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V. A. Burmistrov^a; V. V. Alexandriysky^a; O. I. Koifman^a

^a Faculty of Organic Chemistry, Institute of Chemistry and Technology, Ivanovo, Russia

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Influence of the molecular structure of a nematic solvent on hydrogen bonding with non-mesomorphic proton donors

by V. A. BURMISTROV*, V. V. ALEXANDRIYSKY
and O. I. KOIFMAN

Faculty of Organic Chemistry, Institute of Chemistry and Technology,
F. Engels Av., 153460, Ivanovo, Russia

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The concentration dependence of the orientational order parameter of acetic acid dissolved in nematic solvents has been generated by computer simulation on the basis of an equilibrium model for liquid crystalline solutions containing non-mesogenic solutes. Comparison of this predicted dependence with experiment allows the equilibrium constants, orientational correlation coefficients on non-mesogenic solutes in hydrogen bonded complex and the dimer to be calculated. Data in the structure of H-complexes involving the liquid crystal and the solute have been obtained. Regularities in the influence of H-bonds on the ability of the solute to destabilize the nematic phase. (β_{NI}) have been established. The strengthening of the longitudinal complex is shown to result in a lowering and for the transversal complex — in an enhancing of β_{NI} . The thermodynamic characteristics of alcohols dissolved in nematic Schiff's bases and 4-*n*-hexyloxy-4'-cyanobiphenyl were obtained by gas-liquid chromatography. An even-odd alternation of $\Delta\bar{H}_2$ and $\Delta\bar{S}_2$ alcohol series has been found. It is shown that the direction of the alternation depends on the alignment of the molecular components in the H-complex.

1. Introduction

The problem of providing an adequate description of intermolecular interactions is one of the main questions in the physics and chemistry of liquid crystals (LC) [1]. In order to obtain reliable experimental information about the various forms of intermolecular interactions great difficulties have to be overcome; these are mainly connected with orientational ordering and association processes. For example, specific interactions, such as H-bonding, have not been deeply and seriously investigated in the past.

The results obtained during studies of orientational effects of H-bonds between a nematic solvent-Schiff's bases and model proton-donating solutes-acetic acid and ethanol have been reported in our previous work [2]. An equilibrium model of LC binary mixtures with acetic acid, determining the total solute order parameter has been proposed:



where AA denotes a molecule of acetic acid, $(\text{AA})_2$ an acetic acid dimer, and $\text{LC}\cdots\text{AA}$ a H-complex. Using this scheme we have simulated the concentration dependence of the solute order parameter (S_2) and the equilibrium constant K , as well as the orientational correlation

coefficients in H-complex (a^C) and cyclic dimer (a^D) of acetic acid:

$$a^C = S_2^C/S_1; \quad a^D = S_2^D/S_1 \quad (2)$$

where S is the solvent order parameter, S_2^C and S_2^D are the order parameters of the interprotonic vector of the methyl group of the acetic acid in the complex and the dimer, respectively. The influence of temperature and S_1 on the order of the dimer and complex has been determined.

Nematic LCs are formed not only by Schiff's bases but also by numerous classes of organic compounds. Their tendency for H-bonding may be essentially different because of various factors including their electron-donating capacity, geometry and steric availability of electron pairs, orientational ordering, etc. It is also interesting to find out whether the regularities obtained earlier [2] are applicable to LCs of other classes.

The aim of this paper is to study the influence of the molecular structure of the nematic solvent on the H-complex structure with proton-donating solutes and its influence on different binary system properties (such as orientational ordering, transition temperatures, and thermodynamic parameters).

2. Experimental

Nematic LCs of the following classes: Schiff's bases (I-V), azo- (VI-VII) and azoxy-benzenes (VIII), phenyl

* Author for correspondence.

benzoates (IX-X) and cyanobiphenyls (XI-XIII) have been studied as solvents:

Number	Compound	T_{CN}/K	T_{NI}/K
I	<chem>CCOC1=CC=C(C=C1)/C=C/N2=CC=CC=C2C3=CC=CC=C3</chem>	295	318.0
II	<chem>CCOC1=CC=C(C=C1)/C=C/N2=CC=CC=C2C3=CC=CC=C3</chem>	310	352.0
III	<chem>CCOC1=CC=C(C=C1)/C=C/N2=CC=CC=C2C3=CC=CC=C3</chem>	330	346.5
IV	<chem>CCOC1=CC=C(C=C1)/C=C/N2=CC=CC=C2C3=CC=CC=C3</chem>	340	389.0
V	<chem>CCOC1=CC=C(C=C1)/C=C/N2=CC=CC=C2C3=CC=CC=C3</chem>	314	328.5
VI	<chem>CCOC1=CC=C(C=C1)/C=C/N2=CC=CC=C2C3=CC=CC=C3</chem>	341	391.0
VII	<chem>CCOC1=CC=C(C=C1)/C=C/N2=CC=CC=C2C3=CC=CC=C3</chem>	339	379.0
VIII	<chem>CCOC1=CC=C(C=C1)/C=C/N2=CC=CC=C2C3=CC=CC=C3</chem>	345	393.2
IX	<chem>CCOC1=CC=C(C=C1)C(=O)OC2=CC=CC=C2C3=CC=CC=C3</chem>	341	362.2
X	<chem>CCOC1=CC=C(C=C1)C(=O)OC2=CC=CC=C2C3=CC=CC=C3</chem>	328	359.2
XI	<chem>CCOC1=CC=C(C=C1)C#N</chem>	295	308.1
XII	<chem>CCOC1=CC=C(C=C1)C#N</chem>	326	340.5
XIII	<chem>CCOC1=CC=C(C=C1)C#N</chem>	327	347.1

