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Dielectric Properties of 4-(2,3-Epoxypropoxy)- and 4-Propoxy-4'-alkoxyazoxybenzenes

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Abstract—The temperature dependences of the dielectric permittivity of 4-(2,3-epoxypropoxy)-4'-alkoxyazoxybenzenes (n = 1–10) and 4-propoxy-4'-alkoxyazoxybenzenes (n = 1–10) with mesomorphic properties were measured by dielectrometry. The introductrion of the terminal epoxy group increases the dielectric permittivity and its anisotropy. The dipole moments of molecules of 4-(2,3-epoxypropoxy)-4'-alkoxyazoxybenzenes (n = 1–10) and 4-propoxy-4'-alkoxyazoxybenzenes (n = 1–10) were determined by the second Debye method. The epoxy-substituted azoxybenzenes have higher dipole moments than their structural analogs.

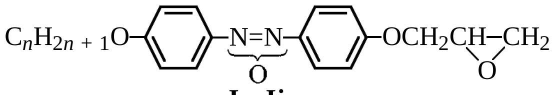
Previously [1, 2] we have studied the effect exerted by the epoxy ring on the volume and optical properties of mesogenic azoxybenzenes. It was shown [1] that introduction of this substituent increases the density of the short-chain homologs (n = 1–5) of disubstituted azoxybenzenes, whereas the density of higher homologs decreases. In addition, the epoxy ring leads to increased jumps of the molar volumes in the nematic–isotropic liquid phase transition and raises the amplitude of the even–odd alternation. At the same time, the introduction of the relatively rigid terminal glycidyl substituent results in less compact packing of azoxybenzene molecules.

As in the case of volume parameters, the introduction of the epoxy ring substantially increases the anisotropy of molecular polarizability of the short-chain (n = 1–5) homologs, whereas lengthening of the chain of the alkoxy substituent levels out this effect. It was also shown that introduction of the glycidyl substituent only slightly affects the orientation order parameters of azoxybenzenes.

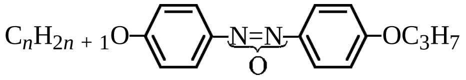
However, to make unambiguous conclusions about the supramolecular structure of the disubstituted azoxybenzenes under consideration, it is necessary to study how the epoxy ring affects their anisotropic dielectric properties. The anisotropy of dielectric permittivity depends on the polarizability of the molecule, its dipole moment, degree of ordering, and the angle between the dipole moment vector and the maximal polarizability axis.

As the liquid crystals under consideration contain no highly polar groups, their dielectric anisotropy should be small [3, 4]. At the same time, as the orientation of the epoxy ring may vary because of the rotation around the axes of the C–O and C–C σ bonds, it is impossible to consider the specific effects of this substituent on the dielectric properties. In addition, it should be noted that we found no data on the behavior of epoxy-containing mesogens in the electric field.

Therefore, we measured the dielectric permittivity of 4-(2,3-epoxypropoxy)-4'-alkoxyazoxybenzenes **Ia**–**Ij** and 4-propoxy-4'-alkoxyazoxybenzenes **IIa**–**IIj** within the temperature intervals of existence of nematic and isotropic liquid phases [5].



Ia–**Ij**



IIa–**IIj**

n = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**), 5 (**e**), 6 (**f**), 7 (**g**), 8 (**h**), 9 (**i**), 10 (**j**).

The temperatures of the nematic–isotropic phase transition in compounds **I** and **II** are listed in Table 1. The temperature dependences of the dielectric permittivity are given in Tables 2 and 3.

