Perturbations caused in the electronic structure of impurity molecules by the orientational order in a nematic liquid crystal

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The changes in the oscillator strengths and in the orientation of the moments of the electronic transitions of impurity molecules of azulene and biphenyl derivatives in a liquid-crystal matrix have been studied experimentally. A universal functional dependence of the oscillator strengths of various electronic transitions on the orientational-order parameter of the mesophase has been established. A phenomenological interpretation of this functional dependence is offered on the basis of an interaction of the order parameter of the liquid crystal with intramolecular degrees of freedom. A general approach to the analysis of the relative orientation of the moments of various intramolecular transitions in the mesophase is proposed. This analysis has been carried out for a sample system. Experiments confirm an earlier prediction of a change in the sign of the anisotropy of the local field tensor in a liquid crystal with a weak birefringence.

1. INTRODUCTION

A topic of considerable research interest in the physics of liquid crystals is the interrelationship between the conformational features and electronic structure of molecules with various types of order in the mesophase. Research on this topic may reveal the effect of the intramolecular degrees of freedom on the nature of phase transitions,[1] and it may make it possible to control transition temperature,[2] macroscopic linear and nonlinear optical properties of liquid crystals,[3] and textural and structural changes[4] through conformational conversions of molecules as a result of chemical substitution or photoexcitation. Here we are seeing a situation typical of the physics of liquid crystals: These effects are being exploited in dynamic holography[3] and information storage[4] even before a detailed study has been made of their features, and before principles for interpreting these effects have been developed on the basis of simpler model systems.

There has been no previous study of the perturbations caused in the electronic structure of molecules (in level positions, in the orientations of transition dipole moments, and in transition oscillator strengths) by the partial ordering of molecules in the mesophase. The extensive literature on the electronic absorption spectra of pure and impure liquid crystals includes determinations of the positions of bands and of the order parameter from measurements of the dichroic ratio $N_1 = D_{\parallel}/D_{\perp}$ of their optical densities; this ratio tells us nothing about the oscillator strength of the transition of interest. The positions of the absorption bands of liquid crystals, however, depend on the static[5] and resonant[6] intermolecular interactions and differ from the positions of molecular levels. To distinguish between these contributions and to determine oscillator strengths from data on the optical densities $D_{\perp,\parallel}$ it is necessary to obtain information about the anisotropy of the local field tensor $\mathbf{f}$ of the lightwave in the liquid crystal. Only very recently has a method been developed[7,8] for experimentally determining the components $f_{\parallel,\perp}$.

Study of the perturbations of the intrinsic electronic absorption spectrum of a liquid crystal is hampered by the experimental difficulties in obtaining polarized spectra from thin liquid-crystal films which have been put in a single domain and by the absence of information on the background values of the optical susceptibility in the bands of interest. This information is required for making accurate local-field corrections.[7] In the present work, in an effort to avoid these difficulties, we have studied the change in the electronic structure (the oscillator strengths and the orientation of the electronic transition moments) of four model impurity molecules in a liquid-crystal matrix with a broad spectral transparency region. In Sec. 2 we describe the systems studied. In Sec. 3 we report the results of measurements of the local-field parameters of the liquid-crystal matrix. These results, of interest in their own right, are also subsequently used to analyze the experiments. In Sec. 4 we develop, and apply to one of the systems studied, a general approach to the analysis of the mutual orientation of the moments of intramolecular transitions in uniaxial liquid crystals. In Sec. 5 we report the results of measurements of the oscillator strengths of electronic transitions in the impurity molecules which we have studied. We have observed various types of changes in the oscillator strengths with increasing orientational order of the mesophase. We offer a phenomenological interpretation of the results in which we incorporate the interaction of the order parameter of the liquid crystal with the intramolecular degrees of freedom.[2]

2. THE SYSTEMS STUDIED AND THEIR SPECTRAL CHARACTERISTICS

As the matrix we selected the liquid crystal CHCA, which is a mixture of cyclohexanecarboxylic acids with a nematic-phase interval between − 17 °C and 92.5 °C. This liquid crystal is convenient for several reasons. The broad mesophase interval makes it possible to study perturbations of the electronic structure of the molecules over a broad range of the order parameter, including the region of a pronounced nonlinear change (near T_c, the temperature of the phase transition from the nematic liquid crystal to an isotropic liquid) and the saturation region (far from T_c). CHCA has a broad transparency region (the long-wave absorption

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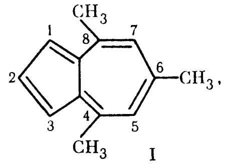
TABLE I. Temperature dependence of the characteristics of pure and impure CHCA liquid crystals: the refractive indices $n_{\|,\perp,i}$, the densities, the dichroic ratios $N_{1,2}$ of the absorption band at $\lambda_{\max} = 336$ nm of impurity molecule I, the component $L_\perp$ of the Lorentz tensor, and the normalized anisotropy of the local-field tensor **f**.

