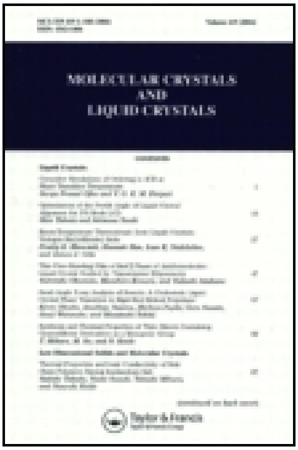

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Low Temperature Reactions of Mesogenic Cyanophenyls in Solid Phase and Inert Matrices

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Abstract. In present work the molecular aggregation and interaction with metallic silver of liquid crystalline 4-pentyl-4'-cyanobiphenyl (5CB), 4-pentyl-4'-cyanophenyl pyridine (5Py), 4-pentyl-4'-cyanophenylcyclohexane (5CH), 4-octyl-4'-cyanobiphenyl (8CB), 4-octyloxy-4'-cyanobiphenyl (8OCB) in molecular condensate films and inert matrices has been studied by low temperature reflection and transmission vibrational spectroscopy in a wide temperature range 80-330 K. The red shift of CN-stretching vibrations band was found to be due to molecular aggregates and low temperature Ag-5CB complexes formation . The factors effecting on their thermodynamic stability are considered. Comprehensive IR- and UV-Vis- study of Ag-5CB film samples of different component ratio at 80K shows the existence of Ag-5CB complexes due to Ag interactions with π-electrons of CN-bond of cyanobiphenyl molecules.

Keywords: liquid crystals, condensate films, molecular aggregation solid phase reactions

INTRODUCTION

Polar liquid crystals such as alkyl/alkoxycyanobiphenyls and their derivatives are widely used as materials for molecular electronics [1]. Molecular aggregation of these compounds considerably influences almost all their physical and chemical properties [2-5]. The direct data on molecular aggregates formation during molecular condensation and its effect on the thermodynamic behavior of self-organizing systems are of great interest for modern supramolecular chemistry [6–8]. Introducing of metals in liquid crystalline systems could stabilize dimeric or higher molecular aggregates [9].

In present work the molecular aggregation of polar liquid crystals: 4-pentyl-4'-cyanobiphenyl (5CB, $T_{K-N}=295K$, $T_{N-I}=309$ K); 4-pentyl-4'-cyanophenylpyridine (5Py, $T_{K-N}=$ 306K, $T_{N-I}=316$ K); 4-pentyl-4'-cyanophenylcyclohexane (5CH, $T_{K-N}=303K$, $T_{N-I}=328$ K); 4-octyl-4'-cyanobiphenyl (8CB, $T_{K-S}=293K$, $T_{S-N}=307K$, $T_{N-I}=314K$); 4-octyloxy-4'-cyanobiphenyl (8OCB, $T_{K-S}=325K$, $T_{S-N}=338K$, $T_{N-I}=352.5K$) in molecular condensate films and inert matrices has been studied by low temperature reflection and transmission vibrational spectroscopy in a wide temperature range 5–10 and 80–330 K. The interaction of metallic silver with 4-pentyl-4'-cyanobiphenyl in low temperature co-condensates was studied by low temperature reflection and transmission IR-spectroscopy and UV-vis spectroscopy in temperature range 80–300 K.

EXPERIMENTAL

Thermal behavior of cyanobiphenyl molecular condensate films of 20–100 μm was studied by low temperature IR-spectroscopy at 77–330 K using special evacuated cryostat [10,11]. The film samples (l = 2–50 μm) were obtained by cyanobiphenyl molecular vapor deposition or metal and cyanobiphenyl vapors co-deposition on polished surface of copper cube, salt (KBr, CaF_2) or quartz windows ,cooled by liquid nitrogen (77 K) and then annealed upto 300–350 K. The deposition rates were 10^{17-18} molecules/cm s. The residual gas pressure in the system did not exceed $5 \cdot 10^{-4}$Torr at all temperatures upto 350 K.

