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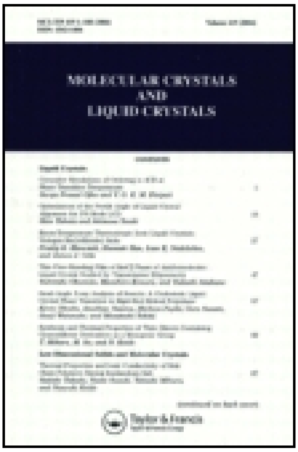

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Far IR Spectroscopic Investigations of Nematic Liquid Crystals with Hydrogen Bonded Molecules. Comparison with Nonoriented Systems

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Version of record first published: 23 Sep 2006.

To cite this article: K. Antonova , M. Petrov , N. Kirov , T. Tenev , H. Ratajczak & J. Baran (1995): Far IR Spectroscopic Investigations of Nematic Liquid Crystals with Hydrogen Bonded Molecules. Comparison with Nonoriented Systems, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 261:1, 63-70

To link to this article: http://dx.doi.org/10.1080/10587259508033452

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Mol. Cryst. Liq. Cryst. 1995, Vol. 261, pp. 63–70
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FAR IR SPECTROSCOPIC INVESTIGATIONS OF NEMATIC LIQUID CRYSTALS WITH HYDROGEN BONDED MOLECULES. COMPARISON WITH NONORIENTED SYSTEMS

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Abstract The 6 - 10th homologues of 4-n-alkoxybenzoic acid, i.e. hexyl-, heptyl-, octyl-, nonyl- and decyloxybenzoic acids (6OBA, HOBA, OOBA, NOBA and DOBA) are used for the present investigations. Far IR spectroscopy is used to study the state of hydrogen bonding at temperature variation of the nematic liquid crystal phase. The observed spectral bands are assigned to different OH deformation vibrations. From the analysis of the temperature dependence of the spectral band widths a cyclic ⟷ open dimer transformation is indicated at different vibration frequencies and polarizations. The activation energy for the dimer and monomer reorientation is calculated and compared with that per hydrogen bond. The correlation lengths parallel and perpendicular to the nematic director ($\xi_{\|}$ and $\xi_{\perp}$) are calculated and an anisotropy is found in the temperature dependence of the critical index of the correlation length. A comparison with nonoriented nematics with hydrogen bonded molecules is presented.

I. Introduction

The optical and electrooptical behaviour of the nematics (N) preceding smectic C (Sc) on cooling is extremely different from that of the conventional nematic liquid crystals [1-3]. Anomalies in the temperature dependence of the electroconductivity, dielectric and elastic constants are observed at a definite temperature T^* [4]. This temperature devides the N phase of 4-n-alkoxybenzoic acid in two subphases: high-temperature N_1 with a classical nematic behaviour and low-temperature N_2 with a smectic-like behaviour. The strong short range smectic order is more pronounced in N_2 than in N_1 [5,6]. Such a behaviour is due to the molecular structure. The molecules of the 4-n-alkoxybenzoic acids tend to associate in dimers by hydrogen

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bonds. Recently, it has been demonstrated [6] that in N_1 subphase the monomers, cyclic dimers and open dimers coexist. These molecular forms have different molecular lengths and their coexistence does not favour smectic-like complex generation. In N_2 subphase, however, the dimer predomination leads to strong smectic order fluctuations. Consequently, the investigation of these processes requires methods very sensitive to molecular interactions.

The known X-ray, textural and depolarized light scattering analyses [4,5,7] are sensitive to the formed quasilayers and work on supramolecular scale. Mid IR spectroscopy [6] gives us the possibility to study the intramolecular vibrations. There exist a few papers on far IR spectroscopic study of some derivativies of benzene, phenol, carboxylic and benzoic acids giving information about the intermolecular vibrations of the hydrogen bond [8-10]. We based our results on the published material since for big molecules like 4-n-alkoxybenzoic acids it is difficult to make band assignment by normal coordinate analysis.

The association-dissociation reactions modulate the macroscopical processes and using the spectroscopic results we succeeded to estimate some supramolecular characteristics like the activation energy for the dimer and monomer reorientation, the correlation length and its critical index.

