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THERMOINDUCED REARRANGEMENT OF THE HYDROGEN BONDED SYSTEMS IN LIQUID CRYSTALLINE CARBOXYLIC ACIDS

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Abstract The properties of H-bonded systems of alkyl- and alkoxybenzene acids have been studied both experimentally (by IR-spectroscopy methods) and theoretically near the solid crystal - liquid crystal phase transitions. Partial dissociation of the cyclic dimers accompanied by formation of open chain-like associates and monomers is found. Their amount depends on the temperature and phase of the sample. The theoretical model of rearrangement of H-bonds is suggested. The rate constant of the cyclic dimer - open associate transition is estimated.

INTRODUCTION

Mesomorphism of alkyl- and alkoxybenzene acids (hereafter referred to as n-ABA and n-AOBA, where n is the number of carbon atoms in the alkyl/alkoxy chain) is explained[1] by association of their molecules into cyclic dimers (CD) by means of hydrogen bonds (H-bonds). Experimental investigations with IR-spectroscopy of H-bond dynamics at phase transitions was executed in number of works[2-7], however there is no theoretical analysis of the peculiarity of the rearrangement of H-bonds at phase transitions.

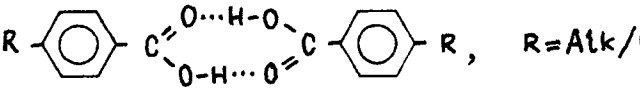
In the present work a peculiar behaviour of H-bonded systems of ABA and AOBA is investigated experimentally (quantitative analysis with the aid of IR-spectroscopy

methods) and theoretically at phase transitions: solid crystal (SC) - liquid crystal (LC) - isotropic liquid (IL).

MOLECULAR ASSOCIATES IN ABA AND AOBA: THE EXPERIMENT

IR-spectra of n-ABA with n=1-9 and n-AOBA with n=3-12 were registered with the aid of IR-spectrophotometer, model UR-20 (Carl Zeiss Jena, Germany) at a resolution of 1-2 cm^{-1} in the 400 to 4000 cm^{-1} spectral region in the temperature range of 100 to 550 K. Sample temperature was maintained constant using automatic thermoregulator with an error of ±1 K.

In IR-spectra the bands at 2900 (ν_{OH}), 1692 ($\nu_{C=O}$) and 940 cm^{-1} (ρ_{OH}) have been found for all phases of ABA and AOBA. They indicate that molecules ABA and AOBA are connected with H-bonds[2-7]:



Enthalpies of H-bonds were estimated by the Iogansen method[8] from shifts of the frequency of twisting vibration ρ_{OH} and of the gravity center of the band corresponding to ν_{OH} of associates with respect to those for monomers. Frequencies ρ_{OH} and ν_{OH} of the ABA and AOBA monomers as determined from spectra of solutions in CCl_4 and of gaseous phase, were about 612 and 3550 cm^{-1}, respectively. In the SC an enthalpy of H-bond was found approximately (36±1) kJ/mol at 100 K and (34±1) kJ/mol at 300 K.

By heating in the SC long before (20-50 K) the SC-LC transition we have been observed the appearance and gradual rise in intensity of bands at 3300 (ν_{OH}), 1703 ($\nu_{C=O}$), 920 (ρ_{OH}), 3550 (ν_{OH}), 1740 ($\nu_{C=O}$), 1090 (ν_{C-O}) and 612 cm^{-1} (ρ_{OH}), of which the first three was attributed to opened associates and the remaining ones - to monomer, while the intensity of CD bands was decreased. All these changes indicate partial dissociation of the CD with formation of open associates and monomers. Their relative amount have

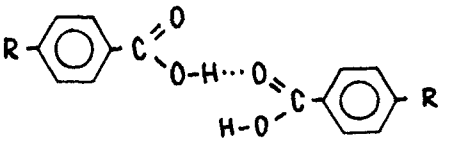
changed depending on the temperature and phase of the sample (see Table).

