (H-bond) formation [18]. Interestingly that the half-width dependences on RES concentration are non-monoto-

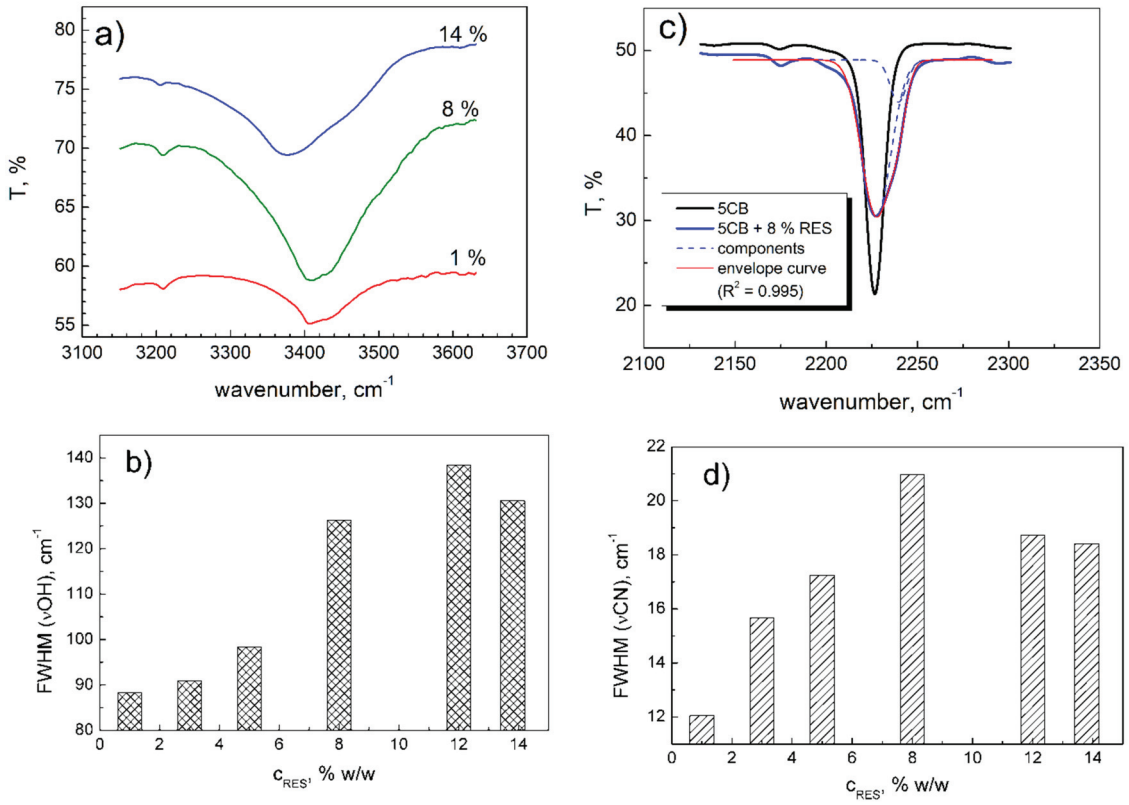

Fig. 5. FTIR data on 5CB+RES systems: a) νOH band of RES for various RES concentrations (specified above the curves); b) νOH band half-width depending on RES concentration; c) changes in νCN band of 5CB in the presence of RES (two-component gaussian decomposition is shown); d) νCN band half-width depending on RES concentration.

nous for both bands (Fig. 5, b, d) indicating that new type of structure becomes prevalent above 8-12 % RES (though these assessments seem to be rather rough due to non-ideal shape of the peaks, especially νOH). Thus, hydrogen bond formation between 5CB and RES is strongly suggested by FTIR data.

The detailed information on 5CB+RES system is provided by DSC technique (Fig. 6). It reveals a number of unusual features. First, it was established that RES is a rare representative of non-mesogenic molecules evoking significant increase in mesophase stability. As it is shown in Fig. 6, 20 % w/w RES causes 15 °C elevation of T_i in 5CB matrix. Then, RES possesses uniquely high solubility in 5CB (up to 30 % w/w) which can serve an additional evidence of involving RES into structurization of the LC matrix, instead of canonical solvation. Besides, RES content above 14 % w/w induces monotropic nematic phase, i.e. that only existing in non-equilibrium supercooled sate.

However, the most intriguing finding provided by DSC is the component ratio corresponding to the maximum T_i elevation. As judged

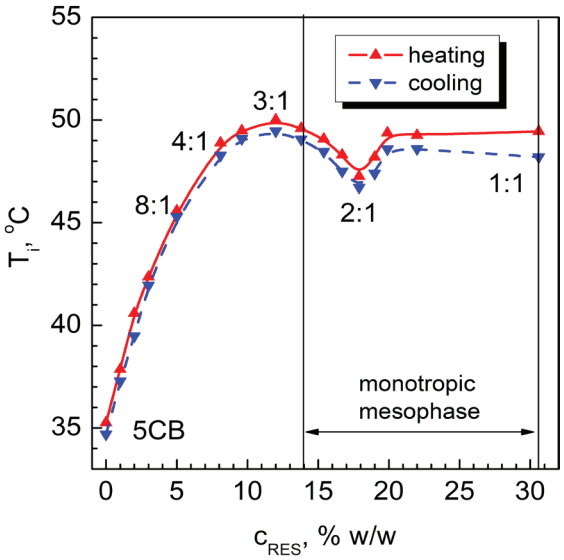

Fig. 6. Nematic-to-isotropic phase transition temperature (T_i) of 5CB+RES systems depending on RES concentration: heating (solid line) and cooling (dashed line). 5CB : RES molar ratios are also indicated. The vertical lines show the concentration margins of monotropic nematic mesophase.

