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Regularities of reversible radical dissociation in liquid crystals

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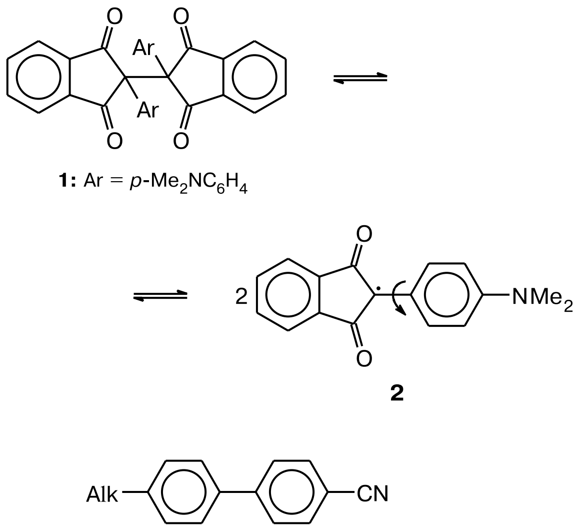
The effect of liquid-crystalline ordering of alkylcyanobiphenyls on the thermodynamic parameters of reversible dissociation of the dimeric 2,2´-bis[2-(*p*-dimethylaminophenyl)indane-1,3-dione] to the 2-(*p*-dimethylaminophenyl)indane-1,3-diyl radicals was found. The angular dependence of the ESR spectra of the radicals in the smectic mesophase is related to their orientation along the liquid crystal director.

Key words: liquid crystals, radicals, ESR spectroscopy, reversible dissociation, equilibrium constants.

Chemical reactions in liquid crystals (LC) and related molecular organized systems are determined by the complicated dynamics of reacting molecules in the highly ordered matrix because both diffusion of the reactants and the chemical act occur in an anisotropic medium. Liquid-crystalline ordering[1] results in self-organization of molecular ensembles with correlation of conformational and orientational degrees of freedom of the associated LC molecules. The interaction of molecules of the liquid-crystalline matrix with structurally isomorphous molecules of the dissolved reactants on going to the mesophase changes the thermodynamic parameters and kinetic regularities of chemical reactions[2,3] and results in an additional anisotropic component of the spectroscopic characteristics.[4,5] "Molecular recognition" in molecular organized systems,[6] which is similar to the "host—guest" interaction in crystals, can depend on the phase state of the medium. This effect is of particular significance for the equilibrium monomer—dimer process when the reactant molecules differ strongly in the spatial structure and electronic state. In liquid-crystalline mesophases, the equilibrium shifts toward the dimer,[7] and the efficiency of radical escape from the cage is reduced.[3]

Scheme 1



1: Ar = *p*-$Me_2NC_6H_4$

2

3a: Alk = *n*-C_5H_{11}
3b: Alk = *n*-C_8H_{17}

In this work, we studied the regularities of reversible dissociation[8,9] of the dimeric 2,2´-bis[2-(*p*-dimethylaminophenyl)indane-1,3-dione] (**1**) to two 2-(*p*-dimethylaminophenyl)indane-1,3-diyl radicals (**2**) (Scheme 1) in different liquid-phase states: nematic (NLC), 5CB—smectic (SLC), and isotropic liquid of 5CB — 4-*n*-pentyl-4´-cyanobiphenyl (**3a**) (T_{NI} = 306 K) and 8CB — 4-*n*-octyl-4´-cyanobiphenyl (**3b**) (T_{NI} = 315 K, T_{SN} = 306 K). The data obtained were compared with the results[8] for *N*-(*p*-methoxybenzylidene)-*p*-butylaniline (MBBA).

Experimental

Solutions with the dimer concentration [**1**] ≈ 10^{-3} mol L^{-1} in a quartz tube 4 mm in diameter were placed in the resonator of a RADIOPAN SE/X-2547 radiospectrometer. ESR spectra were detected at 293—353 K with the error in determination of the absolute and relative concentrations of radicals ≤20 and 10%, respectively. The accuracy of temperature maintenance in a measuring cell was 1 K. Liquid-crystalline materials were used without additional purification.

