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Infrared Absorption Spectra of Liquid Crystals.

IV. Integral Intensity Temperature Dependence of Infrared Bands in Crystal, Nematic Crystal and Isotropic Phases

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The integral intensity temperature dependence of many various IR bands in crystal, nematic crystal and isotropic phases was investigated. It was found that in the crystal phase 20–40° below the phase transition crystal—nematic crystal all bands investigated decrease nonlinearly. From these changes the activation energy V_a for a transition of the molecule from the lattice site into an interstitial one was obtained. In liquid crystal phase the bands, corresponding to the benzene ring deformation, do not change or slightly decrease with temperature while those of O—R and Ph—O stretch vibration decrease very rapidly. An attempt was made to connect the temperature behavior of the integral intensity with intermolecular forces in nematic phase.

INTRODUCTION

The band integral intensity measurement may provide significant information about molecular structure, intermolecular interaction and their changes with temperature and phase transitions. The integral intensity of the ith band

$$A_i = \frac{\pi N}{3c}\left(\frac{\partial \mu}{\partial Q_i}\right)^2 \tag{1}$$

according to the statistical theory of Placzek-Volkenstein[1] supplemented with calculations of the stimulated light emission,[2] should not depend on

temperature in the case when the absorbing center could be considered as a harmonic oscillator. Many experimental investigations[3] show that deviations of theoretical dependence exist for condensed phases. Although some authors[4] reported an intensity increase of the band at 3040 cm^{-1} in liquid benzene spectrum, numerous results show that in liquid and in solutions the integral intensity decreases with temperature. Unfortunately, the results obtained for crystal phases are quite restricted. Lisitza[5] investigated the temperature dependence of some fundamental, combination and overtones from the IR spectrum of crystalline $CHBr_3$ and $CHCl_3$. He indicated that the integral intensity of the 1332 cm^{-1} band decreases with temperature, while the rest of the bands either decrease slightly or do not change at all. Maier and Englert,[6] investigating oriented liquid crystals of the homologous series derived from PAA, observed changes in the extinctions $E_{\parallel}$ and $E_{\perp}$ with the temperature in the liquid crystal phase. Using the relation $E_{\parallel}/E_{\perp}$ they obtained data about the temperature effect upon the molecule arrangement in the nematic phase and its dependence on temperature. Later Bulkin *et al.*[7] studied the temperature effect of the absorption bands which they assigned to combination modes between lattice vibration and intramolecular vibration and which disappear in liquid crystal phase. However, the above authors[6,7] did not investigate the temperature dependence of the integral intensity in crystal, nematic crystal and isotropic liquid. Only Lvova and Sushtinskii[8] reported similar data. They, however, studied only three compounds and a few bands and did not relate the integral intensity temperature dependence to the type of vibration. No changes in the integral intensity at the phase transition liquid crystal-isotropic (C-I) liquid were observed up to now.

EXPERIMENTAL

The apparatus setup was described in detail in part I[9] and part II.[10] In all investigation the reference cell was heated up to the temperature of the sample cell. The temperature difference between the two cells was not more than 2°. By this method window emission is eliminated and there remained only the emission of the substance, which due to the small thickness of the film—10–15 microns, may be neglected. All the instrumental conditions were carefully fixed to remove the systematic errors as far as possible. Particular attention was given to the precision of the mechanical attenuator comb involved in the spectrophotometer. Its linearity was checked by calibrating of the recorder with an external test signal and the absolute intensity calibration was made by the use of the CH out of plane vibration band at 875 cm^{-1} of 1, 2, 4, 5-tetrachlorobenzene in dilute Cs_2 solution. This band is about

100 cm^{-1} from the nearest adjacent band and, thus, is free from the overlap and gives satisfactory agreement with Lambert-Beer's law. The typical band profile is the Lorentzian one and using the Ramsay method[11] we obtained the value of $A = 4{,}55.10^3$ $mol.^{-1}L.cm^{-2}$. Our results was then compared with those, obtained from Shimozawa and Wilson[12]—$4{,}76.10^3$ $mol.^{-1}L.cm^{-2}$ by means of Perkin-Elmer 421. As one can see, in the limits of the error our data coincide well with those of the above authors and hence no significant difficulties were encountered from the mechanical comb.