$T_c - T$, °C	λ=589 nm		λ=355 nm		ρ, g/cm³	N_1	N_2	$L_\perp$	$\Delta f/\bar{f}$, %
	$n_\|$	$n_\perp$	$n_\|$	$n_\perp$					
−0,2	1,441	1,441	1,443	1,443	0,920	1	1	0,333	0
1,0	1,461	1,435	1,462	1,436	0,922	—	—	—	—
2,5	1,465	1,434	1,468	1,435	0,923	1,200	0,943	0,340	0,4
5,0	1,469	1,435	1,473	1,436	0,925	1,255	0,925	0,341	0,7
8,0	1,473	1,435	1,477	1,436	0,926	1,286	0,925	0,342	0,6
10,0	1,475	1,436	1,479	1,437	0,929	—	—	—	—
12,5	1,477	1,437	1,482	1,437	0,931	—	—	—	—
15,0	1,479	1,437	1,483	1,438	0,933	1,306	0,925	0,345	0,3
20,0	1,483	1,439	1,487	1,440	0,936	—	—	—	—
27,0	1,487	1,440	1,491	1,441	0,942	1,347	0,925	0,345	0,4
36,0	1,493	1,444	1,497	1,445	0,949	1,378	»	0,345	0,6
42,5	1,496	1,445	1,499	1,446	0,954	1,408	»	0,346	0,4
47,5	1,498	1,447	1,502	1,448	0,957	1,429	»	0,344	1,0
56,5	1,502	1,450	1,506	1,451	0,964	1,449	»	0,346	0,7
61,5	1,504	1,451	1,508	1,452	0,967	1,469	»	0,347	0,4
65,7	1,506	1,453	1,510	1,454	0,970	1,469	»	0,350	0,4
72,5	1,509	1,455	1,513	1,456	0,975				

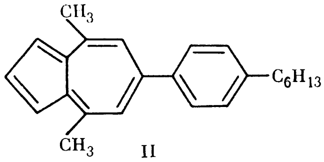
edge is at $\lambda \approx 200$ nm) and is compatible with a wide variety of impurities. The refractive indices $n_{\|,\perp,i}$ of the matrix, measured by an interference method[9] in the visible and UV regions, are listed in Table I. CHCA has a record low birefringence ($\Delta n = 0.04$ at $T_c - T = 10$ °C nad $\lambda = 589$ nm) in comparison with other known thermotropic nematic liquid crystals.[10] The weak optical anisotropy of the matrix significantly reduces the scattering of light by fluctuations of the director and increases the transparency of the matrix; the depolarizing effect of this scattering on the absorption spectrum of the impurity molecules is also reduced.

It was observed in Ref. 8 that the anisotropy $\Delta f = f_\| - f_\perp$ of the local-field tensor in nematic liquid crystals decreases rapidly with decreasing birefringence, and it was predicted that the sign of Δf might change from negative to positive in liquid crystals with small values of Δn. We were interested in testing this possibility in CHCA, with its extremely low value of Δn.

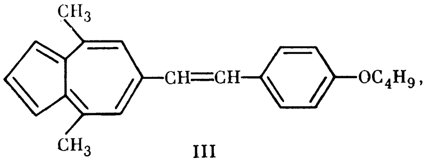
The guiding considerations in the choice of impurity molecules were as follows. Upon phase transitions in liquid crystals and changes in the order within the mesophase, the electronic structure of the molecules may change as a result of the specific intermolecular interactions of complex formation, the appearance of hydrogen bonds, etc.[11] Even in the absence of specific interactions, however, we would expect changes in the electronic structure of the molecules as a result of changes in the conformation of their aromatic skeleton. Such conformational changes, induced by the ordering of molecules in the mesophase, have been seen and are being studied by a variety of physical methods (see the review in Ref. 2). On the other hand, spectroscopic manifestations of conformational changes of the individual fragments making up mesogenic molecules have been recognized for a long time now and have been studied in detail in isotropic solvents.[12,13] Among the various possible conformational changes, the most pertinent are rotations of fragments of a molecule with respect to the single chemical bonds connecting these fragments; these rotations are far more favorable from the energy standpoint than changes in the valence angles or lengths of valence bonds.[14] If such rotations occur around the bonds in a π-electron conjugation of fragments, the change in conjugation has a marked effect on the oscillator strengths of electronic transitions in the molecular spectrum. We accordingly selected the following derivatives of azulene and biphenyl for the experiments:



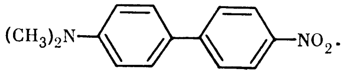
I



II



III



IV

Molecule I has a rigid aromatic ring screened by methyl groups, which reduce its solubility in the liquid-crystal matrix. In the visible and near-UV regions, the electronic spectrum of molecule I consists of two bands. The first is a broad, faint band with a maximum at $\lambda_{\max} = 548$ nm and with a molar extinction coefficient $\varepsilon_{i\,\max} = 280$ liter/(mole · cm) (in the isotropic phase of CHCA). This band corresponds to the first electronic transition of azulene ($\lambda_{\max} = 580$ nm, $\varepsilon = 330$; Ref. 13), which is polarized perpendicular to the 2–6 symmetry axis. The position of this band agrees well with the estimate of 542 nm found from the data of Ref. 13 on the hypsochromic shifts of the first band of azulene upon substitutions of 4-CH_3 or 8-CH_3 ($\Delta\lambda = -12$ nm) and 6-CH_3 (-15 nm) under the assumption that the spectral shifts during polysubstitution are additive.