II. Experimental results and discussion

The liquid crystal was placed between two quartz crystal plates of thickness 400 μm separated with 20 μm thick spacer. Both crystal quartz wafers were covered beforehand by 5 μm polyvinilalcohol layers which were rubbed with a special soft material in order to realize a planar homogeneous orientation of the liquid crystal. The sample was installed into a thermostat with an automatic temperature controller with accuracy of ± 1°C.

Transmittance spectra in the spectral region 200-30 cm^{-1} were recorded on a Bruker IFS 88 Fourier-transform IR spectrophotometer with a spectral resolution of 2 cm^{-1}. The measurements were made in both polarizations: the electric vector $\vec{E}$ parallel (p) and transversal (t) to the director $\vec{n}$ of the oriented nematic texture.

The 6 - 10th homologues of 4-n-alkoxybenzoic acid (6OBA, HOBA, OOBA, NOBA and DOBA) were under investigation. Their phase transition temperatures after [11] are:

6OBA: Solid $\xleftrightarrow{107^{\circ}C}$ N $\xleftrightarrow{153^{\circ}C}$ I (nonoriented system)
HOBA: Solid $\xleftrightarrow{92^{\circ}C}$ S_c $\xleftrightarrow{98^{\circ}C}$ N $\xleftrightarrow{146^{\circ}C}$ I ($T^* = 117^{\circ}C$)
OOBA: Solid $\xleftrightarrow{101,1^{\circ}C}$ S_c $\xleftrightarrow{108^{\circ}C}$ N $\xleftrightarrow{147^{\circ}C}$ I ($T^* = 122^{\circ}C$)
NOBA: Solid $\xleftrightarrow{92^{\circ}C}$ S_c $\xleftrightarrow{117^{\circ}C}$ N $\xleftrightarrow{143^{\circ}C}$ I ($T^* = 128^{\circ}C$)
DOBA: Solid $\xleftrightarrow{97^{\circ}C}$ S_c $\xleftrightarrow{125^{\circ}C}$ N $\xleftrightarrow{143^{\circ}C}$ I (nonoriented system)

The spectra of HOBA, OOBA and NOBA for both polarizations at the temperature (T_{NI} - 10)°C are shown in Fig.1. We chose this temperature in order to compare the microscopical behaviour of the liquid crystals at one and the same temperature distance from the isotropic phase, where dimer molecular forms are generated. The observed bands at 82, 63 and 42 cm^{-1} in p-polarization and at 68 cm^{-1} in t-polarization are well seen and their most essential spectral parameters can

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be determined. The maximum intensity of the band at 68 cm^{-1} in Fig.1a decreases almost two times on going from HOBA to NOBA. The same effect is seen for ν=63 cm^{-1} in Fig.1b. It means that at the temperature (T_{NI}-10)°C there are molecular complexes as a result of smectic order fluctuation. At this temperature the longest dimer molecules of NOBA compact easier than those of HOBA and OOBA in large supramolecular formations with a small energy and a weak spectral band. On the other hand, for ν=82 cm^{-1} the band shape of HOBA and NOBA are similar and differ from that of OOBA (see Fig.1b). If we assign this band to a hydrogen bond stretching vibration, it leads to the fact that the size of the supramolecular formation is not important for the band's intensity since the direction of the resultant vibration always coincides with the long axes of the dimer molecules. Thus the difference probably indicates the known even-odd effect.

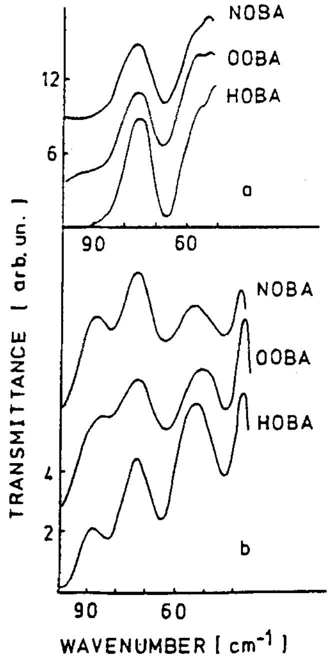

FIGURE 1. Far IR transmittance spectra of HOBA, OOBA and NOBA at T = (T_{NI} - 10)°C : a) t-polarization; b) p-polarization.