The bands investigated were very intense and the thickness of the films used is small—approximately one wavelength. Therefore minor changes in the film thickness, density or refractive index may have a very strong effect on the transmission and different absorption lines may be affected differently. For this reason samples with four different thicknesses—8, 12, 15 and 20 microns were used. Films with thickness of more than 20 microns could be used only under a big ordinate scale suppression, which could increase significantly the error in the integral intensity determination. In the limits of the error the integral intensity determined from the films with different thicknesses were equal. Five-six measurements have been carried out at any temperature and cell thickness as well and the results were averaged in all measurements. This allows a considerable decrease of error. The spectra were recorded on a per cent transmission scale, expanding the axis of wavenumbers 10–20 times. The scanning speed was 12,5 cm^{-1} per minute (with an additional electrometer 1 rpm.). As for the slit width the relation $S/\Delta\nu_{1/2}^2$ was kept between 0,2 and 0,1. Samples were heated very slowly (the mean rate was about 20°/h). The temperature interval was from the temperature of liquid nitrogen up to 400-450°K.

The substances MBBA (*p*-methoxybenzylidene *p*-*n*-butylaniline), EBBA (*p*-ethoxybenzylidene-*p*-*n*-butylaniline), APAPA (*p*-aminophenylacetate) were synthesized and kindly offered to us for investigations by the collaborators of Dr. A. Derzhanski. The chemicals from the homologous series of *p*-azoxyanisole (PAA) were purchased from Eastman Organic Chemical Division. In case when purity of the samples appeared to be in question they were recrystallized several times before use. Purity was checked in two ways: 1) Transition temperature was checked very carefully. Particular attention was paid up to the position of the nematic-isotropic transition temperature since it is very sensitive to impurities, because of very small enthalpy changes. Good agreement with the best temperature value was found.[13] 2) To establish beyond doubt the purity of compounds investigated thin layer chromatography was used as well.

The bands in the region 600–1250 cm^{-1} were mainly investigated. No bands between 1250 and 1600 cm^{-1} were studied due to the complexity of the spectra in this region. All bands investigated had a regular dispersion form

and the Ramsay method with wing correction was used.[11] No data concerning both density and refractive index of investigated compounds are available in the literature except for PAA.[14] Thus only for this substance is the integral intensity given in absolute units ($cm^{+2}sec^{-1}molec^{-1}$). The band intensity from the spectra of all other liquid crystals is in arbitrary units (cm^{-2}). Correction for the refractive index and density changes was made only for PAA, according to.[15]

RESULTS AND DISCUSSION

In the crystal phase the integral intensity of all investigated bands (except 757 cm^{-1} of PAA, whose intensity slowly decreases) does not change with temperature. In the region of 20–40° below the crystal-nematic (C-N) transition temperature nonlinear decrease of the intensity was observed.

Deviations from the theoretical behavior was observed in the isotropic liquid—the integral intensity of all bands investigated decreases with temperature and follows the linear rule $A = A_0 + \alpha T$, where the coefficient α acquires a negative sign. Our results show that α is different for various bands from the spectrum of a given compound, that is, the integral intensity temperature dependence of the bands, which could be assigned to different types of vibrations, have a different temperature behavior. The quickest decrease is that of the end and light atom vibrations and deformation of external angles CCH. Thus, for example, the intensity of the band 1025 cm^{-1} (O—CH_3 stretch), 1249 cm^{-1} (benzene ring-oxygen stretch), 1178 cm^{-1} (CH in plane deformation) and 838 cm^{-1} (CH out of plane deformation) from the PAA spectrum decrease rapidly with temperature. The bands corresponding to the in plane vibrations of the benzene ring—755 and 910 cm^{-1} (PAA) decrease slower; those of the deformation of inner angles with the participation of the substituents—most slowly. This is illustrated in Figure 1 for some bands of PAA spectrum. A similar effect is observed not only in the spectra of such complex molecules, possessing a liquid crystal phase, but for the bands of some more simple molecules as benzonitrile, anisole and phenetole. The integral intensity of the bands 756 cm^{-1} (CH out of plane deformation), 1070, 1160, 1188 and 1284 cm^{-1} (CH in plane deformation) from the benzonitrile spectrum, 735 cm^{-1} (CH out of plane deformation), 1067 cm^{-1} (benzene ring—Br stretch) from the C_6H_5Br spectrum decrease more rapidly than those at 689 cm^{-1} (C_6H_5Br)—out of plane ring deformation, 1001 and 1020 cm^{-1}—breathing modes, 1455, 1478 cm^{-1}—benzene ring stretch vibrations. Rezaev[16] investigating many bands from the Raman spectra of *o*- and *p*-xylene in quite broad temperature limits has obtained the same results.