The second band of molecule I, and intense doublet with $\lambda'_{\max} = 336$ nm ($\varepsilon'_i = 5196$) and $\lambda''_{\max} = 352$ nm ($\varepsilon''_i = 7216$), can be attributed to the doublet structure of the second electronic transition of azulene ($\lambda'_{\max} = 337$ nm, $\varepsilon'_{\max} = 4200$ and $\lambda''_{\max} = 342$, nm, $\varepsilon''_i = 4800$; Ref. 15), polarized along the 2–6 axis. The effect of substitutes on the positions and intensities of the first electronic transition of azulene is known[16] to result primarily from an inductive effect, which is confirmed by the correspondence between the calculated and measured positions of the first band of molecule I, while the inductive and mesomer effects of the substitute on the second electronic transition are comparable. Because of the symmetry of the methyl groups, a possible conformational rotation of these groups in the mesophase around their bonds with the carbon of azulene does not cause changes in their inductive or mesomer effects on the spectrum of molecule I. The oscillator strength of the second electronic transition of molecule I can therefore be assumed independent of the phase state of CHCA, and this transition can be utilized to measure the local-field tensor of the matrix by the method proposed in Refs. 7 and 8. Furthermore, molecule I is small enough that it does not perturb the structure of the liquid-crystal matrix.

Molecules II–IV are model molecules in the sense that their structures are similar to those of typical mesogenic molecules with biphenyl and stilbene aromatic skeletons, which are classical subjects of conformational analysis.[14] Furthermore, molecules II, III, and IV have one, two, and three single bonds, respectively, in their aromatic skeletons; a rotation around each of these bonds changes the π-electron conjugation of the fragments and the oscillator strengths of the electronic transitions of the skeleton.[12,13,16] If a change in the conformation of molecules II–IV in the mesophase of CHCA is possible, and if spectral manifestations of these changes are experimentally observable, we would expect an enhancement of the effects in the order II–IV in accordance with the increasing number of comformational degrees of freedom.

The spectra of molecules II–IV in the mesophase of CHCA were discussed in Ref. 17; in the present paper we will simply summarize their basic features at $\lambda > 300$ nm. In this part of the spectrum, molecules II–IV have a resolved structure and are represented by bands whose positions and intensities are listed in Table II for the isotropic phase of CHCA. The procedure for preparing the samples and that of the spectral measurements are similar to those of Ref. 9.

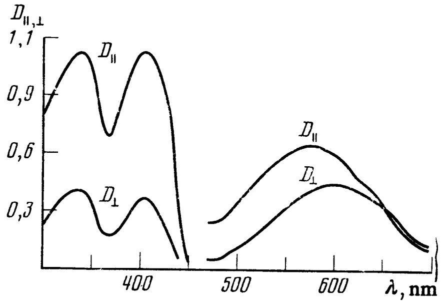


FIG. 1. Spectrum of the optical densities $D_{\parallel,\perp}$ of CHCA ($T = 20$ °C) with impurity molecule III at $\lambda < 460$ nm (cell thickness $d = 18.2\,\mu$m, impurity concentration $C = 0.02$M) and $\lambda > 460$ nm ($d = 68\,\mu$m, $C = 0.14$M).

The spectra of molecules II and III are similar (Fig. 1). The long-wave band of molecules II and III can be attributed to the first electronic transition of azulene, significantly perturbed by the substitutes in position 6. As we go from molecule I to II and III, this band shifts in a bathochromic manner by 17 and 42 nm, respectively. The intensity of this band changes less as we go from molecule I to II than from II to III (Table II). Significantly, the orientation of the transition moment also changes in the series I–III. While the transition in molecule I is polarized perpendicular to the long axis of the molecule, we find $D_{\parallel} \lesssim D_{\perp}$ in molecule II and $D_{\parallel} > D_{\perp}$ in molecule III (Fig. 1), and the transition is polarized predominantly along the long molecule axis. Consequently, the elongation of the conjugation chain of the skeleton in the series I–III leads to changes in three characteristics of the electronic transition localized in the azulene fragment: its energy, its intensity, and the orientation of its transition moment.

The positions of the maxima of the long-wave band in the variously polarized components of the spectrum in the nematic phase of CHCA are not the same (Fig. 1); the quantity $\Delta\lambda = \lambda_{\perp\max} - \lambda_{\parallel\max}$ is larger in molecule III than in molecule II, and in each case it increases with decreasing temperature of the mesophase. It is not yet clear whether this effect is due to a change in the perturbation of the electronic transition of the azulene fragment when the phase state of

TABLE II. Spectral characteristics of impurity molecules II-IV in the mesophase of CHCA: $\varepsilon_{i\max}$, the molar extinction coefficient of the band maximum in the isotropic phase; A_n/K and A_i/K, the normalized oscillator strengths found, respectively, through an extrapolation of the linear behavior in Fig. 4 to the value $S = 0$ and calculated from (2) and the experimental data for the isotropic phase; and $\varkappa$, the parameter in Eq. (15) which corresponds to the straight lines in Fig. 4.