Table 1. Nematic–isotropic liquid phase transition temperatures of 4-(2,3-epoxypropoxy)-4'-alkoxyazoxybenzenes **Ia**–**Ij** and 4-alkoxy-4'-propoxyazoxybenzenes **IIa**–**IIj**

Comp. no.	t_{NI}, °C	Comp. no.	t_{NI}, °C	Comp. no.	t_{NI}, °C	Comp. no.	t_{NI}, °C
Ia	121.2	**If**	131.4	**IIa**	113.8	**IIf**	123.4
Ib	124.8	**Ig**	122.1	**IIb**	144.1	**IIg**	118.4
Ic	125.0	**Ih**	126.3	**IIc**	121.5	**IIh**	117.7
Id	135.5	**Ii**	122.3	**IId**	129.4	**IIi**	115.2
Ie	128.7	**Ij**	123.4	**IIe**	120.6	**IIj**	118.1

Table 2. Temperature dependence of the dielectric permittivity of 4-(2,3-epoxypropoxy)-4'-alkoxyazoxybenzenes **Ia**–**Ij**

T, °C	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$
	Ia		**Ib**		**Ic**		**Id**		**Ie**	
116	9.08	9.90	7.26	10.95	7.42	8.16	4.14	5.08	6.59	8.26
118	9.31	9.82	7.28	12.69	7.42	8.08	4.15	5.06	6.56	8.17
120	9.57	9.74	7.31	14.97	7.42	8.01	4.18	5.03	6.55	8.08
122	9.68	9.66	7.34	9.77	7.42	7.88	4.22	4.99	6.56	8.00
124	9.61	9.60	7.35	8.67	7.44	7.69	4.26	4.94	6.57	7.93
126	9.55	9.54	7.47	8.51	7.47	7.56	4.28	4.91	6.58	7.82
128	9.48	9.47	8.34	8.39	7.44	7.43	4.30	4.89	6.61	7.62
130	9.42	9.42	8.25	8.26	7.31	7.30	4.33	4.84	7.16	7.17
135	–	–	8.01	7.92	6.97	6.99	4.66	4.66	6.98	7.00
140	–	–	7.78	7.59	6.65	6.68	4.66	4.64	6.83	6.82
	If		**Ig**		**Ih**		**Ii**		**Ij**	
116	3.38	4.73	6.25	7.63	3.09	4.23	3.09	3.97	5.46	6.47
118	3.38	4.71	6.31	7.52	3.09	4.22	3.13	3.92	5.47	6.40
120	3.38	4.67	6.35	7.43	3.09	4.18	3.19	3.86	5.47	6.33
122	3.40	4.62	6.40	7.39	3.10	4.13	3.64	3.66	5.46	6.25
124	3.40	4.59	6.63	7.20	3.11	4.13	3.60	3.62	5.56	6.15
126	3.41	4.56	6.89	6.89	3.14	4.02	3.56	3.58	5.99	6.01
128	3.47	4.50	6.85	6.85	3.57	3.58	3.51	3.55	3.93	5.93
130	3.55	4.49	6.81	6.82	3.54	3.53	3.47	3.51	5.86	5.85
135	4.18	4.18	6.71	6.72	3.46	3.41	–	–	5.67	5.66
140	4.14	4.15	6.61	6.62	3.38	3.29	–	–	5.48	5.47

Table 3. Temperature dependence of the dielectric permittivity of 4-alkoxy-4'-propoxyazoxybenzenes **IIa**–**IIj**

T, °C	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$
	IIa		**IIb**		**IIc**		**IId**		**IIe**	
110	11.44	5.49	6.16	6.42	2.11	2.23	4.57	5.56	4.04	4.11
112	5.89	3.90	6.10	6.36	2.15	2.25	4.52	5.41	4.03	4.10
114	3.93	3.89	6.02	6.30	2.22	2.25	4.47	5.32	4.01	4.07
116	3.90	3.86	5.95	6.24	2.26	2.54	4.41	5.22	4.00	4.03
118	3.86	3.83	5.90	6.20	3.54	3.47	4.37	5.09	3.98	4.02
120	3.83	3.80	5.89	6.16	3.27	3.25	4.34	4.98	3.99	4.01
122	3.80	3.77	5.84	6.12	3.16	3.12	4.32	4.90	3.97	3.97
124	3.77	3.74	5.79	6.08	3.05	3.07	4.31	4.81	3.93	3.93
126	–	–	5.76	6.04	3.03	3.06	4.32	4.70	3.89	3.88
128	–	–	5.72	6.00	3.02	3.04	4.31	4.64	3.85	3.84
130	–	–	5.69	5.96	3.01	3.02	4.29	4.30	3.81	3.80
135	–	–	5.61	5.84	–	–	4.09	4.07	–	–
140	–	–	5.58	5.69	–	–	3.89	3.82	–	–
145	–	–	5.59	5.55	–	–	–	–	–	–
150	–	–	5.41	5.44	–	–	–	–	–	–

Table 3. (Contd.)