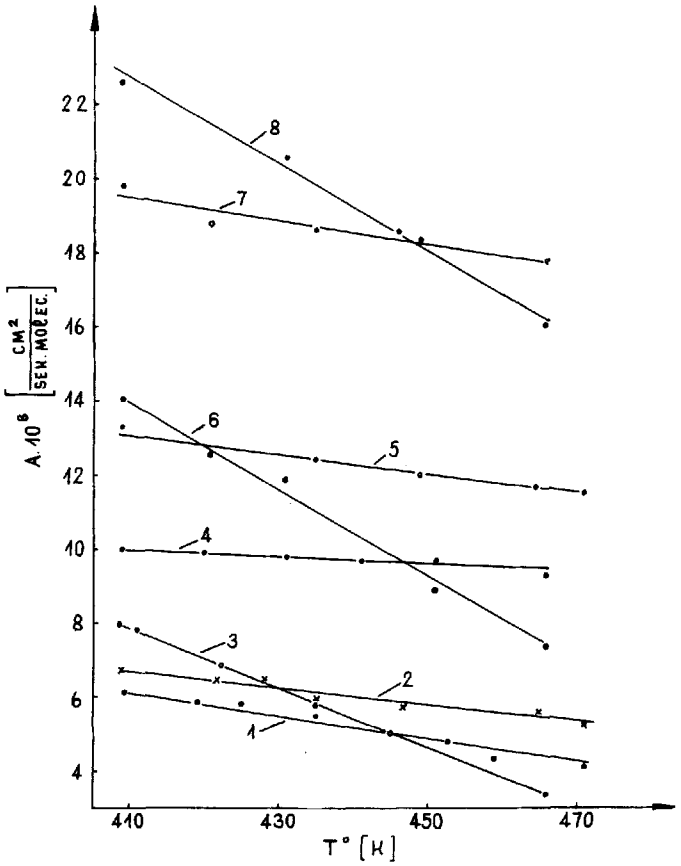

FIGURE 1 The integral intensity temperature dependence of the bands: (1) 910 cm^{-1}; (2) 755 cm^{-1}; (3) 1178 cm^{-1}; (4) 431 cm^{-1}; (5) 612 cm^{-1}; (6) 838 cm^{-1}; (7) 671 cm^{-1}; (8) 1025 cm^{-1} from the IR spectrum of PAA in isotropic phase.

The nematic liquid crystals also show deviation from the theory. Here we observed a difference in the temperature behavior of the bands belonging to the various modes. Bands which can be assigned to the benzene ring vibration have a temperature behavior similar to that in the crystal phase, while those of O—CH_3, Ph—O and CH_3 symmetric deformation (APAPA) decrease fast and have a behavior similar to the one in the liquid phase (Figures 2 and 3).

At present there is no theory explaining satisfactorily the deviation in the integral intensity temperature dependence from the theoretical prediction. However, most probably, the basic reason for the observed deviations are the intermolecular forces. As has been shown,[17] the absorption, induced by