The IR-spectra of the samples were recorded using reflection mode on Specord IR-75 for film condensate samples and using transmission mode on Specord 80 for bulk samples and solutions. Spectroscopic accuracy was upto 0.5 cm^{-1} The temperature of the samples was maintained within ±1 K interval at 77–270 K and ± 0,5K at 290–350 K.

In some cases the molecular vapor of cyanophenyl substance and/or metallic silver were co-deposited with inert matrix molecules: decane (at 80–100 K) and argon (at 5–10 K). The last experiments were made in co-operation with Professor G.Sheina and Dr.A.Ivanov using helium refrigerating system at Institute of Low Temperature Physics and Engineering Ukrainian Academy of Sciences [12].

RESULTS AND DISCUSSION

The IR – spectra obtained for molecular condensate films for example of liquid crystals 5CB and 8CB at 80K and at some temperatures by annealing the samples show the red shift of CN – group band peak at 216 – 270 K .The band of CN – group stretching vibrations was chosen as the most informative for these compounds according to [13]. We consider this transformation in the view of inner dimers(or higher molecular aggregates) formation took place in molecular condensate films of both liquid crystals. Further heating of the samples led to a reversed shift of CN – group stretching vibrations band to higher frequencies according to partial dissociation of cyanobiphenyl dimers and/or higher aggregates in mesophase and isotropic phase . The effect was confirmed by computer modelling of harmonic frequencies of theoretical IR – spectra for cyanobiphenyl monomeric and dimeric structures [14].

Similar results were obtained using special technique for stabilization of monomer and dimer species in inert hydrocarbon at 80 – 130 K and argon at 5 – 10 K matrices [12]. In Figure 4 are presented the data obtained for heteroaromatic derivative of 5CB 2 – p – cyanophenyl – 5 – pentylpyridine (5Py) molecular species stabilized in argon matrix for different values of cyanophenyl/ argon ratio from 1/1000 upto 1/10 and neat cyanophenyl film.

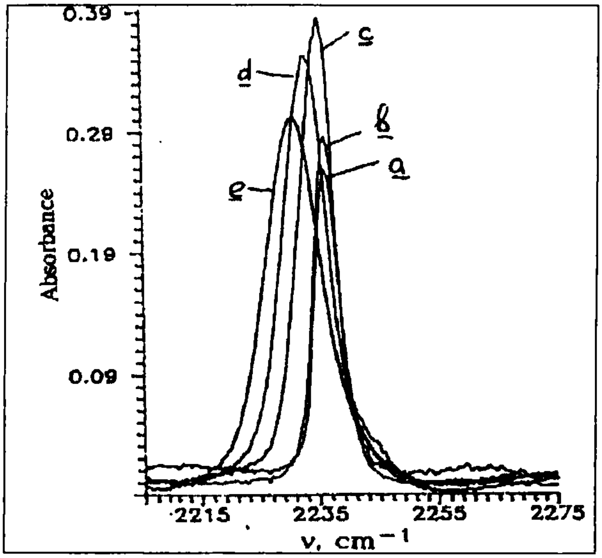

FIGURE 1

C≡N stretching region of 5Py isolated in Ar matrices, T=5K,5Py:Ar:

a) 1:1000;

b) 1:400;

c) 1:50;

d) 1:10;

e) bulk film(l≈20μm).

It was shown that both rising of cyanophenyl contents in the system and increasing of the sample temperature led to CN–band red shift due to inner dimers formation.

The comprehensive study was made for series of cyanophenyls solutions in nonpolar hydrocarbon solvents decane and pentane in a wide concentration range from 0.01 – 1.5 M . It was shown that in high diluted solutions (less than 0.05 M) the maximum absorbance for CN–group grew linear with cyanobiphenyl concentration rising. For more concentrated solutions we had the negative deviation due to molecular association process. In this case CN–group absorbance band was a sum of monomer and dimer (or higher aggregates) absorbencies. Computer treatment of the experimental spectra for a number of cyanophenyl solutions of different concentrations on base of the theoretical modeling approach for a sequence of associative equilibrium's developed in [15] allowed us to obtain line shapes for spectra of monomeric and associative species . In Figure 2 an example is presented .

