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AN EXPERIMENTAL STUDY OF DIELECTRIC PROPERTIES OF NEMATIC LIQUID CRYSTALS

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Dielectric properties of three successive members of the azomethine homologous series are considered in the liquid crystal and isotropic phases. Experimental values are presented for the relaxation time and the dipole relaxation activation entropy and enthalpy.

The majority of published data on dielectric properties of compounds which possess a liquid crystal phase concerns materials with low dielectric anisotropy and transition temperatures for the liquid crystal—isotropic liquid transition far removed from room temperature.

Practical requirements have recently stimulated the synthesis of series of new liquid crystal compounds with a mesophase region near room temperature. A typical representative of this group is p-methoxybenzylidene-p-butylaniline, a member of the azomethine group, the dielectric properties of which have been studied in the radiofrequency and uhf ranges [1-3].

To systematize data on the dielectric characteristics of azomethines we have studied the dielectric properties and calculated certain characteristics of the molecular motion of three members of the homologous azomethine series in the liquid crystal and isotropic liquid phases.

We have studied p-methoxybenzylidene-p-butylaniline (MBBA), p-ethoxybenzylidene-p-butylaniline (EBBA), and p-propoxybenzylidene-p-butylaniline (PBBA) in the radiofrequency and uhf ranges.

The mesophase transition temperatures of these compounds are presented in Table 1.

All the materials studied were produced by methods described in the literature at the All-Union Scientific-Research Institute of Reagents and Special Purity Materials (IREA). The electrical conductivity of the compounds produced was not more than 10^{-9} $\Omega^{-1}\cdot\mathrm{cm}^{-1}$ in the isotropic phase. The impurity content did not exceed 3 mol. %.

The dielectric characteristic measurements in the radiofrequency range were performed with a specially designed low-volume cell and "Tangens-2M" measurement apparatus. The gap between the cell electrodes did not exceed 3 mm. The cell capacitance was 3.2 pF. The error in ε' did not exceed 0.6% and was not greater than 6-7% in ε'' determination in the relaxation range.

Measurements of ε' and ε'' in the uhf range were performed by the cylindrical rod method. The error in ε' determination did not exceed 2%, and in ε'' determination it was not more than 8%.

Temperature was stabilized to an accuracy of ±0.05°.

Experiments were performed over the temperature range 290-355°K and in a magnetic field of intensity up to 4500 G. The experiments revealed that in the rf and uhf ranges in fields of about 2000 G almost complete saturation of ε' and ε'' occurred.

Within the limits of experimental error the results of the MBBA experiments agreed with data in the literature [1-2]. The experimental results were compared with the data from the

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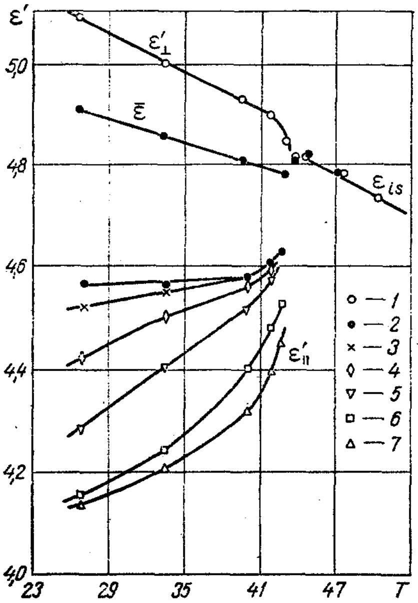


Fig. 1

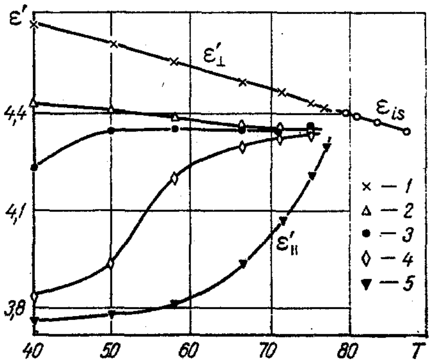
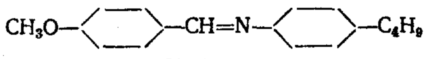
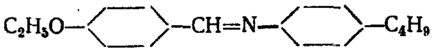
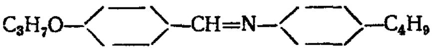


Fig. 2

Fig. 1. Basic dielectric permittivity values $\varepsilon'_\parallel$, $\varepsilon'_\perp$ versus temperature and frequency for MBBA. For B perpendicular to E: 1) f = 0.1-10 MHz; for B parallel to E: 2) f = 0.1 MHz; 3) 0.5; 4) 1.1; 5) 2; 6) 5; 7) 10 MHz. $\bar\varepsilon = (2\varepsilon'_\perp + \varepsilon'_\parallel)/3$; T, °C.