Impurity	λ_{max}	$\varepsilon_{i\ max}$ [10^3 liter/ (mole · cm)]	max (A_i/A_H)	A_n/K (ex trap.)	A_i/K (expt.)	$\varkappa$
II	355	6,09	1,29	1,98	1,91	−0,454
	373	4,71	1,13	1,54	1,48	−0,291
	565	0,34	–	–	–	–
III	340	26,37	1,62	2,49	2,45	−0,689
	404	21,98	1,40	2,00	2,04	−0,425
	590	0,44	0,93	1,07	1,07	+0,216
IV	395	20,71	2,16	3,56	3,67	−0,886

the matrix changes, a difference in the statistical shifts of the observed absorption bands of the impurities in different spectral components,[5,6,17] or a complex vibron structure of the band. The resolution of these questions will require further experiments with impurities II and III in liquid-crystal matrices of different polarities and with homologs of molecules II and III with alkyl chains of various lengths.[6,17,18] We will accordingly analyze only the intensity and orientation of the moment of this transition in the mesophase of CHCA.

Two other pairs of bands of molecules II and III are difficult to identify with the second electronic transition of the azulene fragment, although the positions of the maxima of the short-wave bands differ only slightly from the corresponding values for azulene and molecule I. As we go from molecule I to II, we find that a new band appears at 373 nm, and as we go from II to III we observe, along with a bathochromic shift of this band, an enhancement of both bands by a factor of 4.5 (Table II). Both pairs of bands in molecules II and III are polarized along the π-electron conjugation chain of the skeleton. A similar bathochromic shift of the bands and an increase in their intensity upon an elongation of the π-conjugation bond are characteristic of electronic transitions in a system of π-conjugate fragments. Accordingly, both pairs of short-wave bands in molecules II and III can be attributed to excitations of the π-electron system of the entire aromatic skeleton.

The position and intensity of the long-wave band of molecule IV agree with data in the literature[11,12] for this system, and this band is identified as an electronic excitation of a π-conjugate system of the entire molecule, polarized along its long axis.

In summary, the use of molecules II and IV makes it possible to study perturbations of electronic transitions caused by both individual fragments of the molecules and the collectivized system of π-electrons, spanning several fragments of the aromatic skeleton.

3. LOCAL FIELD OF A LIGHT WAVE IN A LIQUID-CRYSTAL MATRIX

Molecules I–IV are lath-shaped. In analyzing the polarization spectral characteristics, we will accordingly take into account the possibility of a retarded rotation of these molecules around the longitudinal axis. We assume that the z and y axes of the molecular coordinate system lie in the plane of the lath and coincide with the long and intermediate axes of the molecule, respectively. In a uniaxial liquid crystal, the orientational order of the molecular axes with respect to the director, which coincides with Z axis, is described by the traceless diagonal matrix[10]

$$S_{ii}=\langle 3\cos^2\theta_{iz}-1\rangle/2, \qquad i=x,\ y,\ z. \tag{1}$$

In the case of a retarded rotation of the molecule around their longitudinal axes, the parameter $G=S_{yy}=S_{xx}$ is nonzero and describes the two-axis nature of the molecular tensor S_{ii}. Introducing the Euler angles $\theta=\theta_{zZ}$ and ψ, which describe the orientation of the long molecular axis with respect to the director and the rotation of the molecule around its long axis, we find from (1) $G=\langle 3\sin^2\theta\cos 2\psi\rangle/2$. If the polarization of the electronic transition of interest in the molecular system is fixed by the polar angle β and the azimuthal angle ϕ, the measured optical densities of the sample in a uniaxial liquid crystal ($D_{\parallel,\perp}$) and in an isotropic liquid (D_i) are related to the corresponding components of the oscillator strength, $A_{\parallel,\perp}$, by[8]

$$\begin{aligned} &K\frac{n_\parallel}{\rho f_\parallel^2}D_\parallel=A_\parallel=\frac{A_{\text{н}}}{3}\left(1+2SS_\beta-\frac{2}{3}GG_{\beta\varphi}\right),\\ &K\frac{n_\perp}{\rho f_\perp^2}D_\perp=A_\perp=\frac{A_{\mathrm{n}}}{3}\left(1-SS_\beta+\frac{1}{3}GG_{\beta\varphi}\right),\\ &K\frac{n_i}{\rho_i f_i^2}D_i=\frac{A_i}{3}. \end{aligned} \tag{2}$$

Here $K=\text{const}$; $n_{\parallel,\perp,i}$ are the background values of the refractive index in the part of the absorption band under study (in the case of impurity absorption, these would be the refractive indices of the matrix); ρ and ρ_i are the densities of the nematic and isotropic phases; $A_{n,i}$ are the oscillator strengths of the transition of interest in the nematic and isotropic phases;

$$\begin{gathered} S_\beta=(3\cos^2\beta-1)/2, \qquad G_{\beta\varphi}=(3\sin^2\beta\cos 2\varphi)/2,\\ f_{\parallel,\perp}=1+L_{\parallel,\perp}(n_{\parallel,\perp}^2-1) \end{gathered} \tag{3}$$

are the components of the local-field tensor; and $L_{\parallel,\perp}$ are the components of the Lorentz tensor ($\mathrm{Sp}\mathbf{L}=1$).