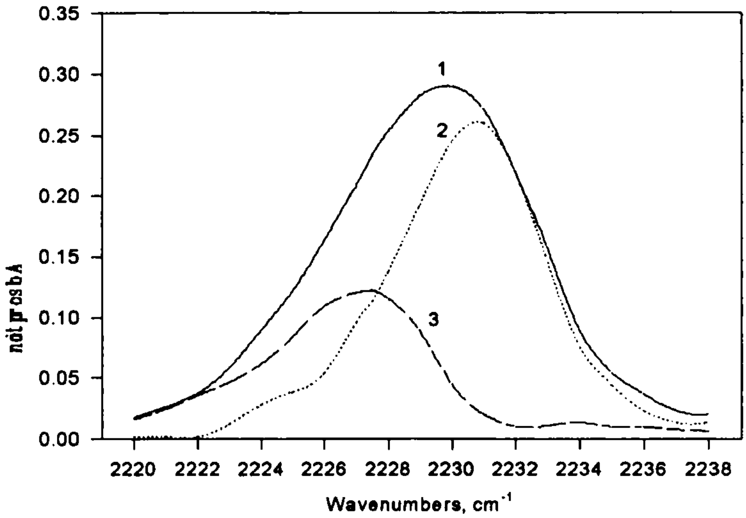

FIGURE 2 Experimental spectrum of 8CB (1) and its computer splitting on monomer (2) and dimer (3) modes., Co[8CB] = 0.548 M, l = 0.0288 mm, T = 294K.

It should be mentioned that the method in use doesn't allow us to distinguish the spectra of dimers and of higher associates if their spectral characteristics do not differ significantly (lower than 0.5 cm^{-1}). The spectroscopic characteristics obtained for monomers (ν_M, ε_M) and molecular associates (ν_D, ε_D) of cyanophenyls under investigation are presented in Table 1.

Table 1. Some spectroscopic and thermodynamic characteristics of cyanophenyls

Substance	υ_M^{max}, cm^{-1}	υ_D^{max}, cm^{-1}	$\varepsilon_M^{max}10^{-3}$, $M^{-1}cm^{-1}$	$\varepsilon_D^{max}10^{-3}$, $M^{-1}cm^{-1}$	Δ H, kJ/mol
5CB	2230 (± 0,5)	2225 (± 0,5)	0.23 (± 0,15)	0.59 (± 0,25)	−19 ± 5
5CH	2232 (± 0,5)	2225 (± 0,5)	0.29 (± 0,15)	0.57 (± 0,25)	− 3 ± 1
5Py	2232 (± 0,5)	2227 (± 0,5)	0.18 (± 0,13)	0.94 (± 0,35)	−12 ± 5
8CB	2231 (± 0,5)	2227.5 (±0,5)	0.19 (± 0,07)	0.87 (± 0,30)	−18 ± 5
8OCB	2231 (± 0,5)	2226.5 (±0,5)	0.21 (± 0,08)	0.67 (± 0,25)	−29 ± 7

It is important that spectroscopic data obtained for monomers in film samples are the same as the values obtained for highly diluted cyanophenyl solutions.

The IR-spectra of cyanophenyl bulk films were recorded at different temperatures within mesophase interval. It was found that CN-group absorption band maximum and line shape depended on the sample temperature. Varying the temperature we changed the monomer/molecular associate ratio. Computer modeling of the experimental spectra as a sum of two modes:

$$I_{exp}(\nu_i) = a_1 I_M(\nu_i) + a_2 I_D(\nu_i)$$

where a_1 and a_2 are the relative quotes of monomeric and associative cyanophenyl species, calibrated using ε_M and ε_D values, allowed us to obtain $\alpha = a_2/(a_1 + a_2)$ — the association degree of cyanophenyl molecules at present temperature. The association enthalpy (Δ H, kJ/mol) of cyanophenyls in mesophase was estimated using temperature dependencies of α-values. The data obtained are also presented in Table 1.