TABLE Contents of H-bonded associates and monomers in 7ABA and 7AOBA (in %)*

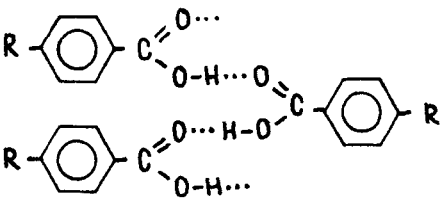
Phase	T (K)	Cyclic dimers	Open associates	Monomers
C_7H_{15}-C_6H_4-COOH:	$SC_2 \xrightarrow{321K} SC_1 \xrightarrow{376K}$ Nematic $\xrightarrow{391K}$ IL			
Solution in CCl_4	298	89	-	11
SC_2	298	100	-	-
SC_2	338	59	39	2
SC_1	363	56	40	4
Nematic	379	52	39	9
Nematic	383	52	39	9
IL	408	49	41	10
IL	423	48	40	12
IL	443	47	42	11
C_7H_{15}-O-C_6H_4-COOH:	$SC \xrightarrow{367K}$ Smectic $\xrightarrow{373K}$ Nematic $\xrightarrow{420K}$ IL			
Solution in CCl_4	295	93	-	7
SC	295	100	-	-
SC	353	58	40	2
Smectic	370	38	29	33
Nematic	386	36	31	33
Nematic	403	35	32	33
IL	425	33	31	36
IL	443	33	31	36

*Calculated by intensities of bands $\nu_{C=O}$ and ρ_{OH}.

Taking into account the peculiarity of ABA and AOBA molecular packing[9-10] in the SC and the weak intensity of bands 612 and 3550 cm^{-1}, which are caused by the absorption of unconnected hydroxyl, one may regard, that the associates are formed not only by means of two molecules (opened dimers):



but three and more molecules too can connected in chain-like associates:



According to our estimates enthalpy of the H-bond in opened associates have been by nearly 4 kJ/mol less than in the CD.

MECHANISM OF OPENED ASSOCIATES FORMATION: THE THEORETICAL STUDY

Let us consider the processes of disruption of two H-bonds in the CD and of formation one H-bond, that have led to the creation of opened associate. Two neighbouring H-bonds of two neighbouring dimeric rings are characterized by a two-wells potential (Figure); the basic parameters of

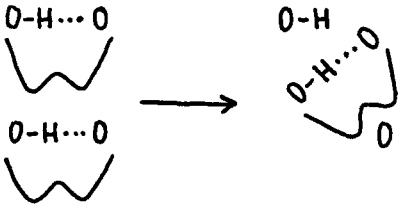


FIGURE. The scheme of hydrogen atom transition from intra-dimeric state into inter-dimeric one.

each well are known (see[11]). Dynamics of crystalline network of that H-bonds may be investigated within the framework of Ising pseudospin model[12]. However in our case there are the experimental evidence of "cross" H-bonds availability (that are opened associates formation).

Therefore it is necessary to use other model which regards for the hydrogen atom jump between H-bonds of neighbouring dimers. For this purpose the protonic polaron model[13] fits. Therefore we investigate the formation interdimeric H-bond in the framework of this model (Figure).

One may suppose that near an SC-LC phase transition H-bonds in the CD are in predissociating-state, in which the transition of hydrogen atom to a new spatial position, i.e. "cross" H-bond, is possible. The availability of intra-dimeric vibrations of proton which are transverse to the O...HO-bonded line: ρ(O...H) ~ 30-50 cm^{-1} (in plane of dimer ring) and $\alpha_{\perp}$(O...H) ~ 30-50 cm^{-1} (normal to plane of dimer ring)[14] have to promote the appearance of such H-bond.

Let us introduce the operator of hydrogen atom transition density

$$\hat{j} = \frac{1}{i\hbar} [\hat{H}_t, (R_1\hat{a}_1^+\hat{a}_1 + R_2\hat{a}_2^+\hat{a}_2)], \qquad (1)$$

where $\hat{H}_t = V_{12}(\hat{a}_1^+\hat{a}_2 + \hat{a}_2^+\hat{a}_1)$ is the tunnel Hamiltonian density of hydrogen atom transition; V_{12} is the matrix element density of transition constructed in protonic wave functions and site vibrations quantum functions, the one takes into consideration the superposition of intra-dimeric vibrations ρ(O...H) and $\alpha_{\perp}$(O...H); $R_{1(2)}$ is the proton (i.e. hydrogen atom) coordinate in intra-dimeric (inter-dimeric) H-bond; $\hat{a}_1^+(\hat{a}_1)$ and $\hat{a}_2^+(\hat{a}_2)$ are the Fermi operators of creation (annihilation) of hydrogen atom in dimeric H-bonds and inter-dimeric H-bond, respectively.