With the molecules in the cell in a planar orientation, we measure the dichroic ratios $N_1=D_\parallel/D_\perp$ and $N_2=D_\perp/D_i$. If the oscillator strength of the transition of interest does not depend on the phase state, i.e., if $A_n=A_i$, then both ratios $N_{i,2}$ can be used to determine the parameter

$$\Sigma=SS_\beta-{}^1/_3GG_{\beta\varphi}, \tag{4}$$

which depends on the orientational order of the molecules and on the intramolecular properties. From (2) we find

$$\Sigma_1=(N_1g_1-1)/(N_1g_1+2), \qquad \Sigma_2=1-N_2g_2, \tag{5}$$

where

$$g_1=\frac{n_\parallel}{n_\perp}(f_\perp/f_\parallel)^2, \qquad g_2=(\rho_i n_\perp/\rho n_i)(f_i/f_\perp)^2. \tag{6}$$

From the solution of the system of equations

$$\Sigma_1=\Sigma_2, \qquad \mathrm{Sp}\,\mathrm{L}=1 \tag{7}$$

we find the actual values of the components $L_{\parallel,\perp}$ in the mesophase.[7,8]

The components $L_{\parallel,\perp}$ in CHCA have been determined with the help of the dichroic ratios $N_{1,2}$ for the doublet band of the second electronic transition of impurity I. The values of $N_{1,2}$ are identical for both components of the doublet. The parameters required for the calculations from Eqs. (5)–(7) are listed along with the results of these calculations in Table I. The experimental values of $L_{\parallel,\perp}$ and $f_{\parallel,\perp}$ show that the anisotropy Δf in the liquid-crystal matrix is slight. This result justifies the suggestion, made previously in connection with nematic[19] and cholesteric[20,21] liquid crystals, that the anisotropy of the tensor $\mathbf{f}$ would be slight in a liquid crystal with a small optical anisotropy. The values found for $L_\perp$ agree well with the dependence $L_\perp(\Delta n)$ established in Ref. 8 for several liquid crystals with molecules of various chemical structures. We see from Table I that the anisotropy Δf is positive over the entire mesophase region, so that we are seeing here the change in the sign of Δf from negative to positive in a liquid crystal with a small optical anisotropy, which was predicted in Ref. 8. The tabulated values of $L_\perp$ have been used to analyze experimental data on other impurity molecules in CHCA. It can be seen from Table I that the dispersion of the refractive indices of the matrix is negligible in the absorption region of impurities II–IV. The dispersion of the components $f_{\parallel,\perp}$ in (3) within the bands studied is similarly small. Consequently, we have used the values of $D_{\parallel,\perp,i}$ and of the components $f_{\parallel,\perp,i}$ corresponding to the maxima of the observed absorption bands to determine the parameters Σ and the normalized oscillator strengths $A_{n,i}/K$.

4. ANALYSIS OF THE POLARIZATION OF ELECTRONIC TRANSITIONS WITH RESPECT TO MOLECULAR AXES IN THE MESOPHASE

Let us examine the possibilities of polarized spectral measurements in a study of the polarization of intramolecular electronic or vibrational transitions with respect to molecular axes. It can be seen from (2) that in order to determine the parameter Σ we should use the dichroic ratio N_1, which does not depend on a possible change in A_n in the mesophase. The values of the parameters Σ for different molecular transitions differ only in the values of S_β and $G_{\beta\phi}$. If we assume as usual[10] $S \gg G$, then the ratio $\Sigma(i)/S$, with known values of S, would determine the angle $\beta(i)$ describing the orientation of the moment of the ith transition with respect to the long axis of the molecule. With constant values of $\beta(i)$ and $\beta(j)$ in the mesophase, the ratios $\Sigma(i)/\Sigma(j)$ should be temperature-independent. In the general case with $\beta(i) \neq 0$ and $G_{\beta\phi}(i) \neq 0$, however, this approach should be too crude for an analysis of possible changes in the parameters $S_\beta(i)$ and $G_{\beta\phi}(i)$ in the mesophase, and we should use the complete expression (4) for Σ. From (4) we find a relation among the temperature-dependent quantities $\Sigma(i)$ for three arbitrary transitions in the molecular spectrum:

$$\Sigma(1)/\Sigma(3) = B\Sigma(2)/\Sigma(3) + C. \qquad (8)$$

If the orientation of the moments of these transitions with respect to the molecular axes does not change in the mesophase, the coefficients B and C will be temperature-independent. Since expression (4) reflects only the uniaxial symmetry of the mesophase, for a constant orientation of the moments the linear dependence in (8) should not change at the nematic-smectic A phase transition or after the transition, in the smectic phase, when the orientational and translational order change. A deviation from the linearity in (8) may be evidence of a change in the orientation of the transition moments in the molecular system.