In such big molecules as 4-n-alkoxybenzoic acids it is difficult to make band assignments by a normal coordinates analysis. In some cases, however, we can compare with the analysis of more simple acids (dimeric formic or acetic) with planar dimer ring structures of C_{2h} symmetry [10]. The dimer form $(R\text{-}CO\text{-}OH)_2$ (where $R=C_nH_{2n+1}OC_6H_6$) has more than 20 internal vibrations, but only six frequencies belong to the intermolecular vibrations involving motion of the hydrogen bond [12]. Considered as Cartesian displacement they can be assigned to stretching, bending, and twisting vibrations.

The OH stretching vibration frequency for the dimeric formic acid has been calculated to be 248 cm^{-1} [10]. Using the equation $\nu_1/\nu_2 = (m_2/m_1)^{1/2}$ which relates the stretching vibration frequency in harmonic approximation and the reduced mass of one molecule with the same parameters of another molecule, a value ν = 82 cm^{-1}

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for the OOBA dimer molecule was obtained and exactly measured. The fact that the same values for the stretching vibration frequencies of HOBA and NOBA were observed obviously means that the influence of the benzene ring is essential and the contribution of the alkyl tail is negligible.

For the assignment of the observed bands we present the oriented crystal system as an ensemble of planar dimer rings with thermal fluctuations strongly correlated in space and time. The dimer molecules of HOBA, OOBA and NOBA can be represented by a molecular quadrupole essentially due to the two central H-bonds with opposite electric dipoles. Accepting this dipole approximation we consider the ensemble of dimer molecules as an overmolecular polyatomic formation with an equivalent transition dipolle moment $\vec{P}$. The direction of $\vec{P}$ deviates by an angle β from the long molecular axis. Angle β was calculated using the IR spectra in p and t polarizations and the equation connecting the anisotropy of the optical absorption of the uniaxial liquid crystal with the order parameter $\langle P_2 \rangle$ [13]. For the band at ν_{OH}=82 cm^{-1} $\beta \approx 10^o$ and for the bands ν_{OH}=63 cm^{-1} and 68 cm^{-1} $64^o \langle \beta \langle \pi/2$ were calculated. Angle β corresponding to the band at 82 cm^{-1} is small implying that the dipole oscillation is approximately along the long molecular axis and thus involves stretching vibration. Taking into account the dichroic ratio $D_{\|}/D_{\perp}$ ($D_{\|}$ and $D_{\perp}$ are the optical densities for IR light polarized parallel and perpendicular to $\vec{n}$, respectively) and the freedom of $\vec{P}$ to rotate in a coordinate system connected with the planar dimer ring, we assigned the bands at 63 cm^{-1} and 68 cm^{-1} to in-plane bending vibration. Our opinion on these peaks is that they correspond to the one and the same frequency and the difference can be due to the spectral resolution. The influence of the vibrations of other molecular formations (e.g., an open dimer) can be also a reason for the difference.

We assigned the band with the lowest frequency at 42 cm^{-1} to the twisting vibration of one monomer unit against the other along the hydrogen bond.

The temperature dependences of the bands halfwidth $\delta\nu$(T) for HOBA, OOBA and NOBA are shown in Fig.2a. They all are different from those of the classical N phase, for which $\delta\nu$ smoothly increases with the temperature increasing. For the substances under investigation $\delta\nu$ fluctuates around an average value in whole nematic region for all observed hydrogen bond vibrations. This average value increases with the temperature increasing or is temperature independent. If it increases, the amplitude of $\delta\nu$ fluctuations increases, too. The positions of the curves extrema depend on the substance and on the vibration frequencies, i.e. on the dimer molecule length and on the type of the deformation vibration respectively. In order to explain the complex character of the $\delta\nu$ temperature dependences we fix first the substance (for example OOBA) and follow the curves for ν=42, 63, 68 and 82 cm^{-1}. The most drastic changes of $\delta\nu$(T) are in the vicinities of T_{NI}, T_{CN} and in the interval 130-122^{o}C. A common feature for all the frequencies is the noticable damping of the curve amplitudes below the temperature T* determined by us using other technics [4,5,14]. For HOBA, OOBA and NOBA these temperatures are approximately 117°C, 122^{o}C and 128°C, respectively.