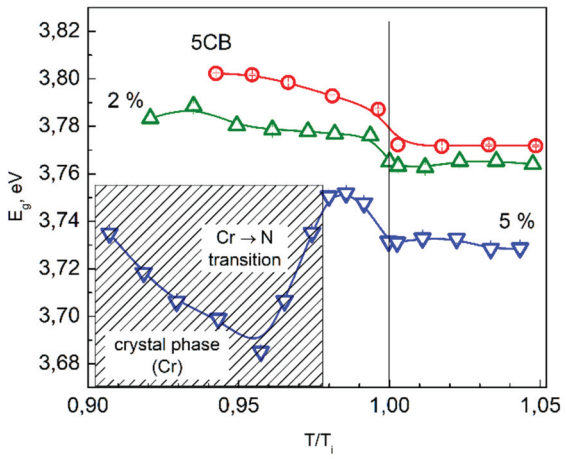

Fig. 7. Dependences of E_g values on the reduced temperature T/T_i for 5CB matrix and mixtures 5CB + RES, 20 μm layer (RES concentration are specified). Temperature ranges of crystal phase (Cr) and Cr → N transition are highlighted. The vertical solid line marks N → I transition. Error bars represent standard deviation of E_g values calculated for data obtained in isotropic phase.

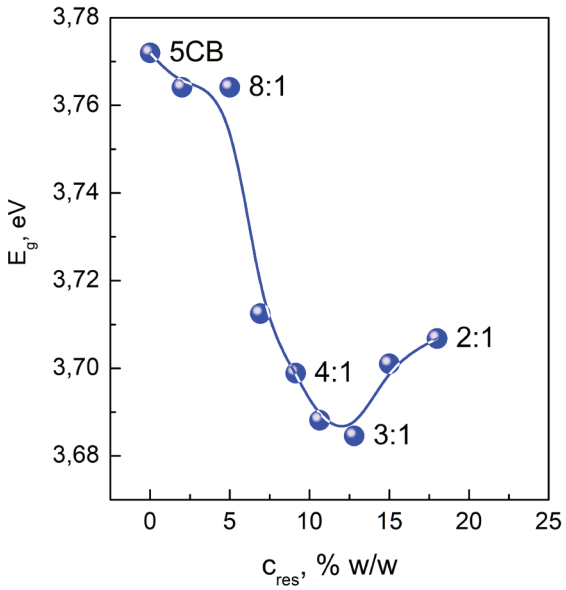

Fig. 8. Concentration dependence of E_g obtained in isotropic phase of 5CB+RES systems (60 °C). Corresponding 5CB : RES molar ratios are indicated near the experimental points. Experimental error is within an experimental point.

from molecular structures (Fig. 1), the maximal 5CB : RES ratio resulted from complex formation should be 2 : 1. Instead, 3 : 1 ratio is experimentally established (see Fig. 6). To our mind, it indicates specific supramolecular ordering in 5CB matrix induced by RES, which we will be discussed further below.

Taking into account the above findings, it seemed fruitful to determine E_g values for 5CB + RES systems. Fig. 7 shows temperature dependences plotted for 5CB+RES systems with RES content up to 5 % w/w. The general trend of decreasing E_g with RES concentration in isotropic phase can be traced. This decreasing may point to lower E_g value for RES as compared to 5CB (direct determining of E_g value for RES in isotropic phase was impossible under the experimental conditions due to high melting temperature, *ca.* 110 °C). Simultaneously, enlarging of E_g jump within N → I transition with RES concentration is observed, which is supported by T_i elevation (see Fig. 6). It is also of note that 5CB + 5 % RES system exhibits crystal phase (Cr) within the explored temperature range, according to DSC data. As we can see, both crystal phase and Cr → N phase transition reflect clearly on the temperature dependence.

Similarly, data on E_g were obtained for various 5CB+RES systems with RES content up to 20 % w/w. Since the nematic mesophase was monotropic in this concentration range, the temperature dependence similar to those in Fig. 7 could not be measured reliably, and we obtained data only for temperatures close to the N → I transition. Based on them, concentration dependence of E_g in isotropic phase was plotted (Fig. 8). This dependence appeared to be pronouncedly non-monotonous, with an extremum at 5CB : RES 3 : 1 molar ratio. This finding is completely in line with DSC data (see Fig. 6) and gives us ground to speculate about possible geometry of molecular packing in the system.