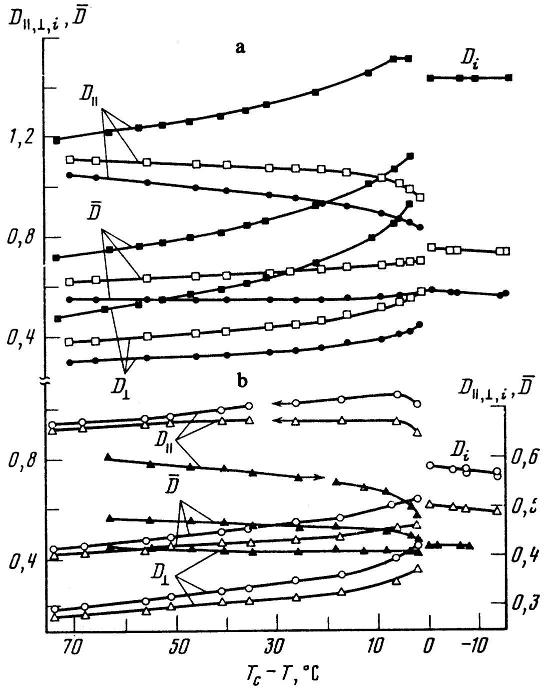


FIG. 2. Temperature dependence of the optical densities $D_{\parallel,\perp,i}$ of the sample in the impurity absorption band. a: □—Impurity molecule II, $\lambda_{\max} = 365$ nm; ●—II, 373 nm ($d = 43$ μm, $C = 0.029$M); ■—IV, $\lambda_{\max} = 395$ nm, $d = 70$ μm, ($C = 0.01$M). b: ○—Impurity molecule III, $\lambda_{\max} = 340$; △—III, 404 nm, ($d = 18$ μm, $C = 0.02$M); ▲—III, $\lambda_{\max} = 590$ nm, $d = 68$ μm, ($C = 0.14$M). The numbers on the scale should be shifted one division downward for part b.

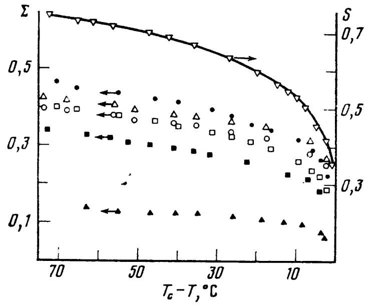


FIG. 3. Temperature dependence of the parameters Σ for electronic transitions of impurity molecules II–IV in the CHCA matrix; macroscopic order parameters S of the matrix. The solid line shows a calculation from Eq. (10). The notation is the same as in Fig. 2, a and b.

Let us take this approach to analyze the experimental data on molecules II-IV in the CHCA matrix. Figure 2, a and b, shows the temperature dependence of the optical densities $D_{\parallel,\perp,i}$ of the mixtures studied in the vicinity of the impurity absorption bands. The parameters Σ found from the dichroic ratios N_1 and expressions (5) and (6) are shown in Fig. 3. For impurity III the ratio $\Sigma(1)/\Sigma(2)$ for the two short-wave bands at 404 (1) and 340 nm (2) varies nonmonotonically with the mesophase temperature. Specifically, it increases from 1.06 ($\Delta T = 74$ °C) to 1.12 ($\Delta T = 6.5$ °C) and then decreases to 1.07 near T_c. A similar behavior is observed for the corresponding pair of bands of impurity II. The ratios $\Sigma(1)/\Sigma(3)$ and $\Sigma(2)/\Sigma(3)$ (transition 3 corresponds to the band at 590 nm) for impurity III then increase from 2.9 and 2.7, respectively ($\Delta T = 68$ °C) to 4.1 and 3.64 ($\Delta T = 3.5$ °C). If we ignored the second term on the right side of (4), these facts would indicate a significant change in the parameters S_β for these transitions. However, a test of relation (8) for the three bands of impurity III shows (see the inset in Fig. 4) that the coefficients $B = 1.28$ and $C = -0.56$ do not change

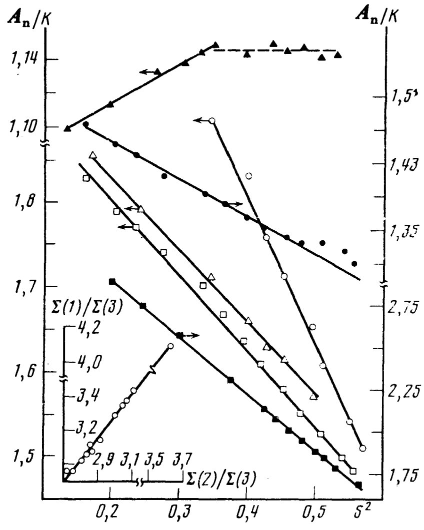


FIG. 4. The reduced oscillator strengths A_n/K, from (11), for electronic transitions of impurity molecules II–IV versus S^2. The notation is the same as in Fig. 2, a and b. The inset shows the ratio $\Sigma(1)/\Sigma(3)$ versus $\Sigma(2)/\Sigma(3)$ for the 404-nm (1), 340-nm (2), and 590-nm (3) transitions of impurity molecule III in the mesophase of CHCA.

with the temperature. Consequently, it is important to take into account the two-axis nature of the molecular tensor S_{ii} in analyzing the polarization of transitions.