Our interpretation of the maxima and minima at fixed molecular length is as follows: the value of the maximum $\delta\nu$ increases with the number of the molecules in excited vibrational state. This value strongly depends on the mixture of different

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hydrogen bond configurations as well. In our case the mixture is realised by cyclic dimers with two linear hydrogen bonds and open dimers with only one linear hydrogen bond. The process of dimer fluctuation between the open and cyclic state with the temperature variation manifests through higher value of $\delta\nu$ with the increasing number of the open dimers. That's why we observed the higher maxima in the N_1 subphase (above T*). The minimum of $\delta\nu$ is connected with the better oscillator arrangement inside the supramolecular complexes. The sensitivity of the frequency 42 cm^{-1} to the mixed character of the smectic-like complexes is very pronounced. Since this vibration mode is twisting of one monomer unit against the other along the hydrogen bond, it demonstrates the process of transformation of the cyclic dimers in open and thus indicates the open dimer contribution in the overmolecular complexes.

Fixing the type of deformation vibration and varying the substance we consider the role of the molecular length in the process of cyclic dimer formation. Fixing ν_{OH}=42 cm^{-1} we find that for NOBA $\delta\nu(T)$ has a maximum at 12 degrees below T_{NI} and a minimum at 20 degrees below T_{NI}. In this range of 8 degrees, very near to T*, a decrease of the open dimers and monomers occurs. The same situation is noticed for HOBA between 20 and 29 degrees and for OOBA between 15 and 26 degrees below T_{NI} and in the vicinity of T*.

Consequently, the two bands at 82 cm^{-1} and 42 cm^{-1} display two boundary states during the building and the breaking of the hydrogen bond, i.e. the cyclic and open dimer states.

We compared the above presented results of oriented HOBA, OOBA and NOBA with nonoriented 6OBA, NOBA and DOBA. The observed spectral bands in the case of nonoriented liquid crystals are at 42, 51, 66 and 81 cm^{-1}. It is seen that the two above mentioned boundary frequencies 42 and 82 cm^{-1} repeat, while the frequencies 63 and 68 cm^{-1} for oriented systems are shifted to 51 and 66 cm^{-1} for nonoriented. The far IR activity indicated by ν=82 cm^{-1} obviously remains the same in nonoriented system implying that the hydrogen bond stretching vibration is collinear with the long dimer axis in both cases. The stable position of the band at 42 cm^{-1} in the two systems indicates that the open dimers due to the twisting vibrations can not be oriented by the boundary conditions.

Using the transition dipole moment distribution we have already assigned the band at 63 cm^{-1} in ordered system to an in-plane hydrogen bond vibration. For nonoriented system the corresponding band is shifted to 51 cm^{-1}. We assume that it indicates a low-energetic bend-twist deformation vibration No damping of the curve amplitudes below T* is observed.

In Fig.2b the $\delta\nu(T)$ dependence for 6OBA is shown. This substance displays only nematic phase. It is seen that the average value of $\delta\nu$ decreases approaching T_{NI} and the solid phases. The maximal fluctuations are in the middle of the N phase as the level of the average $\delta\nu$ value increases. Our interpretation is that in this temperature range the open dimers predominate.

Thus in 6OBA T* is not as emphatic as in the homologues with n≥7. The length of the 6OBA molecules is enough to provoke weak smectic order fluctuations, i.e. a generation of supramolecular complexes but with a small correlation lengths. Concequently, the molecular lengths of 6OBA and HOBA are boundary values at which 4-n-alkyloxybenzoic acids display only N or N and Sc state respectively. So

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the variation of the molecular length from n=6 to n=7 is equivalent to a first order phase transition.

The macroscopical processes characterizing the liquid crystal systems with hydrogen bonded molecules obviously are modulated by the reactions: dimer $\rightleftharpoons$ 2 monomers. The investigation of the macroparameters typical for the N phase requires knowledges of the microscopical details of the hydrogen bond formation processes and the hydrogen bond state as well. Further we'll discuss the processes in the vicinity of T^* only.

The main result we'll present concerns the semi-macroscopic behaviour of the system in a spatial scale ξ (correlation length) much larger than the molecular one l (molecular length). For the interpretation we used our far IR spectroscopy results.

