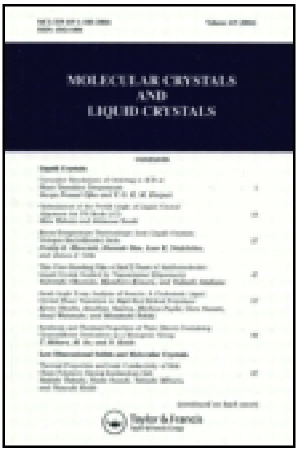

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Dimerization of Some Liquid Crystalline 4′4′-Alkyl-Cyanophenyl Derivatives in Solid Phase and Inert Matrices

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DIMERIZATION OF SOME LIQUID CRYSTALLINE 4'4' – ALKYL – CYANOPHENYL DERIVATIVES IN SOLID PHASE AND INERT MATRICES

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Abstracts Molecular association of liquid crystalline 4,4' – pentylcyanobiphenyl 5CB), 1 – p – cyanophenyl – 4 – parameters of dimerization process have been obtained for nematic pentyl – cyclohexane (5CH) 2 – p – cyanophenyl – 5 – pentylpyridine(5Py) was studied in bulk, solutions and inert matrices at 77 – 330K by low temperature reflection IR – spectroscopy and isothermal Calve calorimetric methods. The thermodynamic and kinetic mesophase. The factors effected the dimer stability were considered.

Introduction Liquid crystalline alkylcyanobiphenyls and some related compounds are widely used in materials for electronics [1]. Dimerization of polar cyanobiphenyl molecules greatly influenced almost all properties of these liquid crystals [1–3]. There are only few reports [4–6] presented thermodynamic data, the data on kinetics are not available at all. At the same time the dimerization constants obtained by direct methods can provide grounds for understanding of reaction mechanism and supply information for further investigation of the dimer bond nature. We studied the dimerization process of some cyanophenyl derivatives : 4,4' – pentylcyanobiphenyl(5CB), 2 – p – cyanophenyl – 5 – pentylpyridine (5Py), ! – p – cyanophenyl – 4 – pentylcyclohexane(5CH) in bulk, solutions and inert matrices at 77 – 330 K by low temperature reflection IR – spectroscopy and isothermal Calve calorimetric method.

IR – study of cyanophenyl dimerization

The samples for IR study of thermal behaviour of monomeric liquid crystalline system in solid phase were obtained by condensation of monomer molecular beam on cooled by liquid nitrogen polish copper surface using special cryostat for low temperature IR–spectroscopy [7]. The registration of IR–spectra was carried out on Specord IR–75 in the regime of reflection for condensed and matrix isolated samples and on Specord–80 in the regime of transmission for solutions and bulk samples .

It was shown that at 270–290 K the effective process of inner dimers formation took place in monomeric sample. This transformation was accompanied by CN–stretch band shift to lower frequencies. The effect was confirmed by computer modelling of theoretical IR spectra of dimer and monomer of 5CB and its derivatives. The experimental spectroscopic characteristics obtained for monomer and dimer of cyanophenyls are presented in Table 1. The spectroscopic data for bulk monomeric liquid crystals are the same as for high diluted solutions of liquid crystals in nonane and pentane. Similar data were obtained by matrix isolation technique for IR spectroscopy of studied liquid crystals monomers and dimers in argon matrices (LC:Ar = 1:2500 and 1:10) at 5–10K.

Further heating of the samples led to reversed transition of CN–stretch band to higher frequencies according to partial dissociation of cyanophenyl dimers in mesophase and isotropic phase. The IR–spectra of the named liquid crystals were registrated at different temperatures in interval of nematic mesophase existence. In this case CN–stretch band is a sum of the monomer CN–stretch mode and dimer form stretch mode.

Table 1.

Monomer and inner dimer spectroscopic characteristics of liquid crystals 5CB, 5CH, 5Py (CN–stretch mode)

Subst.	ν_{max} mon. film, cm^{-1}	ν_{max} dimer film cm^{-1}	ν_{max} mon. solution cm^{-1}	$\varepsilon_{max} x 10^{-3}$ mon. film M^{-1}.	$\varepsilon_{max} x 10^{-3}$ mon. solution M^{-1}.	$\varepsilon_{max} x 10^{-3}$ dimer film M^{-1}.

				cm^{-1}	cm^{-1}	cm^{-1}
5CB	2229.0	2225.5	2230.0	0.6±0.3	0.33±0.3	4.2±3
5CH	2232.5	2225.0	2232.0	0.5±0.3	2.95±0.3	3.7±0.3
5Py	2230.0	2227.0	2230.0	1.8±0.6	1.1±0.3	9.4±0.3

Using computer modelling of the spectra the sum vibration were divided on the modes of monomer and dimer forms:

$$I'_{sum}(\nu_i) = \alpha_1 I'_1(\nu_i) + \alpha_2 I'_2(\nu_i) \qquad (1)$$

The experimental band was set by ν_{max}, I_{max} and $\nu_{1/2}$–values and approximated by Lorenz shape line. The calculated values of dimerization degree ($\alpha 2$) and dimerization equilibrium constant (K_{dim}) are presented in Table 2. The dimerization enthalpy–values estimated using IR–spectra temperature dependence in nematic mesophase are also in Table 2.

Table 2.

Dimerization equilibrium constant K_{dim} and enthalpies of dimerization

Substance	5CB	5CH	5Py
T,K	298	304	308
α_{dim}	0.88	0.69	0.78
K_{dim}, M^{-1}	7.6±0.5	0.9±0.1	2.1±0.3
ΔH, kJ/mol	19±5	3.0±1.0	12±5

Calorimetric study of dimerization kinetics

The kinetics of liquid crystalline cyanophenyls was studied by isothermic Calve calorimetry [8]. Using temperature jump method allowed us to obtain the dimer concentration higher than equilibrium value at experimental temperature. The analysis of experimental data in assumption of the simple kinetic scheme of the dimerization process: 2M<=>D allowed us to obtain the kinetic parameters in nematic mesophase. The data obtained are presented in Table 3.

Table 3.

Kinetic constants of cyanophenyl derivatives dimerazation in nematic mesophase

Substance	k_1x10^4,s^{-1}	$k_2x10^3,M^{-1}s^{-1}$
5CB	3.0±0.6	2.3±0.5
5CH	10±3.0	1.3±0.3
5Py	2.1±0.4	0.67±0.12

The data presented in table 3 show that the characteristic time of the dimerization process in mesophase can be estimated as about 300 s. This value is significantly more than specific time of diffusional motions and molecular reorientational processes in studied liquid crystals.

The analysis of kinetic and thermodynamic data obtained allowed us to make some conclusions about bond nature in cyanophenyl dimers and about chemical structure influence on relative bond stability. The fact that dimer of 5CB is much more stable than 5CH dimer led us to conclusion that forces of dispersive attraction are significant for dimer formation. The second aromatic ring in monomer structure of 5CB strongly stabilise the dimer structure. This evidently occurs not only due to the increase of effective dipole moment of the molecule but due to the increase of dispersive attraction. In cyclohexane derivative the slight destabilisation can also occur due to unfavourable interaction of different cyclohexane confirmations. The inserting of nitrogen atom in aromatic center of 5Py molecule doesn't lead to dimer structure stabilisation. It is possibly due to lowering of effective value of cyanophenyl molecule dipole.

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