Fig. 9 represents some our ideas concerning possible molecular arrangement in 5CB+RES systems. Two main possibilities are considered: in-plane and out-of-plane arrangement of the components. Both arrangement types are able to provide elevated T_i values, as it was established experimentally (see Fig. 6), due to more condensed packaging of 5CB molecules than in the nematic phase itself. Besides, they are mainly stabilized by H-bonds and dipole-dipole interactions, which can exist not only in nematic but also in isotropic phase (see Fig. 8), where elements of short-range order are maintained. One can also suggest that these more condensed structures can serve as an additional tightening factor for surrounding LC molecules or tend to phase separation from canonical nematic phase due to great difference in their molecular arrangement.

In-plane arrangement (Fig. 9, a) seems intuitively clear. It comprises two H-bonded 5CB molecules with an extra one inserted between them in opposite direction. Nonetheless, such a

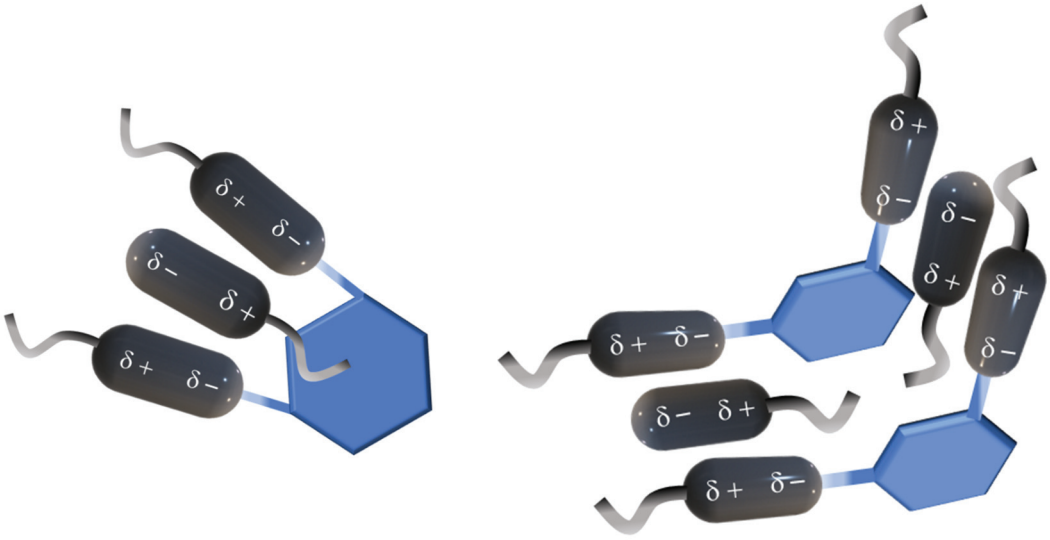

Fig. 9. Possible molecular arrangements in 5CB+RES systems which fit to 5CB : RES 3 : 1 molar ratio observed experimentally: a) in-plane; b) out-of-plane. 5CB molecules are schematically presented as sticks with flexible moieties, RES molecules are presented as rigid hexagons. H-bonds between OH-groups of RES and CN-groups of 5CB are schematically shown with straight segments. Partial charges localization in 5CB molecules is marked as δ– and δ+.

model has several obvious disadvantages. First, both valence angles of RES hydroxylic groups and H-bonds appears essentially distorted. As far as we see, such arrangement lowers significantly the energy and hence sustainability of the supramolecular aggregate. Then, the flexible alkyl moieties of the extra 5CB molecule being in plane with benzene core of RES should face certain steric hindrances. Finally, a question remains open how such supramolecular subunits can pack with each other to form continuous phase.

All the mentioned matters are absent in the case of out-of-plane arrangement (Fig. 9, b), where extra 5CB molecules are displaced between stable aggregates 5CB : RES 2 : 1. As one can see, there are no bonds distortion or steric hindrances in such arrangement which may result to its reduced sustainability. Instead, hydrophobic interactions between the benzene core of RES and alkyl chains of 5CB provide increased stabilization to the structure. It is also obvious that the subunits can be freely translated in two dimensions to form a condensed macroscopic phase. Thus, out-of-plane arrangement seems more realistic for 5CB+RES system, though additional experiments and proper quantum-mechanical calculations are clearly needed. Naturally, certain refinements of this basic model are quite possible. In particular, helical structure instead of columnar could conceivably form. Generally, it seems to be a rare case when a non-mesogenic dopant causes spatial nanostructurization of LC matrix.

4. Conclusions

Our studies of LC systems based on 5CB with non-mesogenic dopants salicylaldoxime (SA) and resorcinol (RES) have shown that E_g values substantially depend on the phase state and specific intermolecular interactions in the system. In 5CB+RES system, E_g value non-monotonously depends on dopant content and has a local extremum at the concentration point (3:1 molar ratio) corresponding to the eventual complex formation suggested by differential scanning calorimetry. The DSC data showed a non-trivial increase in the nematic-to-isotropic phase transition temperature in 5CB+RES system, with the highest temperature stability at the same (3:1) concentration. All these features can be ascribed to hydrogen-bonded supramolecular aggregates, as well as dipole-dipole interactions with additional contribution of supramolecular ordering ensuring the densest packing in the anisotropic liquid phase.

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