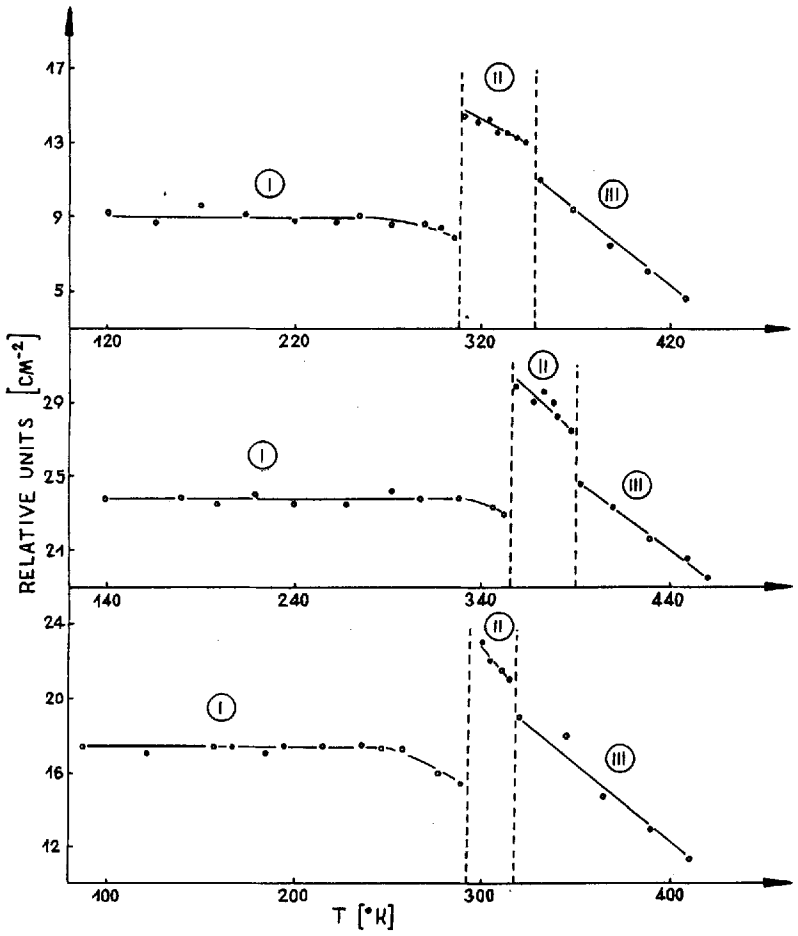

FIGURE 2 A comparison between the integral intensity of the bands assigned to O—R stretch vibration in different liquid crystals (from below): 1029 cm^{-1} (MBBA); 1022 cm^{-1} (APAPA) and 1042 cm^{-1} (EBBA); (I) crystal phase; (II) liquid crystals phase; (III) isotropic liquid.

the intermolecular forces, could be considered as an addition to the fundamental one. Formula (1) shows that the integral intensity of a given band for an isolated molecule (gaseous phase) does not depend on temperature. In the presence of intermolecular interaction the dipole moment of a corresponding vibration could be considered as being composed of two parts: the one, which is defined by the dipole moment of an isolated molecule and the other—the so-called "induced" dipole moment, depending on the effect of the electric field of the surrounding molecules on the corresponding

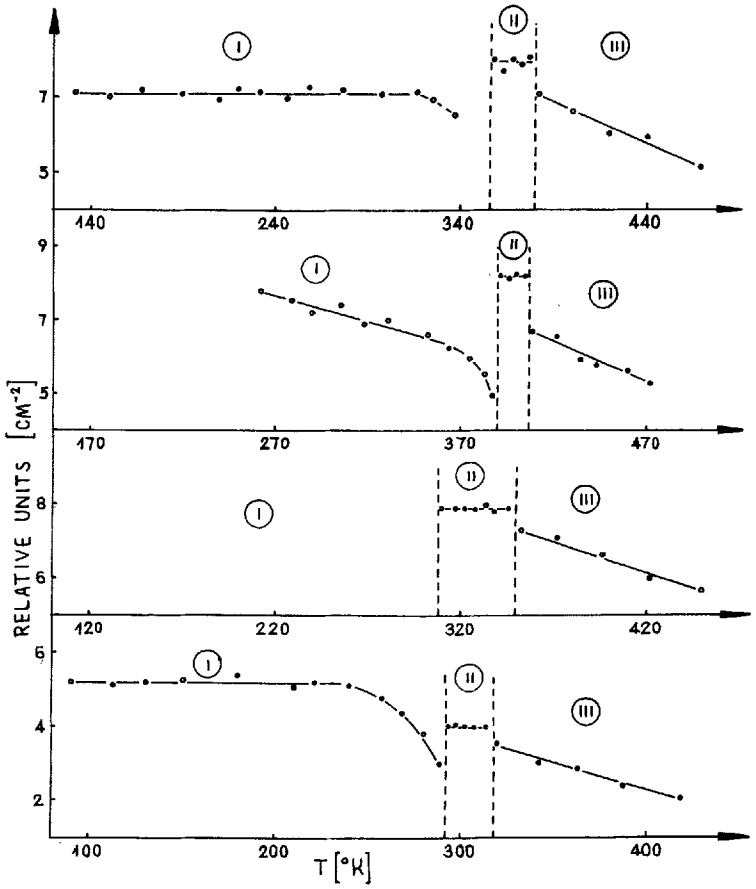

FIGURE 3 A comparison between the integral intensity of the bands assigned to the benzene ring vibrations in different liquid crystals (from below): 600 cm^{-1} (MBBA); 532 cm^{-1} (EBBA); 757 cm^{-1} (PAA) and 912 cm^{-1} (APAPA); (I) crystal phase; (II) liquid crystal phase; (III) isotropic liquid.