with acetic acid, ethanol, *n*-propanol, *n*-butanol and *n*-pentanol as proton-donating non-mesogenic solutes. Nematic solvents were purified by recrystallization; acetic acid and the alcohols were purified by known techniques [3].

Nematic-isotropic transition temperatures were measured visually and were checked by ^1H NMR with a rate of the temperature change equal to 2 K h^{-1} . The coefficients β_N , β_I were determined from the phase diagram using linear regression with 2 per cent error. The order parameters (S_1) and (S_2) were measured as in [2] with 5 and 3 per cent error, respectively. The solution thermodynamic parameters were obtained by gas-liquid chromatography according to the known procedures [4]; the errors obtained are 3.5 per cent for $\Delta\bar{H}_2$ and 3 per cent for $\Delta\bar{S}_2$.

3. Results and discussion

3.1. *H*-complexes structure of azo- and azoxy-benzenes

The concentration dependences of the orientational order parameter of the interprotonic vector for the methyl group of acetic acid in the nematic solvents I-X are shown in figure 1. Table 1 gives computer simulated

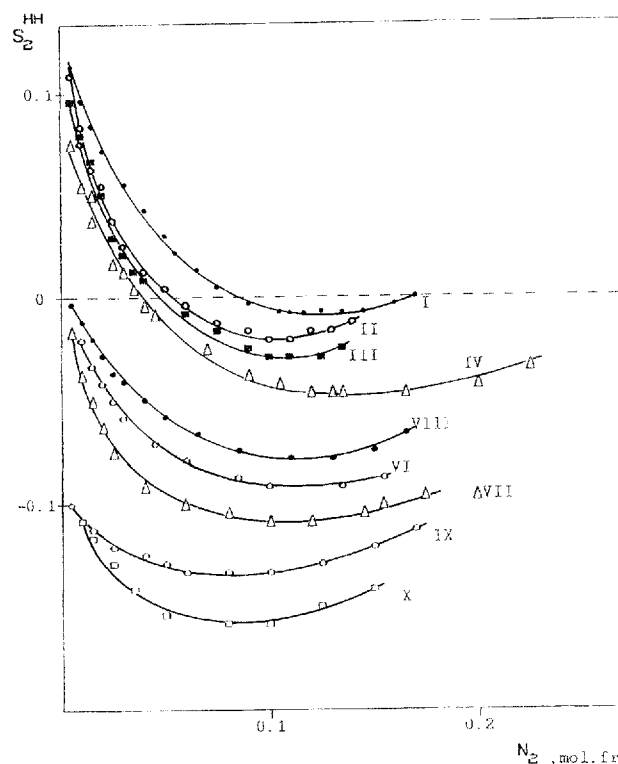


Figure 1. The concentration dependence of the order parameter of acetic acid in the solvents: I ($T=295\text{ K}$), II (328 K), III (329 K), IV (358 K), VI (368 K), VII (354 K), VIII (367 K), IX (343 K), X (338 K).

Table 1. Calculated characteristics of acetic acid dissolved in nematic LCs.

Compound	T/K	$K/\text{l mol}^{-1}$	$-a^D$	a^C
VI	343	0.019 ± 0.003	0.39 ± 0.01	0.028 ± 0.003
	353	0.030 ± 0.004	0.40 ± 0.01	0.023 ± 0.003
	363	0.048 ± 0.006	0.43 ± 0.01	0.020 ± 0.003
VII	342	0.013 ± 0.002	0.34 ± 0.01	0.034 ± 0.004
	348	0.016 ± 0.002	0.34 ± 0.01	0.036 ± 0.004
	354	0.028 ± 0.002	0.41 ± 0.01	0.029 ± 0.003
VIII	346	0.038 ± 0.005	0.40 ± 0.01	0.015 ± 0.003
	352	0.041 ± 0.006	0.38 ± 0.01	0.015 ± 0.003
	358	0.044 ± 0.006	0.36 ± 0.01	0.017 ± 0.003
IX	344	0.042 ± 0.008	0.46 ± 0.02	-0.095 ± 0.008
	350	0.046 ± 0.008	0.45 ± 0.02	-0.083 ± 0.008
	363	0.055 ± 0.008	0.46 ± 0.02	-0.085 ± 0.008
X	343	0.055 ± 0.008	0.40 ± 0.02	-0.140 ± 0.008
	348	0.041 ± 0.008	0.48 ± 0.02	-0.107 ± 0.008
	351	0.034 ± 0.008	0.43 ± 0.02	-0.081 ± 0.008

Table 2. Orientational order parameters of individual nematic LCs at $T_{sh} = 5$ K.

