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Molecular Polarizability Anisotropies and Order Parameters of Di-n-Alkyl 4-[4-(4-N-Octyloxy-Benzoyloxy)-Benzoyloxy]-Benzylidenemalonates

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MOLECULAR POLARIZABILITY ANISOTROPIES AND ORDER PARAMETERS OF DI-N-ALKYL 4-[4-(4-N-OCTYLOXY-BENZOYLOXY)-BENZOYLOXY]-BENZYLIDENEMALONATES

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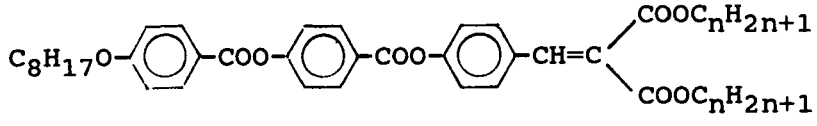
Abstract For the homologous series of the swallow-tailed compounds the relative molecular polarizability anisotropies and the temperature dependence of the order parameter in the nematic and smectic A phases were determined from refractive indices using the isotropic internal field model of Vuks and the mean field fitting method of Tough and Bradshaw. The Maier-Saupe mean field interaction parameter is in the nematic phase nearly constant and shows in dependence on alkyl chain length a strong alternation in the smectic A phase. The relative polarizability anisotropy is decreasing alternately in both phase types with extension of the alkyl chains of the swallow tails.

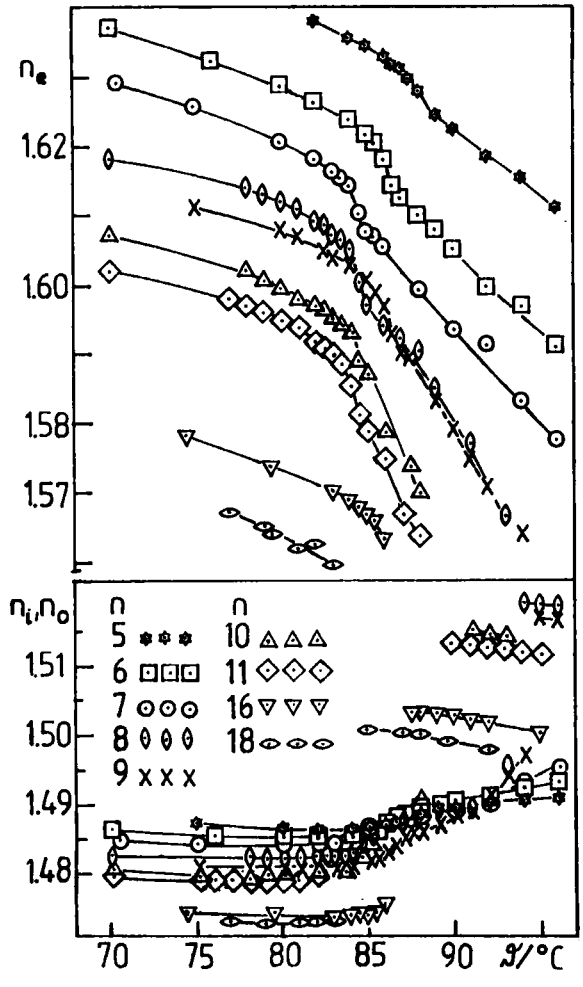
Introduction

The Maier-Saupe order parameter[1] has been defined in the nematic phase. According to the Mc Millan theory[2] of smectic A liquid crystals, in which two order parameters are defined, the Maier-Saupe orientational order parameter is used to describe the alignment of the molecular long axes and the smectic order parameter indicates the strength of the smectic planes. The temperature dependence of refractive indices may be used for the calculation of the the orientational order parameter, the mean field interaction parameter and the molecular polarizability anisotropy.

Substances and experimental data

Synthesis, phase transition temperatures, enthalpies and entropies of the homologous series of di-n-alkyl 4-[4-(4-n-octyloxybenzoyloxy)-benzoyloxy]-benzylidene-malonates are given by Weissflog et al.[3].





The refractive indices were measured with an Abbe refractometer and are shown in Figure 1.

FIGURE 1

Refractive indices of the di-n-alkyl 4-[4-(4-n-octyloxybenzoyloxy)-benzoyloxy]-benzylidene-malonates vs. the temperature, n = number of the carbon atoms in the alkyl chain of the swallow tails.