T, °C	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$
	IIf		**IIg**		**IIh**		**IIi**		**IIj**	
110	3.86	4.00	3.49	3.68	5.74	5.32	3.40	3.46	4.50	4.65
112	3.86	3.97	3.48	3.65	6.61	5.24	3.40	3.43	4.50	4.62
114	3.85	3.94	3.46	3.63	5.69	5.08	3.40	3.41	4.49	4.60
116	3.84	3.92	3.45	3.61	4.65	4.93	3.38	3.37	4.49	4.56
118	3.83	3.90	3.49	3.57	4.84	4.84	3.37	3.37	4.54	4.52
120	3.82	3.87	3.51	3.51	4.76	4.74	3.37	3.36	4.48	4.47
122	3.82	3.84	3.49	3.49	4.62	4.63	3.36	3.36	4.42	4.41
124	3.81	3.81	3.46	3.47	4.50	4.52	3.35	3.36	4.34	4.35
126	3.81	3.80	3.44	3.45	4.40	4.42	3.36	3.36	4.31	4.30
128	3.80	3.80	3.42	3.43	–	–	–	–	4.26	4.24
130	3.80	3.80	3.40	3.41	–	–	–	–	4.20	4.18
135	–	–	3.35	3.35	–	–	–	–	–	–

Our experimental data show that epoxy-substituted azoxybenzenes **Ia**–**Ij** have higher dielectric permittivities (Tables 2, 3) and anisotropies (Figs. 1, 2) than their structural analogs **IIa**–**IIj**.

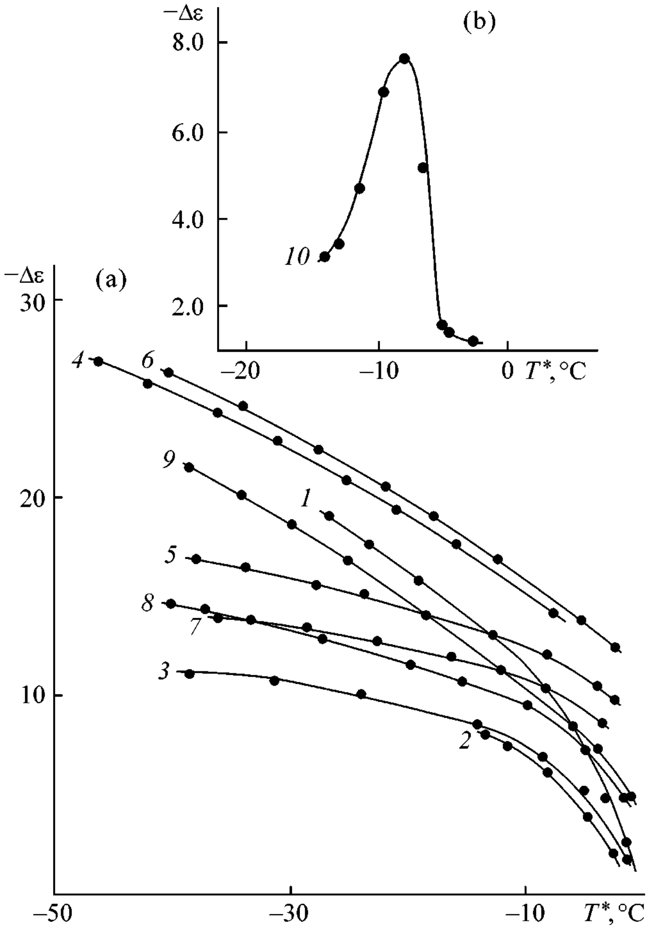


Fig. 1. Anisotropy of dielectric permittivity of 4-(2,3-epoxypropoxy)-4'-alkoxyazoxybenzenes vs. temperature T^* ($T^* = T - T_{NI}$). (a) Homologs (*1*) **Ia**, (*2*) **Ic**, (*3*) **Id**, (*4*) **Ie**, (*5*) **If**, (*6*) **Ig**, (*7*) **Ih**, (*8*) **Ii**, and (*9*) **Ij**; (b) (*10*) homolog **Ib**.