LC	S_1	LC	S_1
I	0.50	VIII	0.51
II	0.56	IX	0.50
III	0.62	X	0.50
IV	0.50	XI	0.57
V	0.52	XII	0.49
VI	0.49	XIII	0.47
VII	0.53		

results for K , a^C , a^D . These calculations were carried out as in [2]. Because of the strong influence of the LC orientational ordering on the characteristics summarized in table 1 [2], the order parameters S_1 have been measured. Since the nematic-isotropic transition temperatures differ, we have chosen for the analysis S_1 values only at a single shifted temperature $T_{sh} = 5$ K ($T_{sh} = T_{NI} - T$) which normalized the S_1 value with respect to the phase transition temperature (see table 2).

The data analysis given in table 1 shows some differences in the behaviour of K for Schiff's bases I-IV [2] and azo- and azoxy-benzenes (VI-VIII). Although the equilibrium constant for Schiff's bases do not change significantly with temperature, a definite increase of K is observed for the azo- and azoxy-derivatives VI-VIII. The reason for such behaviour may be explained by a reduction of the LC-acetic acid H-complex formation enthalpy (according to the absolute value) caused by steric hindrance on complex formation because of the coplanarity of substituted azobenzenes [5]. Thus, accepting, that

$$\Delta \bar{H}_2 = 2 \Delta \bar{H}_2^C - \Delta \bar{H}_2^D, \quad (3)$$

where $\Delta \bar{H}_2$ is the enthalpy process (1) and $\Delta \bar{H}_2^C$, $\Delta \bar{H}_2^D$ for complex formation and acetic acid dimerization, respectively, the differences in $\Delta \bar{H}_2^D$ are not great for LCs VI-VIII because of the similarity of the dielectric and orientational properties of the solvents (see table 2); the decreasing in $\Delta \bar{H}_2^C$ must result in positive $\Delta \bar{H}_2$ values and an increase in K with temperature (see table 1).

This assumption is confirmed by the 3-5 times reduction of the orientational correlation coefficients for the non-mesogen in the H-complex (a^C) when going from Schiff's bases (I-IV) to azobenzenes (VI-VII) (see table 1). Reduction of the orientational correlation of the components in the 'solute-LC' complex in this case is due to spatial restrictions caused by the planar rigid core of the substituted azobenzenes (see figure 2(b)). The latter evidently results in the disturbance of the H-bond linearity and an increase of the mobility of the solute.

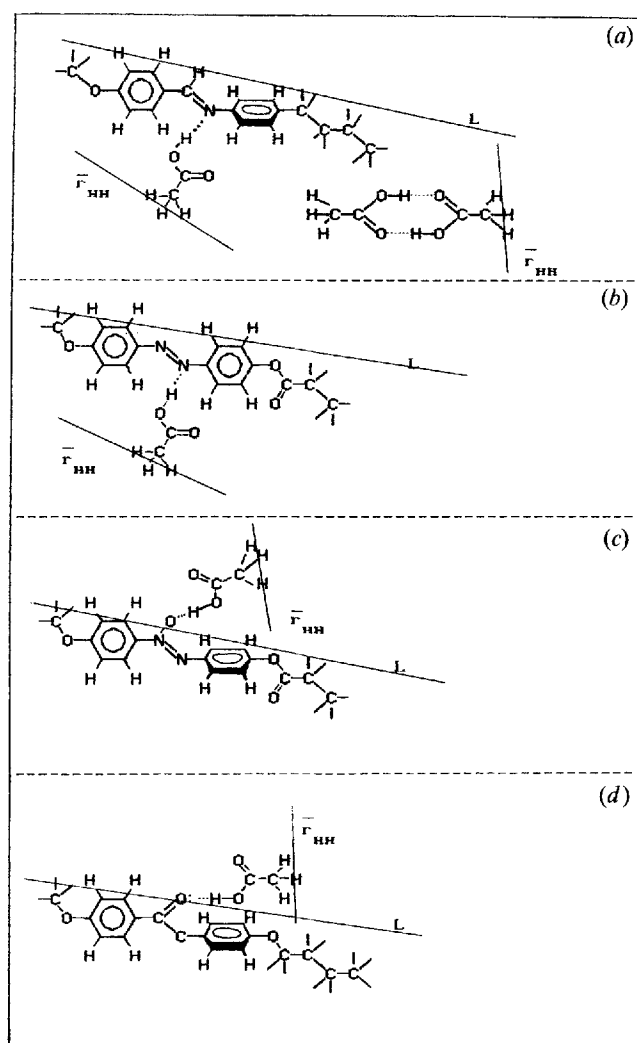


Figure 2. The molecular structures of the LC-acetic acid complexes.

