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TEMPERATURE DEPENDENCES OF THE ELASTIC CONSTANTS IN THE p-ALKOXYBENZYLIDENE-p'-n-BUTYLANILINES HOMOLOGOUS SERIES

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Abstract Temperature dependences of the three elastic constants in the title compounds are reported and discussed.

To obtain temperature dependences of the helical pitch which would be at least qualitatively correct and to ensure realistic relationship between splay and bend elastic constants (K_{11}/K_{33}), one has to account for third-order terms in the free energhy density expansion over the orientational order parameter Q and its spatially non-uniform fluctuations:

$$F_{eff} = \frac{L_1}{2} \partial_\alpha Q_{\beta\gamma} \partial_\alpha Q_{\beta\gamma} + \frac{L_2}{2} \partial_\alpha Q_{\alpha\gamma} \partial_\beta Q_{\beta\gamma} + \frac{L_3}{2} Q_{\alpha\beta} \partial_\alpha Q_{\gamma\delta} \partial_\beta Q_{\gamma\delta} + \frac{a}{2} (T-T_o) \mathrm{Tr}(Q^2_{\alpha\beta}) + \frac{b}{3} \mathrm{Tr}(Q^3_{\alpha\beta}) + \frac{a}{4} \mathrm{Tr}(Q^4_{\alpha\beta}) \quad (1)$$

In this case, combining the Oseen-Frank and Landau-de Gennes theories, one obtains [1]

$$K_{11} = Q^2 (2L_1 + L_2 - \frac{2}{3} Q L_3)$$
$$K_{22} = Q^2 (2L_1 - \frac{2}{3} Q L_3) \quad (2)$$
$$K_{33} = Q^2 (2L_1 + L_2 + \frac{4}{3} Q L_3)$$

K_{ii} temperature dependences calculated using (2) were found to be in a good agreement with experimental data for p-azoxyanizole in a narrow temperature range (up to 4°C) below the isotropic transition point[1].

In the present work we have studied temperature dependences of the elastic constants for the first four members of the 4-alkoxybenzylidene- 4'-n-butylaniline homologous series (MBBA, EBBA, PBBA, and BBBA).

K_{11} and K_{33} were determined using the Frederiks transition in the magnetic field[2]. Planar boundary conditions were ensured by standard cleaning procedure of glass substrates[2] and subsequent coating by thin polyvinyl alcohol layer. Homeotropic alignment was obtained using the lecytine solution. K_{22} was determined using NMR broad lines spectroscopy upon addition of a small amount (<0.35 mol.%) of chiral dopant[3].

The results obtained are shown in Figs. 1-4. Solid lines are model $K_{ii}(T)$ curves calculated according to Eqs. (2) using the orientational order parameter values obtained in a separate NMR experiment[4]. Values of K_{iiexp}/K_{iicalc} (which are, in fact, relative deviations of experimental elastic constants from the 'ideal' dependences) vs. carbon atom number in the alkyl chain are presented in Fig. 5. The following characteristic features are to be noted:

(a) K_{22} values are in excellent agreement with the model calculations and, moreover, show no apparent dependence upon the alkyl chain length.

(b) K_{33} values show a slight decrease with longer chains, unaccounted for by the theory used. This can be understood in terms of possible 'internal bend' related to intramolecular degrees of freedom, i.e., molecules with

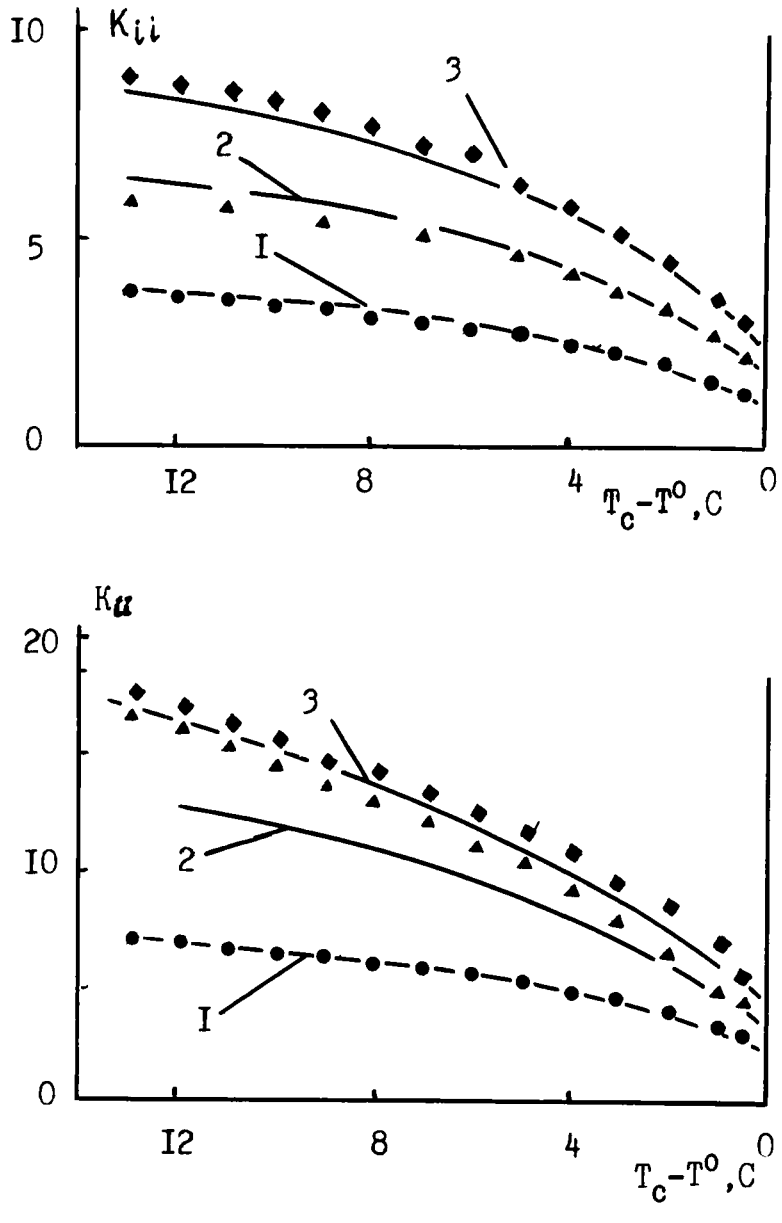

FIGURE 1. Temperature dependences of K_{11} (▲ curve 2), K_{22} (● curve 1), and K_{33} (◆ curve 3) for MBBA (a) and EBBA (b)