In both homologous series, the dielectric anisotropy varies only slightly with the length of the alkoxy chain (Fig. 3). The exceptions are the second homolog **Ib** of the 4-(2,3-epoxypropoxy)-4'-alkoxyazoxybenzene

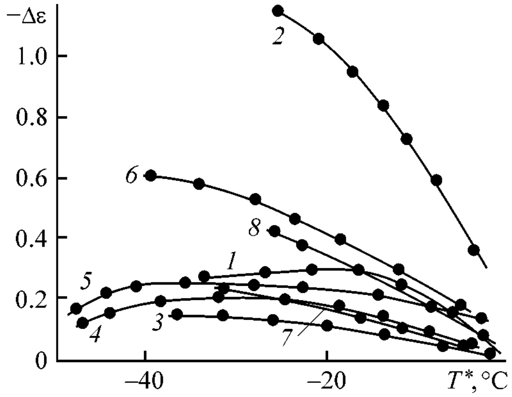


Fig. 2. Anisotropy of dielectric permittivity of 4-alkoxy-4'-propoxyazoxybenzenes vs. temperature T^* ($T^* = T - T_{NI}$). Compound: (*1*) **IIb**, (*2*) **IId**, (*3*) **IIe**, (*4*) **IIf**, (*5*) **IIg**, (*6*) **IIh**, (*7*) **IIi**, and (*8*) **IIj**.

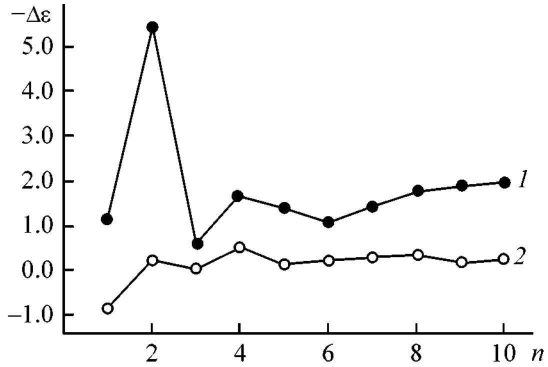


Fig. 3. Anisotropy of dielectric permittivity vs. the number of carbon atoms n in the terminal alkoxyl substituent of (*1*) 4-(2,3-epoxypropoxy)-4'-alkoxyazoxybenzenes and (*2*) 4-alkoxy-4'-propoxyazoxybenzenes at T^* –10°C in the nematic phase.

series and the first (**IIa**) and second (**IIc**) homologs of 4-alkoxy-4'-propoxyazoxybenzenes. The abnormally high dielectric anisotropy of **Ib** (Fig. 1b) is probably due to a combination of several factors [6]. For example, the molecular polarizabilitiy, dipole moment, and degree of orientation order of 4-(2,3-epoxypropoxy)-4'-ethoxyazoxybenzene **Ib** are noticeably higher than those of the other glycidyl-substituted azoxybenzenes.

Of all the studied mesogens, only 4-methoxy-4'-propoxyazoxybenzene **IIa** has a small positive dielectric anisotropy (Table 3). Presumably, in this compound the component of the dipole moment directed along the long axis of the molecule, $\varepsilon_{||}$, is greater than that of the lateral dipole moment, $\varepsilon_{\perp}$. The only homolog with zero dielectric anisotropy is 4,4'-dipropoxyazoxybenzene **IIc** (Table 3), which is probably due to the equal contribution of the orientation component to $\varepsilon_{||}$ and $\varepsilon_{\perp}$.

In both series of azoxybenzenes, the anisotropy of the dielectric permittivity decreases with increasing temperature.