Fig. 2. Basic dielectric permittivity values $\varepsilon'_\parallel$, $\varepsilon'_\perp$ versus temperature and frequency for EBBA. For B perpendicular to E: 1) f = 0.1-10 MHz; for B parallel to E: 2) f = 0.1 MHz; 3) 0.5; 4) 2; 5) 10 MHz.

TABLE 1. Structural Formulas and Transition Temperatures of the Compounds Studied

Structural formula	Melting point, °C	Clarification point, °C
MBBA 	22	44
EBBA 	36	78
PBBA 	39,5	56,5

literature by comparing static values of $\varepsilon'_s\|$, $\varepsilon'_\infty\|$ due to the absence of data on dielectric characteristics in the dispersion region at the frequencies used. The $\varepsilon'_s\|$, $\varepsilon'_\infty\|$ values were obtained by processing the dispersion curve.

For the remaining compounds the present study was the first to produce results over such a wide frequency range.

The behavior of the azomethine dielectric characteristics in the rf range is shown in Figs. 1, 2.

For all the compounds studied a low-frequency dispersion region was observed for the basic $\varepsilon'\|$ values, as illustrated in Figs. 1 and 2, with a characteristic dipole relaxation time of the order of 10^{-7}-10^{-8} sec, as calculated by the Cowl—Cowl relationships, which satisfactorily describe the experimentally observed function $\varepsilon' = \varphi(\varepsilon'')$. The parameter values

TABLE 2. Characteristics of Dipole Relaxation Process

T, °K	$\tau \cdot 10^{6}$, sec	$\varepsilon'_{s\parallel}$	$\varepsilon'_{\infty\parallel}$
In MBBA (ΔH=101,4 kJ/mol; ΔS=226,8 J/mol·deg)			
299,95	0,0880	4,564	4,096
306,65	0,0518	4,573	4,115
313,05	0,0239	4,594	4,144
315,00	0,0152	4,615	4,157
In EBBA (ΔH=64,2 kJ/mol; ΔS=88,54 J/mol·deg)			
313,65	0,1814	4,444	3,750
323,45	0,0835	4,414	3,748
331,55	0,0441	4,354	3,726
339,95	0,0247	4,339	3,727
In PBBA (ΔH=93,6 kJ/mol; ΔS=201 J/mol·deg)			
314,55	0,0961	4,530	3,682
320,65	0,0615	4,475	3,708
326,25	0,0322	4,447	3,720
328,45	0,0252	4,435	3,739

as calculated from the Cowl – Cowl diagram are presented in Table 2.*

The theory of absolute reaction rates was used to determine the enthalpy and entropy of dipole relaxation activation from the experimentally calculated function $\tau = f(T)$.

An insignificant (within the limits of processing error) change in these parameters with temperature was noted. The high values of activation enthalpy, significantly exceeding such values in normal liquids [4], indicates the significant correlation of molecules in the oriented mesophase.

The high $\varepsilon'_\parallel$ values outside the low-frequency dispersion region and the increase in $\varepsilon''_\parallel$, $\varepsilon''_\perp$ losses with growth of temperature suggest the presence of at least one more dispersion region for each of the above quantities in the higher frequency range. Using the data on $\varepsilon^*_\parallel$, $\varepsilon^*_\perp$ in the uhf range with the assumption of Debye relaxation in this region, we calculated the dipole relaxation times, and these proved to lie in the range of hundreds of picoseconds, characteristic of a normal liquid [4]. The similarity of the values obtained for the different relaxation processes ($\varepsilon^*_\parallel$, $\varepsilon^*_\perp$, ε^*_{is}) permits the assumption that the mechanism of thermal motion in the mesophase with times of the order of 10^{-10} sec is close to the mechanism of thermal motion in the isotropic phase. Such motions may be related to rotation of molecules about their axes.

The significant braking in molecular motions in the mesophase, leading to relaxation times of 10^{-7}–10^{-8} sec, is related to dipole interaction in the mesophase as compared to the isotropic liquid, which can significantly affect rotation of molecules about their short axes.

We note that for all the azomethines a change in the sign of the anisotropy occurs in the frequency range of 10^{10} Hz. In the isotropic liquid it was observed that with increase in the number of carbon atoms the dielectric permittivity decreases.

NOTATION

$\varepsilon'_\parallel$, $\varepsilon'_\perp$, basic values of dielectric constant; ε'_∞, dielectric constant values at high frequency limit of dispersion region; τ, dipole relaxation time; ΔH, ΔS, enthalpy and entropy of dipole relaxation activation; f, frequency; ε_{is}, dielectric constant in isotropic phase.

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*Since the relaxation time spectrum is broadened only insignificantly upon approach to the transition point, the calculated values agree with values obtained with the Debye equations.