It should be noted that the nitrogen lone pair in the benzylideneaniline core must be available due to their non-coplanarity [6].

For the substituted azoxybenzene VIII another situation is noted. A priori it might be supposed that incorporation of the oxygen into the linkage would reduce the steric hindrance for H-bond formation, however the a^C (VIII) coefficients are even lower. This observation may be explained by an analysis of the azoxybenzene molecular structure [5], according to which one of the oxygen lone pairs can not be available for H-bonding with a proton donor (see figure 2(c)), because aromatic ring I is turned out from the plane of the N=O bond by a small angle (about 20° in *p*-azoxyanisole [5]). The direction of the second available lone pair is such that the interproton vector for the CH_3 group of acetic acid is orientated at an angle much closer to the magic angle in comparison

with azobenzene and azomethine (see figure 2(c)). This explains a substantial decrease in the dipolar couplings in the NMR spectra and a decrease of a^C . At the same time the enthalpy of complex formation has to stay high, because K is independent of temperature.

The ordering of the acetic acid dimer (a^D) in LCs VI–VIII is similar because of the similarity of the orientational ordering of the solvents.

It should be noted that the presence of one or more proton-acceptor centre (group –OCOR) does not give a noticeable change to the total orientational ordering (S_2) because of the low order of the aliphatic chains [7].

3.2. Structure of ester complexes

Comparison of the concentration dependences of S_2 for acetic acid in LC esters IX–X and previously studied Schiff's bases [2], azo- and azoxy-benzenes (see figure 1), indicates an essential difference. The dependence of $S_2 = f(N_2)$ (IX, X) (see figure 1) has an extreme character but unlike nitrogen containing LC, the order parameters of the interproton vector for the solute methyl group has a large negative value even for very low solute concentrations. This may be explained by, for example, the weakening of H-bonds with the LC and the arrangement of the non-mesogen in the complex.

The results of computer simulations of the curves (see figure 1) according to the model described earlier, are given in table 2. The similarity of the molecular structure of the solvents IX, X, their orientational order (see table 2) and T_{NI} (see experimental part) results in the closeness of K , a^C , a^D parameters for these solvents. The most interesting conclusions may be made when analysing the a^C coefficients, which define the orientational correlation between the solute and LC in the H-complex; a^C , IX, X (see table 1) values unlike LCs with other linkage groups have a negative sign, which determines the type of concentration dependence (see figure 1). Negative a^C values indicate a predominantly parallel arrangement of long molecular axes of the components in the complex. To explain this fact we refer to X-ray data on the molecular structure of phenylbenzoate derivatives [8], according to which the benzoic ring is disposed practically in the plane of the carbonyl bond, but the phenol ring is rotated out of this plane at an angle of more than 60° . That is why it is clear, that one of the lone pairs on the oxygen atom is sterically screened and the second is relatively available and directed at a small angle ($\approx 10^\circ$) to the long molecular axis of the LC. Interaction of the acetic acid with this lone pair leads to perpendicular alignment of the interproton vector relative to the LC long axis (see figure 2(d)) and to negative values for a^C . Complex formation with the participation of the second oxygen atom of the carboxyl group might have resulted

in perpendicular arrangement of the long axis of the solute and positive a^C values as for solvents I–VIII.

It should be noted that the reason for acetic acid ordering less in the H-complex in comparison with the dimer and the maximum $S_2 = f(N_2)$ for the IX, X curves may be both in the deviation of the direction of the oxygen pair from the LC long axis and in a non-linear hydrogen bond as a consequence of steric restrictions from the phenol core.

3.3. Structure of cyanobiphenyl complexes

All of the information described in the previous sections refers to lateral specific interactions with the participation of the electron-donating linkages. In connection with this the study of the properties of H-complexes in solvents having no linkage groups in the rigid molecular core is of interest. The well-known 4-*n*-alkyl and 4-*n*-alkoxy-4'-cyanobiphenyls are of this type. These compounds possess an electron-donating terminal substituent, the cyano-group, the lone pair of which is directed along the long molecular axis.