Along with the dielectric permittivities of 4-(2,3-epoxypropoxy)-4'-alkoxyazoxybenzenes **Ia**–**Ij** and 4-propoxy-4'-alkoxyazoxybenzenes **IIa**–**IIj**, we also determined their dipole moments (Table 4). As can be seen from these data, compounds **Ia**–**Ij** have higher dipole moments than their structural analogs. It is worth noting that, in both homologous series, dipole moments are only slightly dependent on the number of the homolog. The only exception is the first homolog **Ia** in the series of glycidyl-substituted azoxybenzenes. The lower, as compared to the other compounds of this series, dipole moment of 4-(2,3-epoxypropoxy)-4'-methoxyazoxybenzene **Ia** is evidently due to partial compensation of the vector components of its dipole moment. In the series of 4-alkoxy-4'-propoxyazoxybenzenes **Ia**–**Ij**, an odd–even alternation of dipole moments is observed, which is manifested in the saw-tooth plot of μ vs. the number of carbon atoms in the alkoxy chain.

Table 4. Dipole moments of 4-(2,3-epoxypropoxy)-4'-alkoxyazoxybenzenes **Ia**–**Ij** and 4-alkoxy-4'-propoxyazoxybenzenes **IIa**–**IIj**

Comp. no.	μ, D	Comp. no.	μ, D
Ia	2.22	**IIa**	2.21
Ib	3.66	**IIb**	2.53
Ic	3.34	**IIc**	2.12
Id	2.88	**IId**	2.17
Ie	3.21	**IIe**	1.88
If	3.01	**IIf**	2.10
Ig	2.91	**IIg**	2.14
Ih	3.06	**IIh**	2.44
Ii	3.34	**IIi**	1.98
Ij	3.40	**IIj**	2.26

EXPERIMENTAL

The liquid crystals were prepared by the procedures published in [5, 7]; their structure was confirmed by elemental analysis and by ^{1}H NMR and IR spectroscopy. Compounds **Ia**–**Ij** and **IIa**–**IIj** were purified by column chromatography on alumina with chloroform–heptane (1 : 1) as eluent, followed by vacuum drying to constant weight.

The dielectric permittivity was measured by the bridge method with an R-5058 ac bridge at 1000 Hz. The liquid crystals were oriented by a stationary magnetic field with a strength of 5000 G. The cell for measuring the dielectric permittivity was a 0.25 mm thick plane capacitor with an area of 0.44 cm^2, which was thermostated with the accuracy of ±0.1°C. The dielectric constants were determined at the cell voltage of 1.2 V. The cell was calibrated with benzene of chemically pure for spectroscopy grade. Checking the performance of the unit with a series of solvents [8] of chemically pure for chromatography grade showed that the measurement error in determination of the dielectric permittivity did not exceed 0.7%.

The dipole moments of disubstituted azoxybenzenes were determined by the second Debye method [9] from the dielectric permittivity, density, and refractive index of infinitely dilute solutions of the liquid crystals in benzene at 25°C. Because of small amounts of the solutions, it was impossible to determine their density with sufficient accuracy. Therefore, we calculated the dipole moments by the Guggenheim–Smith formula (1) [6].

$$\mu = 0.02208 \frac{1}{(\varepsilon_1 + 2)d_1^{1/2}} [M_2(\alpha - \beta)T]^{1/2}. \quad (1)$$

Here ε_1 is the dielectric permittivity of benzene, d_1 is the density of benzene, M_2 is the molecular weight of a liquid crystal, and T is the temperature. The parameters α and β were found from Eqs. (2) and (3) by the least-squares method.

$$\varepsilon_{1,2} = \alpha\omega_2 + \varepsilon_1, \tag{2}$$

$$n^2_{D1,2} = \beta\omega_2 + n_{D1}. \tag{3}$$

Here $\varepsilon_{1,2}$ is the dielectric permittivity of the solution of a liquid crystal, $n_{D1,2}$ is its refractive index, n_{D1} is the refractive index of benzene, and ω_2 is weight fraction of the liquid crystal in the solution.

The absolute error in determination of the dipole moments was ±0.05 D.

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