Two monomers tending to associate in a cyclic dimer follow separately their own local order $\vec{n_1}$ and $\vec{n_2}$ with an angle α between them. The life-time of the hydrogen bond is connected with the temperature averaged angle $\langle\alpha\rangle$ by the relation: $\tau^{-1} = (\langle\alpha^2\rangle)^{1/2}$ [9,12]. Using the relation $\delta\nu \sim \tau^{-1}$ we obtained the temperature variation of τ giving indirectly the temperature dependence of α in the N phase. α can variate as $0\langle\alpha\langle 2\pi$. When $\langle\alpha\rangle = \pi/2$ the probability for the hydrogen bond realisation is minimal. For ν_{OH}=63 cm^{-1} $\langle\alpha\rangle$ increases with the temperature increasing while for ν_{OH}=42, 68 and 82 cm^{-1} it is temperature independent. $\langle\alpha\rangle$ is temperature independent for all substances and for all frequencies below T^* too, which indicates a saturation of the hydrogen bond formation in the low-temperature N_2 subphase.

We calculated the equilibrium constant K for the equilibrium 2 monomer $\longleftrightarrow$ dimer using the formula $K = c_A/2c_C^2$ [15], where c_A and c_C are the equilibrium static concentrations of the cyclic dimers and the monomers. From the temperature dependence of K we estimated the enthalpy of dimerization, $\Delta H = 4.8$ kJ/mol, which is comparable with the energy per hydrogen bond.

The dimerization can be realized only if the oxigen atom forming the hydrogen bond posesses an energy enough to overcome the monomer's energy barrier. The rate of the dimerization reaction is connected with its activation energy by an exponential dependence: $\tau^{-1} \sim \exp(W/k_B.T)$, from where the activation energy of the dimer-monomer reorientation in the high- and the low-temperature nematic regions was calculated. The results are given in the Table 1.

It is seen that W depends on the molecular structure and on the type of vibration as well.

The far IR absorption bands at different polarizations give a possibility to calculate the correlation lengths $\xi_{\|}$ and $\xi_{\perp}$ - parallel and perpendicular to the optical axis of the supramolecular complex, confirming its anisotropic properties.

The temperature dependence of ξ is characterized by the critical index μ [16]. The variation of I^{max}: $\Delta I^{max} = I_m^{max} - I_o^{max}$ in the temperature interval $\Delta T = |T - T^*|$ can be presented as $\Delta I^{max} = A|\Delta T|^{\mu}$, where A is a constant including the molecular length and $|\Delta T| \ll T^*$. In Table 1 it is seen that for a fixed substance, i.e. molecular length, the value of $\mu_{\perp}$ at 68 cm^{-1} is bigger than that of $\mu_{\|}$ at 63 cm^{-1}. This fact indicates a strong anisotropy of the complexes. The ratio $\mu_{\|}/\mu_{\perp}$ for NOBA is about 0.7, implying that the quasilayer area increases rapidly in the N region and forms smectic-like state.

This work is fulfilled in the frames of Contract F39 between the Institute of Solid State Physics and the Bulgarian National Science Foundation.