The order parameters for acetic acid dissolved in substituted cyanobiphenyls XI–XIII are very high (see figure 3) in comparison with those in solvents I–X. It is interesting to note that the temperature dependence of S_2 is approximated for each solvent by the only curve independent of concentration (see figure 3). This points to a predominantly common mechanism for solute alignment in the solvent structure [9]. The efficiency of LC orientational correlation of solvent and solute may be estimated, considering both S_2 and S_1 . That is why we have estimated, the temperature averaged coefficients

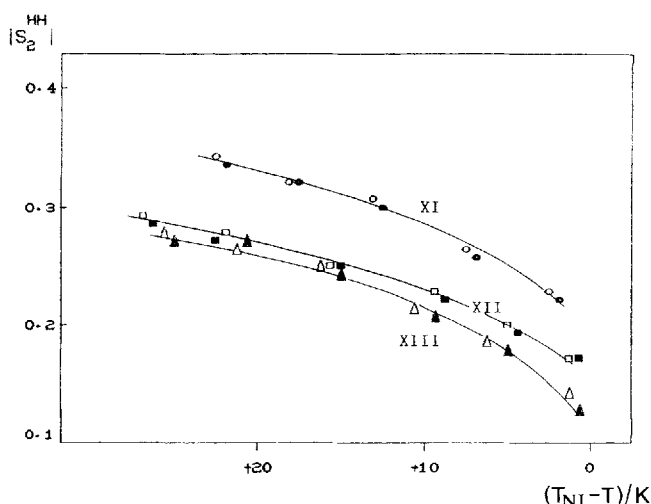


Figure 3. The temperature dependence of the order parameter for acetic acid dissolved in the cyanobiphenyls XI–XIII as solvents (mol fractions of acetic acid: (○) 0.045, (●) 0.126, (□) 0.055, (■) 0.105, (△) 0.046, (▲) 0.139).

Table 3. Characteristics of the binary system LC-acetic acid.

LC	β_N	β_I	a^c
I	0.68	0.62	0.169
II	0.53	0.43	0.160
III	0.39	0.33	0.139
IV	0.34	0.25	0.115
V	0.64	0.54	—
VI	0.29	0.24	0.020
VII	0.31	0.26	0.035
VIII	0.32	0.28	0.015
IX	0.24	0.21	-0.095
X	0.23	0.22	-0.140
XI	0.23	0.21	-0.470
XII	0.22	0.19	-0.400
XIII	0.20	0.18	-0.420

$a = S_2/S_1$, which is equal to 0.47 ± 0.02 , 0.40 ± 0.02 and 0.42 ± 0.02 for LCs XI, XII and XIII, respectively. These data show that the ordering of acetic acid is close to the value of the LC order parameter because $S_2^{HH} = -\frac{1}{2} S^{C_3}$ (S^{C_3} is the order parameter for the C_3 axis of the methyl group). Such a high ordering of a non-mesomorphic solute is possible only because of the formation of strong H-bonds of the $-\text{CN}\cdots\text{HOOC}-\text{CH}_3$ type; the equilibrium of dimer-complex (1) is moved to the side of the latter in comparison with LCs inclined to lateral specific interactions (I-VIII). In this case the reason for the high solute ordering is the absence of any noticeable steric hindrance during the formation of longitudinal complexes.

3.4. Influence of H-bonds on the nematic-isotropic transition

The characteristics of phase transitions of nematic LCs particularly, the nematic-isotropic transition temperature T_{NI} , are one of the fundamental LC parameters [10]. T_{NI} determines the temperature mesophase interval and makes it possible to estimate the influence of solute addition on the nematic phase. The slopes

$$\beta_N = -(dT^*/dN_2)_N; \beta_I = -(dT^*/dN_2)_I, \quad (4)$$

are used for this purpose [11]: where $T^* = T/T_{NI}$ and N_2 is the mole fraction of solute. The majority of non-mesomorphic solutes are known to destabilize the nematic phase so decreasing T_{NI} . The influence of a specific interaction on the nematic-isotropic transition has not been investigated previously. For this reason we have determined the phase diagrams of binary systems of LCs (I-XIII) with proton-donating solutes (for example acetic acid and alcohols); the β parameters so obtained are shown in table 3 were estimated.

Solvent orientational order plays an important role in the mesomorphic properties of LC solutions [11]. As a

rule, the addition of a non-mesomorphic solute dissolved in a highly ordered solvent is accompanied by a smaller depression of T_{NI} . Thus, when investigating the influence of H-bonds on the nematic-isotropic transition it is also necessary to consider the influence of S_1 for these solvents (see table 2). The data analysis summarized in tables 2 and 3 shows that there is no common dependence $\beta_N = f(S_1)$. This is not surprising because of different tendencies for complex formation by nematic LCs of different classes. It is worth considering the correlation between β_N and S_1 within one LC class namely Schiff's bases I-V, due to the fact they are the largest number of solvents studied and have a wide S_1 interval (from 0.47 up to 0.62 at $T_{NI} - T = 5$ K).

The data given in figure 4 indicate that similar $\beta_N = f(S_1)$ dependencies are observed for all proton-donors, the experimental points for LC IV solutions do not follow the general tendency of the change in β_N . This is not surprising, because unlike other solvents IV has an electron withdrawing substituent in the aniline ring, leading to a lowering of electron density on the nitrogen atom thus decreasing the tendency for H-complex formation with proton-donors. These conclusions are confirmed by the lowering of values of this deviation in the series: acetic acid > propanol > butanol (see figure 4) coupled with the increasing of the length of the solute molecule and reduction in the tendency for complex formation.