It is interesting to compare the results found for the parameters Σ with the macroscopic order parameter of the matrix,

$$S=(n_{\parallel}{}^2-n_{\perp}{}^2)/(n_{\parallel}{}^2-n_{\perp}{}^2)_{max}, \tag{9}$$

where $(n_{\parallel}^2-n_{\perp}^2)_{\max}$ corresponds to the value $S=1$. Analysis of the data in Table I shows that the temperature dependence of the anisotropy $\Delta=n_{\parallel}^2-n_{\perp}^2$ can be approximated well over the entire temperature interval studied, $T_c-T=1$–75 °C, by

$$\Delta=\Delta_{max}(1-T/T_1)^{\beta}, \tag{10}$$

where the parameter values $T_1=T_c+0.3$ °C and $\beta=0.177$ do not depend on the wavelength λ at which $n_{\parallel,\perp}$ are measured; for $\lambda=589$ nm, we have $\Delta_{\max}=0.216$. Figure 3 shows values of S. Since the anisotropy of the local field of the matrix is small, expression (9) also determines the average degree of order of the matrix molecules.[8] There are significant discrepancies between the values of S and Σ. In estimating the values of the parameters S_{imp} and G_{imp} for the elongated impurity molecules of type II and III, we can set $S_{\text{imp}}\gg G_{\text{imp}}$ in (4) (Ref. 10). Furthermore, for the transition of interest in molecule IV we have $S_{\beta}=1$ and $G_{\beta\phi}=0$. The difference between D and Σ (aside from the 590-nm transition in molecule III) should thus be attributed to the relative disorder of the impurity molecules in comparison with the matrix molecules.

5. CHANGE INDUCED IN THE OSCILLATOR STRENGTHS OF ELECTRONIC TRANSITIONS BY THE ORIENTATIONAL ORDER OF THE MOLECULES IN THE MESOPHASE

Returning to the analysis of Fig. 2, a and b, we note that the temperature dependence of $D_{\parallel}$ is anomalous for the absorption bands of impurity molecules III and IV. Instead of the decrease in $D_{\parallel}$ with decreasing Σ (at $A_n=$ const) expected on the basis of (2), we see that $D_{\parallel}$ remains constant or increases toward T_c; the average optical density is $\overline{D}=(D_{\parallel}+2D_{\perp})/3<D_i$. This anomaly becomes more pronounced as we go from molecule II to molecule IV, i.e., as we increase the number of intramolecular conformational degrees of freedom. Because of the insignificant relative change in the parameters $n_{\parallel,\perp}$, $f_{\parallel,\perp}$ and ρ in (2), this behavior of $D_{\parallel}$ and $\overline{D}$ is evidence of a decrease in the oscillator strengths A_n of the corresponding transitions with increasing orientational order of the mesophase. Furthermore, we see from Fig. 2b that for the absorption band at $\lambda_{\max}=590$ nm of impurity molecule III there is a slight increase in $D_{\perp}$ with increasing Σ instead of the decrease expected on the basis of (2), and here we find $\overline{D}>D_i$, which may indicate an increase in A_n.

On the basis of the experimental data available, we can determine the normalized oscillator strengths

$$\frac{A_n}{K}=\frac{1}{\rho}\left(\frac{n_{\parallel}}{f_{\parallel}{}^2}D_{\parallel}+\frac{2n_{\perp}}{f_{\perp}{}^2}D_{\perp}\right), \tag{11}$$

working simply from the measured parameter value resorting to any model. The effects of a change in A_n/K mentioned above differ in magnitude for the different impurities and also for the different bands of a given impurity. Table II shows the maximum value of the ratio A_i/A_n of the parameters found from (2) and (11). The greatest effect is observed for the transition in IV, which has the longest π-conjugation chain. With decreasing length of the π-conjugation chain, in molecules III and II, the amplitude of the change in A_n within the mesophase decreases rapidly. For the long-wave transition in III, localized in an azulene fragment and more sensitive to the inductive effect of the substitutes,[16] the change in A_n is small and has the sign opposite that for the other transitions in III and the transitions in II and IV.

The microscopic reasons for the changes in the parameters A_n are not yet clear. We can, however, point out that the significant changes observed in the intensities of bands with a slight change in the band positions (these position changes were not observed experimentally for molecules II-IV) are characteristic of cases in which the conformational rotations of the fragment around the bonds connecting them weaken the π-electron conjugation of the molecules.[12,13] On the other hand, we see from Fig. 2, a and b, that the temperature dependence $\overline{D}(\Delta T)$, the temperature dependence $D_i(\Delta T)$, and the signs of the derivatives $d\overline{D}/dT$ and dD_i/dT are substantially different in the nematic and isotropic phases of CHCA. For this reason, the observed changes in A_n are due to the appearance of a macroscopic long-range orientational order in the system, not a change in the density of the medium.