bond. That's why in condensed phases the value A_g (integral intensity corresponding to the isolated molecule in gaseous phase) will change as a result of the interaction with its near neighbors. It could be presumed that the change of A_g as a result of the perturbing effect of intermolecular forces are:

$$A = A_g + \Delta \tag{2}$$

where A is the integral intensity in a condensed phase while Δ is determined by the character and energy of intermolecular interaction. Therefore, investigating different bands we can obtain valuable data about the character, orientation and participation of various atoms and groups in the

intermolecular forces and their changes with temperature and phase transitions. In the solid state, due to the presence of a crystal lattice, the intermolecular interactions are strong and Δ acquires its maximum value and reaches saturation. At the same time the integral intensity of all bands studied does not change, which shows that the intermolecular interactions do not change significantly with temperature.

As one can see from Figures 2, 3 and 4 the intensity begins to decrease well below the transition temperature crystal—nematic crystal (C-N). It should be noted that the decrease of the integral intensity is observed in spite of the increasing of the half-band width.[9,10] The similar effect was

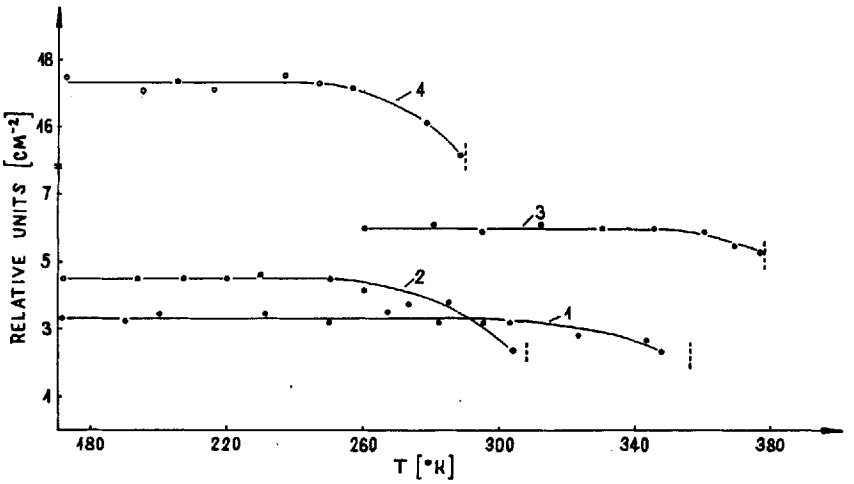

FIGURE 4 The integral intensity temperature dependence of the bands: (1) 763 cm^{-1} (APAPA); (2) 924 cm^{-1} (EBBA); (3) 696 cm^{-1} (*p-n*-hexoxybenzoic acid) and (4) 1029 cm^{-1} (MBBA) in crystal phase.

observed by Bulkin *et al.*[7] who have investigated the absorption in the maximum of the band assigned to the combination modes between lattice and intermolecular vibrations in the IR spectrum of some molecules from the PAA-homologous series. Besides, Borer[18] and Billard[19] investigating Raman spectra of MBBA, mentioned the observed rapid decrease of peak heights of some lattice modes approx. 30° before the transition temperature. However, as far as we know, there are no data in the literature concerning the integral intensity changes before the phase transition crystal—nematic crystal. Furthermore, as can be seen from Figures 2, 3 and 4 the lower melting crystals have the more gradually decreasing intensity. It should be underlined that similar phenomenon has not observed in the band integral intensity temperature dependence from the spectra of related substances,