The data summarized in figure 4, show only indirectly the influence of specific interactions on the phase transition. To find a direct correlation it is necessary to choose a parameter which would simply reflect H-bond properties. Such a characteristic is given by the correlation coefficient a^c (see § 2) [2] because it describes not only H-bond with the strength, but also its orientation. In addition the a^c values normalized LC order parameters, strongly influencing β_i [11] (see figure 4).

Taking into account the influence of temperature on a^c (see table 1), some coefficients at approximately equal shifted temperatures ($T_{NIsh} = T - T = 25-30$ K) which are shown in table 3, have been chosen. The $\beta_N = f(a^c)$ dependence is given in figure 5. It should be noted that the experimental points corresponding to 13 nematic LCs can be approximated by the same curve. This enables us to consider the a^c coefficients to be a reliable characteristic of H-complexes in an anisotropic solvent. Analysing the plot given in figure 5, we can see that the destabilizing influence of a proton donating solute on the nematic mesophase can be determined not only by the strength but also the H-bond (LC-proton-donor) orientation, the latter playing the main role. Thus, if the strengthening of the longitudinal complex (esters, cyanobiphenyls) results in a small decrease in the destabilizing influence (β_N), since a similar effect occurs for the con-

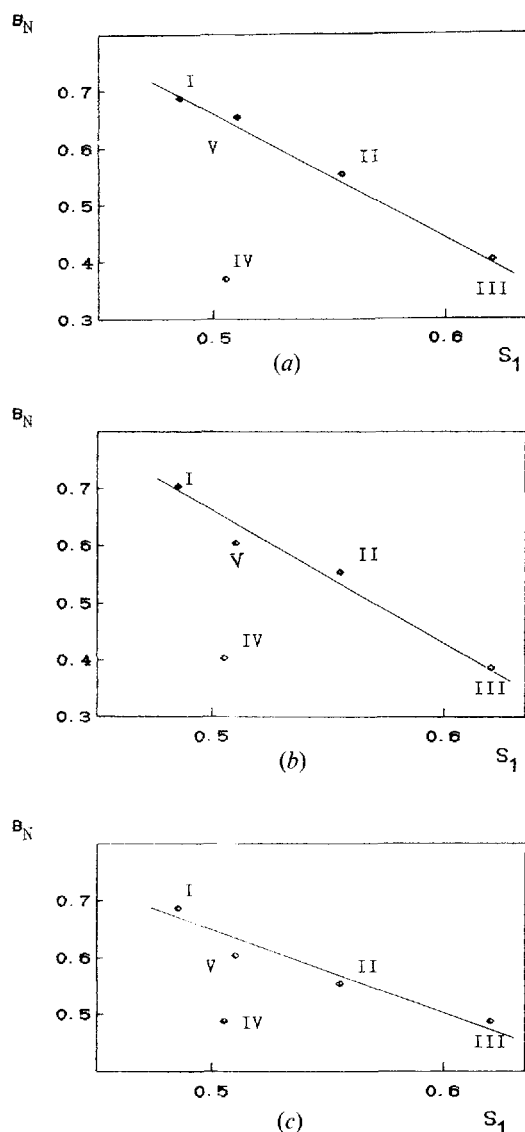


Figure 4. The parameters β_N plotted against the solvent order parameter (at $T_{sb} = T_{NI} - T = 5$ K): (a) acetic acid, (b) *n*-propanol, and (c) *n*-butanol.

ditions of transversal H-complex which caused the strong destabilization of nematic mesophase by a non-mesogenic solute.

3.5. Influence of H-bonds on the thermodynamics for alcohols in nematic liquid crystals

The thermodynamic parameters for aliphatic alcohols dissolved in nematic liquid crystals, have been obtained using gas-liquid chromatography. One of the advantages of this method is that the solute is at infinite dilution which excludes its self-association and so makes it possible to investigate the solution thermodynamics from the standpoint of the solvent-solute interaction only [12].

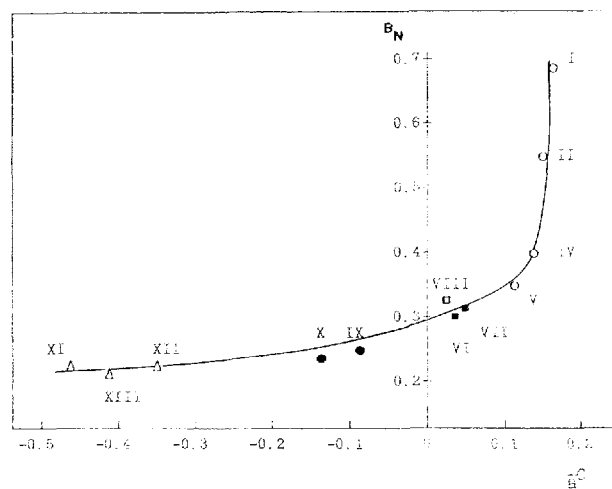


Figure 5. The dependence of β_N , for solutions of acetic acid in nematic solvents, on the orientational correlation coefficients a^C .