Results and Discussion

Reversible dissociation of the dimer in the ordered LC mesophase of **3a**,**b** is characterized by an increase in the

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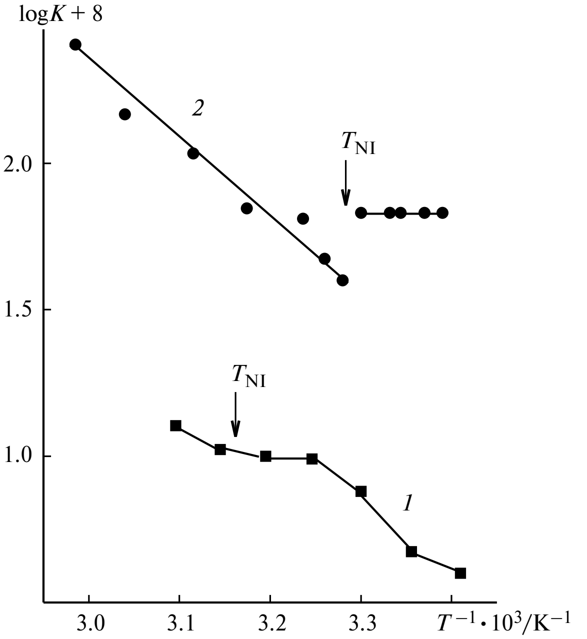

Fig. 1. Temperature dependences of the equilibrium constants (K) of the radical—dimer interaction in MBBA (*1*) and **3a** (*2*).

efficiency of radical escape from the cage compared to isotropic solutions, which dramatically differs from the earlier[7] observed effects. For the dimer in the nematic mesophase of **3a**, the equilibrium constant of dissociation $K = [\mathbf{2}]^2/[\mathbf{1}]$ is two orders of magnitude higher than that in acetonitrile ($6.7 \cdot 10^{-7}$ and $4.4 \cdot 10^{-9}$ mol L^{-1} at 295 and 293 K,[8] respectively) and remains almost unchanged in the whole temperature region of NLC phase (Fig. 1). A ~1.5-fold decrease in K, which is reliable at the 10% relative error of determination of [**2**], in the region of phase transition to the isotropic liquid is accompanied by the disappearance of the additional anisotropic splitting of the HFC components in the ESR spectra of the radical (Fig. 2). Solvate stabilization of the radical is retained even in the isotropic phase of **3a** because the enthalpy and entropy of dissociation of the dimer (46±5 kJ mol^{-1} and 23±10 J mol^{-1} K^{-1}) to radicals are much lower by the absolute value than those for standard isotropic solutions.[9] In the ordered SLC phase of **3b** prepared by cooling from the isotropic liquid and NLC phase in a magnetic field, the formed confocal texture fixes the predominant direction of LC molecular layers arrangement and also incorporated radicals **2**. A remarkable difference in their ESR spectra for the initial and orthogonal positions of the sample (Fig. 3) at a small width of the components of the ESR spectra proves that the radicals with a great persistent length are incorporated into a system of the rigid π-conjugated fragments of alkylcyanobiphenyl. The angular dependence of the ESR spectra of the radicals in SLC of **3b** and additional splitting of the HFC components in the nematic mesophase of **3a**,**b** are caused by the anisotropic character of HFC interaction on the nitrogen atom in the radical.