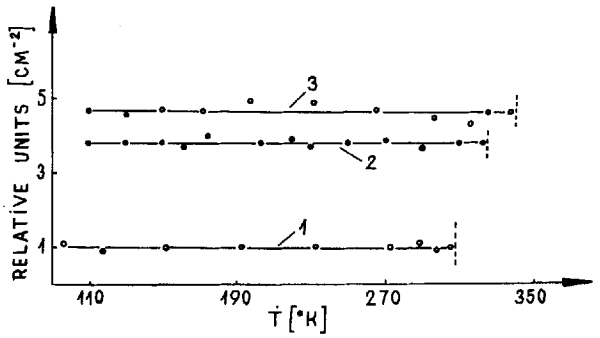

FIGURE 5 The integral intensity temperature dependence of the bands: (1) 1076 cm^{-1} (azoxybenzene); (2) 1067 cm^{-1} (benzyliden-aniline) and (3) 760 cm^{-1} (azobenzene) in crystal phase.

not possessing liquid crystal phase. Figure 5 shows the changes in the integral intensity of some bands from the spectra of benzylideneaniline (BA), azo- and azoxybenzene (related nonmesomorphic compounds). As one can see from it, no changes in the intensities are observed even close to the phase transition crystal—isotropic liquid. Hence, the observed nonlinear decrease of the integral intensities well below the phase transition crystal—liquid crystals is the peculiarity of the compounds possessing a nematic phase and may be explained probably with formation of lattice defects, i.e., with the molecule transition from the lattice site in the interstitial one. Many aspects of the nematic phase favor this explanation. In the nematic phase the crystal structure is replaced by one in which there is a long range order only with respect to the orientation of long axes. Such a structure could be reached from the crystal by taking molecules from the lattice site and moving them into the interstitial site, creating defects in the lattice. Bulkin *et al.*[7] reached the same conclusion. During this transition the interaction of the molecules with its nearest neighbors decreases, hence the value Δ will decrease and therefore the integral intensity. As it is known the probability for defect formation is given with the formula

$$\frac{n}{n_0} = A \exp\left(-\frac{V_a}{\kappa T}\right) \tag{3}$$

where n_0 is the total number of the molecules in the crystal site, n—in the interstitial site, and V_a is the potential barrier which the molecule has to overcome in transition from the crystal site into the interstitial one. We can introduce the so-called fractional change of the integral intensity β at a given temperature. This is the difference between the integral intensity in the last point of the linear dependence and that at a higher temperature, when the integral intensity decreases significantly. Hence β is proportional to

n/n_0 and the formula (3) may be written in the form:

$$\beta = A \exp\left(-\frac{V_a}{\kappa T}\right) \tag{4}$$

Plotting ln β as a function of $1/T\ 10^3$, V_a may be obtained from the slope of the straight lines. The results for all investigating crystals are summarized in Table I, where our data are compared with those of Bulkin[7] obtained by means of decreasing of peak heights and thermodynamic data of Haller and Cox.[20] Each value is averaged in several bands corresponding to a different type of vibration. The mean error is about 1 kcal/mol. for the lowest melting substance (MBBA) to 8 kcal/mol. for *p*-azoxyphenetole (PAF), which has the highest temperature for the C-N transition—406°K. As one can see from Table I, the activation energy V_a is bigger the higher the temperature of crystal—nematic transition is i.e., the larger the intermolecular interactions are in the solid phase. A similar effect was observed in the pre-orientation potential barrier V_{0R} of the same molecules in crystal phase.[10] In addition our investigations show, that the lattice defects are forming earlier when the melting temperature of the substances is lower. For example, in the crystal MBBA (melting temperature 293°K) the defects began to form at about 40° before the phase transition C-N, while for PAF (highest melting compound) the similar effect is observed only at 15° below the C-N transition. This also shows that V_a is connected with the intermolecular forces in the crystal phase. The activation energy follows the same alternating pattern, characteristic of many properties of the liquid crystals, viz., rotational diffusion,[10] entropy,[20] distribution of the ultrasound.[21] In fact, this result indicates that the alternation in transition temperature is possibly a more intimate property of the

TABLE I

The activation energy V_a[kcal/mol] for transition of the molecules from the lattice site into interstitial one.