Schiff's bases II-IV and 4-*n*-pentyloxy-4'-cyano-biphenyl (XII) were used as solvents. The solvent choice is due to the fact that Schiff's bases form the strongest H-complexes with mutually parallel alignment of the two components. Taking into account the influence of the molecular geometry on H-bonds, especially under the conditions of an orientationally ordered solvent, we have analysed the influence of the length of the non-mesogen molecule on the solution thermodynamics.

The activity coefficients for the alcohol dissolved in both the nematic and isotropic phases of LCs II-IV and

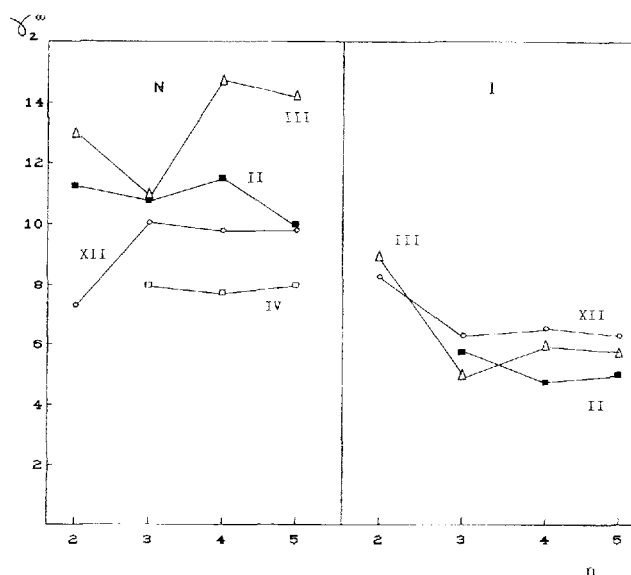


Figure 6. The infinite dilution activity coefficients (298.15 K) of alcohols ($C_nH_{2n+1}OH$) in both nematic and isotropic phases (II-IV, XII).

Table 4. Thermodynamic parameters of *n*-alcohols dissolved in nematic LCs†.

LC	Structure	Nematic phase		Isotropic phase	
		$-\Delta\bar{H}_2/\text{kJ mol}^{-1}$	$-\Delta\bar{S}_2/\text{J mol}^{-1} \text{K}^{-1}$	$-\Delta\bar{H}_2/\text{J mol}^{-1} \text{K}^{-1}$	$-\Delta S_2/\text{J mol}^{-1} \text{K}^{-1}$
II	C ₂ H ₅ OH	26.5	109	—	—
	C ₃ H ₇ OH	28.2	114	33.0	125
	C ₄ H ₉ OH	30.0	121	39.6	145
	C ₅ H ₁₁ OH	35.8	138	39.5	146
III	C ₂ H ₅ OH	21.8	94	25.7	105
	C ₃ H ₇ OH	25.9	106	31.2	120
	C ₄ H ₉ OH	21.7	95	34.3	130
	C ₅ H ₁₁ OH	24.9	106	37.8	141
IV	C ₃ H ₇ OH	26.8	107	—	—
	C ₄ H ₉ OH	31.1	121	—	—
	C ₅ H ₁₁ OH	32.4	126	35.1	127
V	C ₂ H ₅ OH	28.5	112	23.2	96
	C ₃ H ₇ OH	21.9	93	28.8	111
	C ₄ H ₉ OH	28.0	113	32.3	124
	C ₅ H ₁₁ OH	32.5	127	36.1	137

† Relation error of measurement ΔH_2 3.5 per cent and ΔS_2 , 3 per cent.

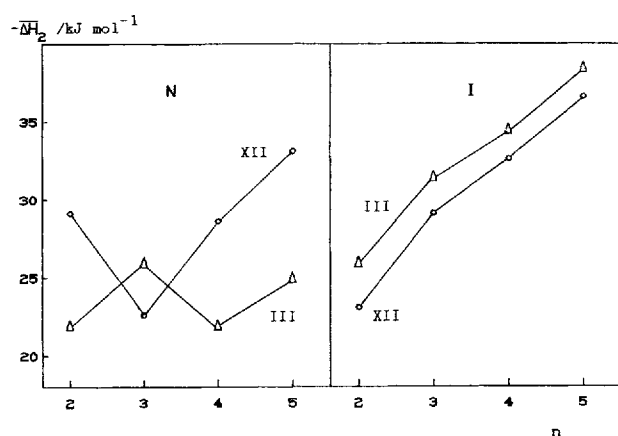


Figure 7. The partial molar enthalpy of *n*-alcohols in liquid crystalline solvents II and XII.