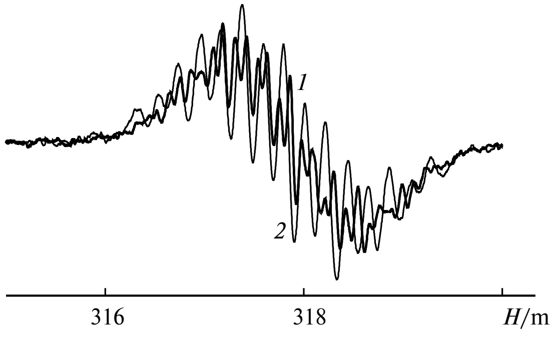

Fig. 2. ESR spectra of radical **2** in the nematic at 295 K (*1*) and isotropic at 335 K (*2*) mesophases of **3a**.

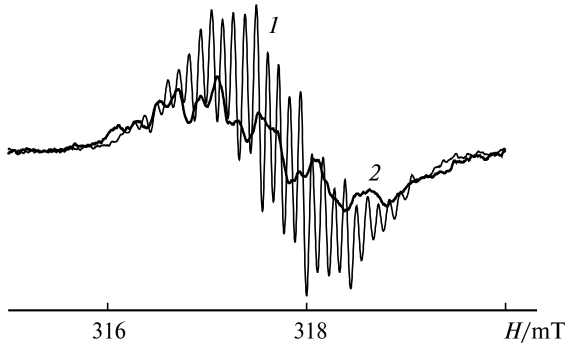

Fig. 3. ESR spectra of radical **2** in the smectic mesophase of **3b** at 296 K. The mesophase was prepared by cooling of the sample in the magnetic field from the isotropic phase in the orientation parallel (*1*) and perpendicular (*2*) to the magnetic field.

Since the polarities of the terminal groups in alkylcyanobiphenyls differ and due to the rigid aromatic fragments of the mesogenic molecules, strong intermolecular interactions appear to produce the "tail-to-head" molecular pairs.[10] Orientational coordination of the molecules of the liquid-crystalline matrix with the strongly polar CN group to form donor-acceptor pairs with antiparallel arrangement of dipoles[10] (indicated by the strongly anisotropic HFC on the N atom in the radical) plays an important role for the radical. A similar effect increasing the temperature of the phase transition occurs in **3a** when 4-aminobiphenyl is introduced.[7] On the contrary, at high orders of the liquid-crystalline matrix, incorporation of a bulky dimer molecule into the uniaxial NLC phase is sterically hindered. The "compensation effect" found in the log$K$—1/T plot (see Fig. 1) for NLC phase of **3a** is due to a sharp change in the character of the reactant—matrix interaction of the "host—guest" type in a narrow temperature interval. In standard isotropic liquids, the enthalpy of dimer dissociation is ~80 kJ mol^{-1}, and the K values obtained by extrapolation of K in the isotropic LC phase for **3a** should more than twofold increase in NLC. The effective entropy of dissociation decreases most significantly on going from the NLC phase to isotropic liquid due to the disappearance of orientational correlation of the liquid-crystalline environment, which is likely the most important reason for a decrease in K with temperature. The elevated efficiency of radical escape in the NLC phase is explained by the mutual orientation of the radicals unfavorable for the anisotropic liquid environment during recombination with formation of the bulky dimer molecule. In standard liquids or rigid matrices, by contrast, an increase in the medium viscosity sharply decreases the efficiency of radical escape from the reaction cage during dissociation of the molecules. For alkylcyanobiphenyls K is more than 15-fold higher[8] than that in the nematic mesophase of MBBA at 295 K, which can be attributed to the radical solvation. Since the permittivity of LC is much lower than that of acetonitrile, the observed effect is related to the orienting influence of the LC matrix for the donor-acceptor radical—molecule interaction in the LC environment. These results demonstrate that the liquid-crystalline ordering can exert a substantial effect on the thermodynamic parameters of processes accompanying dissociation of the carbon—carbon covalent bond. It is also noteworthy that the processes are reversible for both increasing and decreasing temperature and the "temperature hysteresis" [4,5] in the region of phase transition can occur at a much higher experimental accuracy taking into account a low heat of the NLC—isotropic liquid transitions.[11]

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