The analysis of the data in Table 1 allowed us to compare the relative stability of the liquid crystalline aggregates in the view of the molecular structure of polar mesogen. The most stable molecular associates were formed in the case of cyanobiphenyls as opposed to their hydrogenated or heteroaromatic derivatives [16]. This is possibly due to the strong parallel stacking of two benzene rings and overlapping of the π−aromatic systems of two mono−meric units. Only one benzene unit is in 5CH molecular structure, and this leads to the significant decrease of the ΔH−association value. For 5Py molecules we obtained ΔH−association value that is lower than for 5CB, this could be connected with the less planar dimeric structure formation. In the case of differently substituted cyanobiphenyls (Table1) we can see that the most stable dimers were formed in the case of alkoxycyanobiphenyl 8OCB in com−parison with alkylcyanobiphenyls 5CB and 8CB. It could be pos−sibly due to the increased of conjugation with of oxygen atom.The increased length of the alkyl chain did not influence significantly on the molecular association parameters.

The Ag−5CB films obtained after co−condensation were pale yellow color. In the IR−spectra of co−condensate film compared to the IR−spectrum of neat 5CB ligand two new bands in the field of CN−stretching vibrations at 2030 and 2130 (2080) cm−1 were founded. We have assigned these bands to CN stretching vibra−tions in Ag−5CB π−complexes of two types that differed by metal−ligand ratio [7]. The shift of about 100cm^{-1} to lower fre−quency is the characteristic of formation of π−complexes of ze−rovalent transition metal with π−donating ligands [8]. We also determined the appearance of new band at 650cm^{-1} and assigned it to metal ligand vibration [8]. The disappearance of new bands by heating the sample up to 200 K shows the stability of Ag−5CB complexes only at low temperatures 80−200K.

The UV−Vis spectra of 5CB and Ag−5CB co−condensate films as compared to the spectra of 5CB films at 80 K show the wide absorption band in the range of 370−440nm. This leads to the pale yellow color of the Ag−5CB films and is connected with charge transfer in Ag−5CB π−complexes. During heating the film samples along with the band at 370−440nm the new intensive band in the region 520−600 nm was detected. The aggregation of the metal atoms was probably the cause of the appearance of the last band. These new bands in the spectra of Ag−5CB film samples also disappeared as samples were heated up to the room tem−peratures proving instability of Ag−5CB complexes.

CONCLUSIONS

In present work we made the IR–spectroscopic study of the thermal behavior of the mesogenic cyanobiphenyls: 4–pentyl–4–cyanobiphenyl (5CB), 4–pentyl–4'–cyanophenylpyridine (5Py), 4–pentyl–4'–cyanophenylcyclohexane (5CH) 4–octyl–4–cyanobiphenyl (8CB), 4–octyloxy–4–cyanobiphenyl (8OCB) in molecular condensate films, bulk phase and inert matrices . It was found that CN–group absorbance maxima and line shape were dependent on the monomer/dimer(or higher associates) quantitative ratio, that was changed by varying the temperature of the liquid crystalline sample. The thermodynamic data obtained for the molecular association process of the named polar liquid crystals revealed that the most stable associates were formed in the case of cyanobiphenyl molecules in comparison with their hydrogenated or heteroaromatic derivatives. The higher thermodynamic stability was shown for aggregates of alkoxycyanobiphenyls in comparison with alkylcyanobiphenyls. The increased length of the alkyl chain did not influence significantly on the molecular association parameters. Comprehensive IR– and UV–Vis– study of Ag–5CB film samples of different component ratio at 80K shows the existence of Ag–5CB complexes due to Ag interactions with π–electrons of CN–bond of cyanobiphenyl molecules.

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