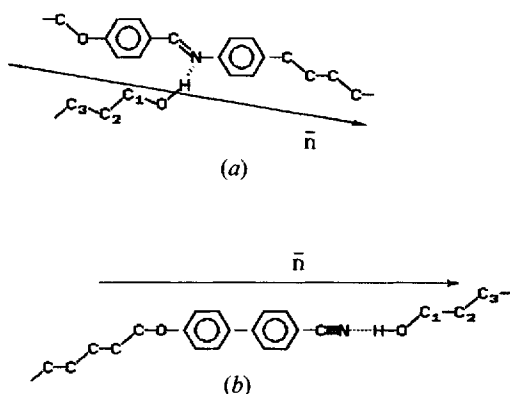


Figure 8. The molecular structures of the 'LC-*n*-alcohol' H-complex.

XIII are given in figure 6. This analysis shows that γ_2^∞ in the isotropic phases (II-IV, XIII) is weakly dependent on the LC nature. This may be explained by the similarity of the dielectric and electron-donor properties of these solvents. This situation changes (see figure 6(a)) when going to the nematic phase, in which the solvent properties differ due to their different orientational order.

A direct comparison of the solute activity coefficients is rather difficult considering the compensation effect [13] which is expressed by a strong correlation of the enthalpy and entropy parameters. Thus the strengthening of the solvent-solute interactions and the associated increase in the partial mole enthalpy (in absolute value) is accompanied by entropy losses because of the restriction of the translational motion of the non-mesomorphic solute [13]. Partial molar enthalpy and entropy of the alcohols dissolved in nematic and isotropic phases (II-IV, XII) (see table 4 and figure 7) have been studied in this connection. These data confirm that solution of short chain alcohols in nematic phases of Schiff's base III and cyanobiphenyl XII is accompanied by a distinct even-odd alternation of $\Delta\bar{H}_2$ and $\Delta\bar{S}_2$ (see figure 7). Alternation of different LC characterizations is well known [1] and is said to be caused by different contributions of even and odd atoms of the aliphatic terminal substituent to the anisotropy in the molecular polarizability and consequently to the intermolecular anisotropic interactions [1]. Taking into account the existence of an orientational correlation with the liquid crystalline solvent it is supposed that even-odd alternation may be revealed in an homologous series of non-mesomorphic solutes. It is interesting to note that in our case these effects are

opposite for LCs **III** and **XII** and do not exist for nematic phases **II** and **IV**. To explain these data it is necessary to consider the solvent orientational order (see table 2) and the solute order at infinite dilution. All of these solvents may be arranged according to S_1 in the following order: **III** > **II** > **IV** > **XII**.

The highest alcohol orientational ordering is observed in solvents **III** and **XII** as well as S_2 for acetic acid (see previously). In the first case (**III**) it exists because of a high S_1 , and in the second it is due to effective solute alignment into the terminal H-complex structure (see §3.3). Thus we can conclude that a high orientational order for the non-mesomorphic proton-donors give an effective orientational correlation of the components and this is necessary for an even-odd effect for a homologous series of solutes.

The different directions of even-odd alternation in LCs **III** and **XII** can be explained in terms of the differences in H-complex properties with the participation of Schiff's bases [2] and cyanobiphenyls (see §3.3). The formation of a transverse H-complex **III** (see figure 8 (a)) results in odd alcohol carbon atoms having a greater contribution to the intermolecular interaction energy between LC and solute. In contrast even atoms have a greater contribution for the longitudinal complex (see figure 8 (b)).

Thus it may be noted that H-bond structure greatly influences not only the orientational and mesomorphic properties, but also the non-mesomorphic solute thermodynamics.

4. Conclusions

The noticeable influence of the molecular structure of the nematic solvent on the structure of the H-complexes with proton-donating solutes has been shown. It has been established that Schiff's bases possess the largest tendency for lateral H-complex formation. Strong steric restriction to the H-complex formation weakening the H-bond are observed for azobenzene derivatives. The steric factor becomes weaker on going to azoxybenzenes but changes in the H-bond orientation and the angle between the long molecular axes of the components in

the complex becomes less. Phenylbenzoate derivatives form mutually parallel lateral complexes with the proton-donor, and with the cyanobiphenyls longitudinal alignment of the components is due to the orientation of terminal electron-donating cyano-group. The influence of H-bond properties on the nematic-isotropic transition temperatures of binary systems have been stated, due to which the strengthening of transversal complexes results in an increasing destabilization by the solute while longitudinal H-complex formation gives the opposite effect. The thermodynamic characteristics for alcohol solutes dissolved in nematic LCs at infinite dilution together with the order parameters show the existence of an even-odd alternation of $\Delta\bar{H}_2$ and $\Delta\bar{S}_2$ in a homologous series of solutes. The structure of the H-complex was shown to determine the direction of the even-odd effect.

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