A macroscopic density J of hydrogen atom transition probability between neighbouring dimers per unit of time in the crystal in the pre-transition temperature region can be calculated by means of the standard method of small polaron model[13]. In that model J is determined in accordance with formula

$$J = Sp(\hat{\rho}_t \hat{j}), \tag{2}$$

where $\hat{\rho}_t$ is the correction to basic statistic operator and the Hamiltonian $\hat{H}_t$ is used for its builds.

The calculations give (compare with[13]):

$$J = 2^{3/2}\pi^{1/2} n_0 g |V_{12}|^2 \sinh(\Delta\mathcal{E}/k_B T) \exp(-E_a/k_B T)$$

$$\times \left(\hbar^2 u^2 \left[\omega_1^2 \cosh\frac{\hbar\omega_1}{2k_B T} + \omega_2^2 \cosh\frac{\hbar\omega_2}{2k_B T}\right]^{1/2}\right)^{-1}, \tag{3}$$

where n_0 is the concentration of opened H-associates; g is the length of OH...O bond; u^2 is the dimensionless constant describing a relative displacement of oxygen atoms that formed the H-bond from their equilibrium positions due to the hydrogen atom localization between them, i.e. the parameter u^2 characterizes the local change of lattice energy and in the small polaron model $u^2 \gg 1$. $E_a = \sum_{i=1}^{2} u^2 \hbar\omega_i$ is the energy of polaron displacement and the one relates to the H-bonded energy in dimer (35 kJ/mol); $\omega_1 = 2\pi c \cdot 165$ cm^{-1} and $\omega_2 = 2\pi c \cdot 290$ cm^{-1} are the most intensive polarized low cyclic frequencies of benzene ring: γ(CCC) and β(CCH), respectively[14-15]. Taking into account that there are two H-bonds in dimer from relation $2E_a = u^2 \sum_{i=1}^{2} \hbar\omega_i$ we find $u^2 \approx 35$. The parameter $\Delta\mathcal{E}$ is the difference between energy for two type of H-bond. For the appraisal one takes $\Delta\mathcal{E} = k_B T_c$ where T_c is the phase transition temperature. In (3) the activation energy

$$E_a = k_B T u^2 \sum_{i=1}^{2} \tanh\frac{\hbar\omega_i}{4k_B T} - \frac{3}{2}\Delta E. \tag{4}$$

Let us estimate the value J for the 7ABA crystal at the SC_2-SC_1 transition temperature $T_c = 320$ K and for the 7AOBA crystal at the SC - smectic phase transition temperature $T_c = 367$ K (see Table). Assuming that the frequency of superposition of intra-dimer vibrations

ρ(O...H) and $\alpha_{\perp}$(O...H) are approximately equal $\Omega = 2\pi c \cdot 40$ cm^{-1} one finds the magnitude of matrix element

$$V_{12} = V_0 \coth\frac{\hbar\Omega}{2k_B T_c} \approx 12V_0. \quad (5)$$

So far as $V_0 \ll \hbar\Omega, \hbar\omega_{1(2)}, k_B T_c$ then $V_0 \approx 2{,}5 \cdot 10^{-2} k_B T_c \approx 10^{-23}$J. Let the value of $g \approx 0{,}26$ nm; a concentration n_0 of opened associates is equal to $1{,}6 \cdot 10^{21}$ cm^{-3} for 7ABA and $1{,}5 \cdot 10^{21}$ cm^{-3} for 7AOBA. Using the expression (2) the rate constant K of the cyclic dimer - opened associate transition is found

$$K = J \cdot S, \quad (6)$$

where S is the effective cross section for the channel of interaction between the tunneling hydrogen atom and an oxygen of neighbouring dimer. Supposing $S \approx 0{,}1 \times 0{,}1$ nm^2 with regard for aforesaid we find

$$K \approx 10^{-2}\ s^{-1}. \quad (7)$$

In our experiment by heating of sample to T_c the associate formation finished in the course of 2-3 min (establishment time of thermal equilibrium in the cell) that corresponds to $K_{exp} \approx 10^{-2}\ s^{-1}$. Consequently, the calculated value of K conforms to experimental one.

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