We can offer a phenomenological interpretation of the experimental data, derived from an interaction of the order parameter of the system with noncritical intramolecular degrees of freedom.[2] Corresponding to these degrees of freedom are the generalized coordinates Q_k ($k=1, 2, \ldots$), which may, in particular, also describe changes in the conformation of the molecular fragments. For a relative rotation of two fragments through an angle ϕ around the single chemical bond connecting the two fragments, for example, we would have[2] $Q = \cos^2\phi$. A change in the parameters Q_k is accompanied by a change in the molecular properties and in the particular features of the intermolecular interaction, which affect the temperatures of the phase transitions and the degree or orientational order of the system.[2-4] There is accordingly an interaction of the parameters Q_k with the tensor order parameter of the liquid crystal, $S_{\alpha\gamma} = S(n_\alpha n_\gamma - \delta_{\alpha\gamma}/3)$ ($n_{\alpha,\gamma}$ are the components of the director $\mathbf{n}$), and the optimum values of Q_{ki} (in the isotropic phase) differ from those of Q_{kn} (in the nematic phase). The invariant terms of the interaction are proportional in lowest order to the products $Q_k\,\mathrm{Sp}(\mathbf{S}^2)$, and the corresponding increments in the free-energy density of the nematic liquid crystal are

$$\Delta F_{SQ_k} = -\lambda_k \Delta Q_k S^2, \tag{12}$$

where the parameters λ_k may be either positive or negative. A molecular contribution to the energy of the mesophase comes from the terms

$$\Delta F_{Q_k} = (\Delta Q_k)^2/2\chi_k, \tag{13}$$

where χ_k are the susceptibilities of the molecule with respect to a change in Q_k. Minimizing the sum of the terms in (12) and (13), we find

$$\Delta Q_k = \lambda_k \chi_k S^2. \tag{14}$$

In general, the oscillator $A = A(Q_k)$ of any electronic transmission of a molecule is a complicated function of the parameters Q_k, and this functional dependence is not known at the outset. Expanding this function in a series in ΔQ_k around $Q_k = Q_{ki}$, and restricting the discussion to the linear approximation, we find, using (14),

$$A_n = A_i(1 + \varkappa S^2), \tag{15}$$

where the parameter $\varkappa$ can be either positive or negative. In deriving (15) we did not specify the miscroscopic reasons for the changes in the parameters Q_k or the nature of the transition in question.

Figure 4 shows experimental values of A_n/K for the transitions studied vesus the square of the macroscopic order parameter S (Fig. 3). These plots are linear, in agreement with (15), over the entire mesophase interval. The values of A_n/K extrapolated to $S = 0$ agree well with the experimental values of A_i/K (Table II). Systematic deviations from linearity are observed only for the bands at 590 nm (molecule III) and 373 nm (molecule II), far from T_c. These deviations may be caused by a violation of the condition $\chi_k = \text{const}$, and they may correspond to the more probable case in which χ_k decreases with distance from T_c.

The parameter $\varkappa$ is a measure of the extent to which the electronic structure of the impurity molecules is perturbed by the orientational order of the matrix. We see from Table II that this parameter increases in absolute value with increasing length of the conjugation chain as we go from molecule II to IV, or it increases with decreasing wavelength of the electronic transition for molecule II or III. For the long-wave transition of molecule III localized in an azulene fragment, the parameter $\varkappa$ has the sign opposite that for other transitions in molecule III. It is important to note that the values of the parameters $\varkappa$ for all the transitions studied differ significantly less in magnitude than do the oscillator strengths of these transitions, and there is no correlation between the oscillator strength of a transition and its perturbation in the mesophase. Accordingly, perturbation mechanisms involving the polarization interaction of the excited impurity molecules with the matrix[11] are improbable in this case. On the other hand, the fact that we are far from the spectral region of intrinsic absorption of the matrix rules out a mechanism involving the mixing of molecular configurations of the impurity due to a reasonant interaction with the matrix.

This set of experimental results and their analysis indicate a change in the conformation of the impurity molecules in the mesophase as the most probable reason for the observed effects. The constancy of the orientation of the transition moments of impurity molecule III in the mesophase, mentional above, results from the circumstance that the two short-wave transitions of molecule III are polarized along the conjugation axis, which makes a small angle with the axes of possible rotations of the fragments around the single chemical bonds of the skeleton. The perturbation of the long-wave transition of molecule III in the mesophase is small in comparison with its perturbation as we go from molecule II to III (cf. the values of the parameter ε_i), so that the experiments also do not reveal a possible change in the parameters S_β and $G_{\beta\phi}$ for this transition. The signs of the changes in the angles ϕ_k through which the fragments of one molecule or of different molecules rotate are determined by the particular features of the intermolecular interaction in the mesophase, especially close-packing effects. In molecule IV, for example, the fragment $N(CH_3)_2$ is nonplanar, and a minimization of the energy of the steric intermolecular interaction can be achieved by rotating this fragment around the bond connecting it to the benzene ring. Such a rotation is known[12,13] to lead to the same spectral changes as were observed above for this molecule in the CHCA matrix.

We note in conclusion that the approach developed above could be used to analyze the changes in the orientation of moments and in the oscillator strengths of vibrational transitions in mesogenic molecules. It would be interesting to see similar studies for the nematic-smectic A phase transition and for phase transitions between different metastable states of uniaxial vitrified phases of liquid crystals. Finally, as part of the study of the conformation changes of complex molecules and for practical applications, it would be interesting to use this approach in analyzing the electrooptical and spectral properties of the new class of T-, h-, and H-shaped dyes with spatially separated chromophores.[22,23]

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