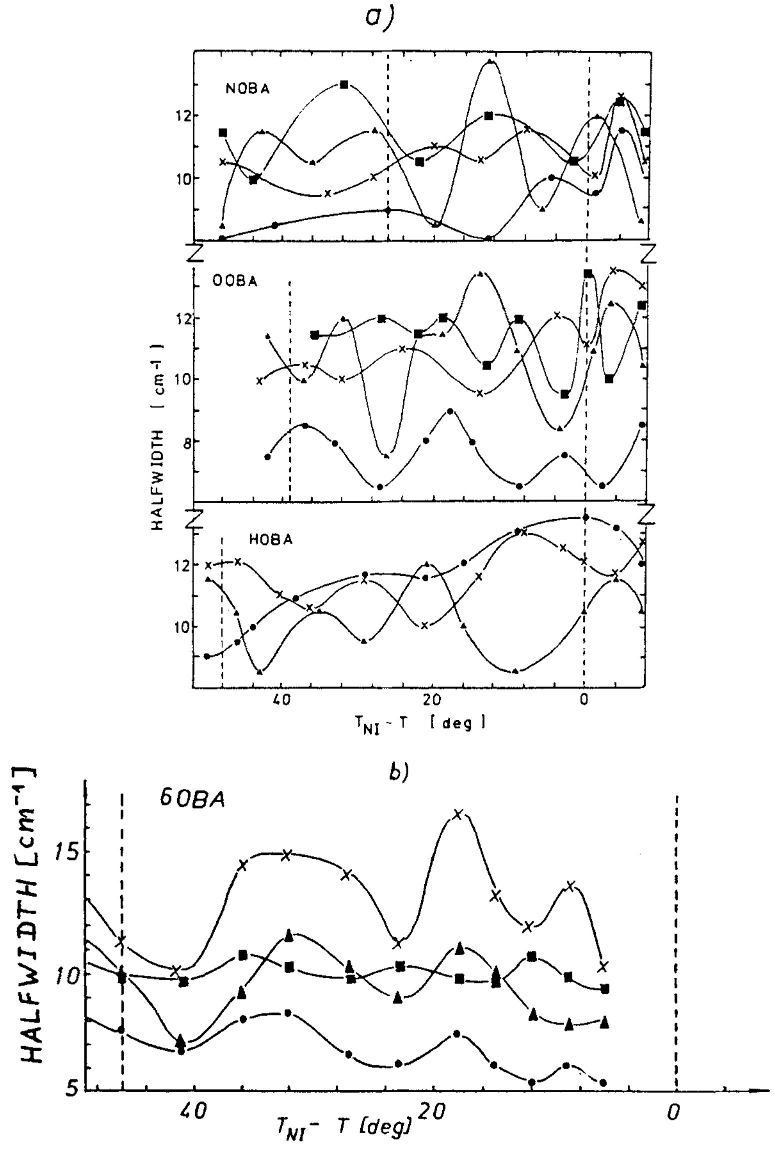

FIGURE 2. Temperature dependence of the halfwidth of the spectral bands $\delta\nu(T_{NI} - T)$: a) for oriented HOBA, OOBA and NOBA: ▲ - 42 cm^{-1}, × - 63 cm^{-1}, ■ - 68 cm^{-1}, ● - 82 cm^{-1}; b) for nonoriented 6OBA. Left dashed lines correspond to T_{CN}.

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Table 1. Frequency dependence of the activation energy for dimer —monomer reorientation and of the critical index μ for HOBA, OOBA and NOBA.

substance	W kJ/mol	μ	polarization	ν cm^{-1}
HOBA	3,680	0,663	∥	42
HOBA	5,965	0,730	∥	63
HOBA	4,310	-	⊥	68
OOBA	6,670	0,816	∥	42
OOBA	4,725	0,811	∥	63
OOBA	8,940	0,860	⊥	68
NOBA	8,240	0,775	∥	42
NOBA	4,375	0,750	∥	63
NOBA	4,310	1,036	⊥	68

References

1. F. Rondelez, Solid State Commun., 11, 1675 (1972).
2. H. Gruler and G. Meier, Mol. Cryst. Liq. Cryst., 23, 261 (1973).
3. E. F. Carr, Phys. Rev., A12, 327 (1975).
4. M. Petrov and P. Simova, J. Phys, D18, 239 (1985).
5. P. Simova and M. Petrov, Mol. Cryst. Liq. Cryst., 182B, 225 (1990).
6. M. Petrov, E. Anachkova, N. Kirov, H. Ratajczak and J. Baran, J. Mol. Liq., in press.
7. A. de Vries, Mol. Cryst. Liq. Cryst., 10, 31 (1970); 10, 219 (1970); 11, 361 (1970).
8. A. E. Stanevitch, Optika and Spectroscopya, XXI, 5 645 (1966).
9. G. Allen, J. G. Watkinson and K. H. Webb, Spectrochimica Acta, 22, 807 (1966).
10. R. J. Jakobsen, J. Mikawa and J. W. Brasch, Spectrochimica Acta, 23A, 2199 (1967).
11. A. J. Herbert, Trans. Far. Soc., 63, 555 (1967).
12. L. Colombo and K. Furic, Spectrochimica Acta, 27A, 1773 (1971).
13. A. Saupe, Z. Naturforsch, 18a, 336 (1963); Mol. Cryst. Liq. Cryst., 16, 87 (1972).
14. M. Petrov, A. Braslau, A. Levelut and G. Durand, J. Phys.II Fr. , 2, 1159 (1992).
15. B. Deloche and B. Cabane, Mol. Cryst. Liq. Cryst., 19, 25 (1972).
16. P. E. Cladis, Phys. Rev. Lett., 31, 1200 (1973).

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