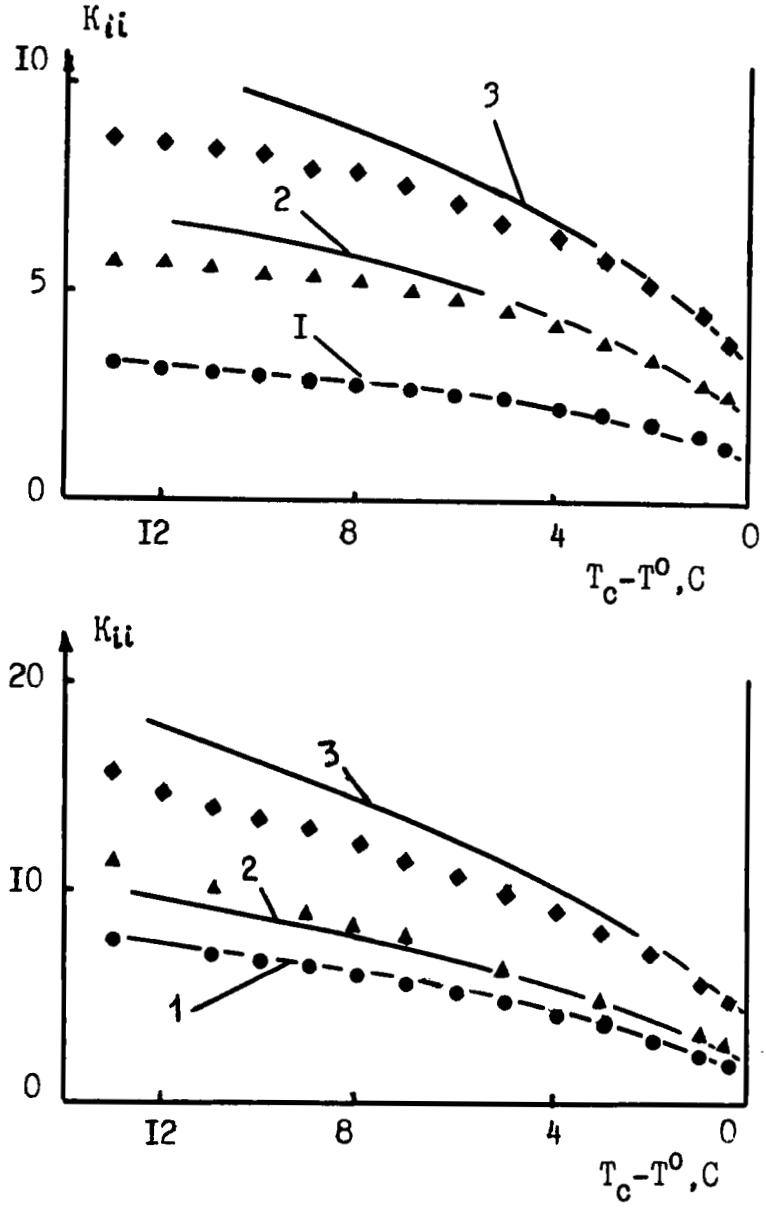

FIGURE 2. Temperature dependences of K_{11} (▲ curve 2), K_{22} (● curve 1), and K_{33} (◆ curve 3) for PBBA (a) and BBBA (b)

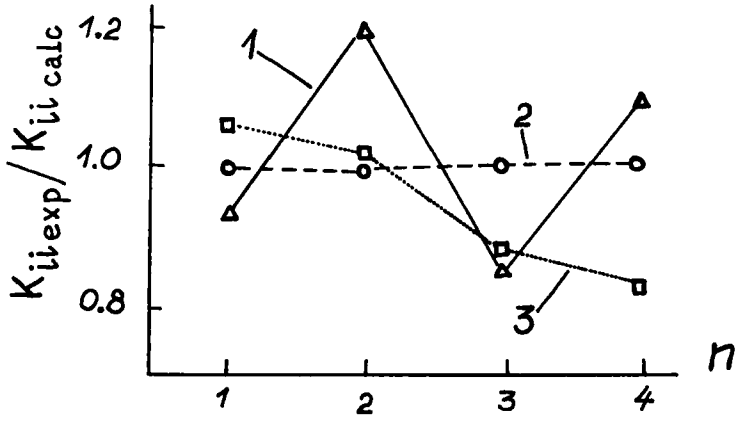

FIGURE 5 Experimental and calculated K_{ii} values ratio: 1 - K_{11}, 2 - K_{22}, 3 - K_{33}.

longer alkyl chains, when submitted to bend deformations, assume alkyl chain conformations making the effective molecular shape more 'banana-like'. The possibility of such an effect has already been predicted[5].

(c) As for K_{11}, it is characterized by a pronounced odd-even effect, indicating that splay deformation, accompanied by the rapprochement of the adjacent ends of neighbouring molecules , is especially sensitive to packing characteristics determined by molecular geometry.

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