substance	T[°K] cryst.-liq. cryst.	V_a our results	[kcal/mol] other data
PAA	390	28 ± 5	42 ± 6(7)
PAF	406	36 ± 8	
4,4′-dipropoxy-azoxybenzene	388	25 ± 5	
4,4′-dibuthoxy-azoxybenzene	381	19 ± 3	19 ± 2(7)
4,4′-dipenthoxy-azoxybenzene	349	14 ± 2	11 ± 2(7)
4,4′-dihexoxy-azoxybenzene	354	15 ± 2	16 ± 2(7)
MBBA	293	9 ± 1	7 (20)
EBBA	309	12 ± 2	
APAPA	356	14 ± 2	
p,n-penthoxy-benzoic acid	398	25 ± 6	
p,n-hexoxy-benzoic acid	378	20 ± 5	

crystal and liquid crystal as a whole. Our results confirm the earlier indication,[22] that the C-N transition is connected with effects which appear 20–40° below the observed capillary transition temperature. The same result was obtained by means of neutron diffraction measurements of deuterated PAA.[23] It must be noted that the activation energy V_a for MBBA and EBBA molecules is close to the enthalpy of phase transition crystal—nematic crystal for similar compounds alkoxybenzylidene-*p*-aminoacetophenones.[20]

At the phase transitions the interaction of the molecule with its neighbors is changed and consequently the integral intensity will change. A great number of investigations show, that the intensity of almost all bands increases in the transition gas-liquid.[24] The integral intensities of the bands, corresponding to vibrations of O—CH_3 and Ph—O increase approximately 30% at the phase transition C-N in all studied compounds (Figure 2), while the bands related to the benzene ring deformation do not change or slightly increase (Figure 3). In the isotropic liquid the integral intensity of O—CH_3 and Ph—O decreases 15–20% while that of the aromatic ring vibration slowly decreases. Bands, which can be assigned to the benzene ring deformation in the nematic phase have a temperature behavior similar to that in the crystal phase, while the one of O—CH_3 and Ph—O decreases very fast. As far as we know similar effects have not been observed up to now. Keeping in mind the different temperature dependence and the changes at phase transitions of various IR bands, one can consider that in the first approximation in the nematic phase two kinds of intermolecular forces are acting. The end molecule groups take part in such an interaction, which decreases fast with temperature. In the liquid crystal phase the molecular freedom is greater. This favors such a distribution of the molecules where the end group of one PAA molecule comes to the center of the neighboring molecule. Hence it is possible for dipole interaction between the alkoxy group of one molecule and azoxy or azomethyne groups in the center of the other to arise. Actually X-ray investigations of PAA and PAF confirm this assumption.[25,26] At higher temperatures the thermal movement of the molecules increases and this hinders the mutual orientation of the molecules. As a result, the dipole interactions decrease rapidly.

Between the benzene rings of two neighboring molecules other types of intermolecular forces are acting, most probably dispersion. These forces slightly depend on temperature.[1] In fact the integral intensity of all bands corresponding to the benzene deformation do not change or slightly decreases with temperature in nematic phase.

Taking into account that the dipole interactions decrease very fast with the temperature, while the dispersion interactions do not change, one can assume that the more important role in mesophase stability determination is played by the dispersion forces. In fact, our investigations show that the frequencies

of the end and central atom bands in the limits of the error ($\sim 0{,}5\ cm^{-1}$) do not change at phase transition N-I, but those out of the plane skeletal vibration of the benzene ring (600–500 cm^{-1}) change about 1 cm^{-1}.[27] That the dispersion forces and thus the polarizability of the molecule determined the mesophase stability is indeed very likely. Many mesomorphic compounds contain benzene rings that are easily polarizable because of the presence of π-electrons. Haller and Cox,[20] investigating the connection between the dipole moment and polarizability on the one hand and the nematic mesophase stability of *p*-alkoxybenzylidene-*p*-amino-acetophenones on the other, reached the same results.

CONCLUSION

In the crystal phase the integral intensity of all bands does not change with temperature up to 20–40° below the phase transition C-N. The activation energy V_a for molecular transition from the lattice site into an interstitial one was determinated. Our results coincide very well with those of Bulkin, who investigated decrease of peak heights with temperature and thermodynamic data of Haller and Cox.

In the liquid crystal phase the bands corresponding to the benzene ring deformations do not change or slightly decrease with temperature but these of O—R and Ph—O decrease rapidly and have a behavior similar to that in the isotropic liquid. Having in mind the different temperature dependence of the integral intensity, a qualitative conclusion that dispersion forces prevail over the permanent dipole interaction in determination of mesophase stability was made.

These results demonstrate the power of infrared spectroscopy as a tool for the study of defect formation in the crystal phase, the intermolecular interactions in condensed phase, and their changes with temperature and phase transition.

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