Calculation of polarizabilities and order parameters

For the calculation of polarizabilities from refractive indices the isotropic internal field model of Vuks[4] was first applied to nematic liquid crystals by Chandrasekhar and Madhusudana[5]. According to Dunmur et al.[6] and Madhusudana[7] the Vuks model should be preferred. It may be applied with success also to uniaxial smectic phases[8]. Tough and Bradshaw[9] have proposed an extrapolation method to obtain the relative polarizability anisotropy and the order parameter. They used the Maier-Saupe mean field theory[1] to calculate the temperature dependence of the order parameter S. Contrary to the Maier-Saupe theory[1] where A/T_{NI} is a constant (4.541), Tough and Bradshaw[9] have introduced A as adjustable parameter. A complete description of this mean field extrapolation method is given in[9].

Discussion

Generally in the considered homologous series we observe an alternating decrease of the relative polarizability anisotropy of the nematic and smectic A phase with elongation of the alkyl chain (Figure 2). The relative polarizability anisotropies and the mean field interaction parameters A/T_{NI} show an opposite behaviour (Figure 2,3). In the nematic phase the mean field parameter has nearly the same value as in other nematic compounds[10]. For the considered homologous series the envelope of the family of curves of the order parameter of the nematic phase vs. the reduced temperature is shifted to smaller values in comparison to compounds with two benzene rings[10]. In all cases the curve of the temperature dependence of the order parameter is shifted to lower order parameter values in comparison

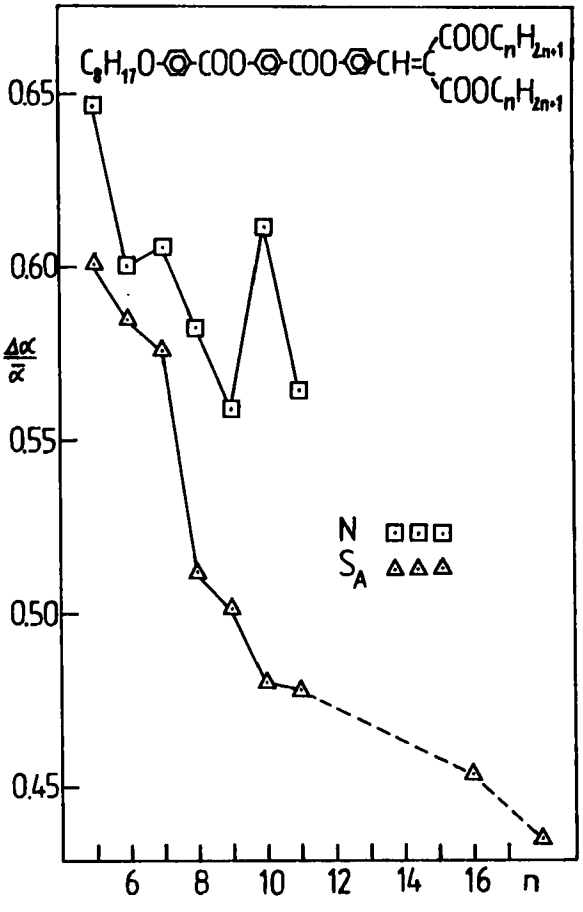


FIGURE 2

The relative polarizability anisotropy vs. the number n of carbon atoms in the alkyl chains of the swallow tails.

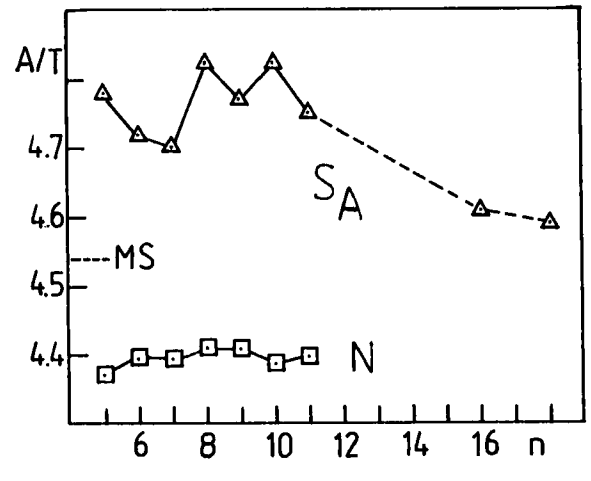


FIGURE 3

The mean field interaction parameter vs. the number n of carbon atoms in the alkyl chains of the swallow tails.

to the values obtained from[1](MS) (Figure 4).

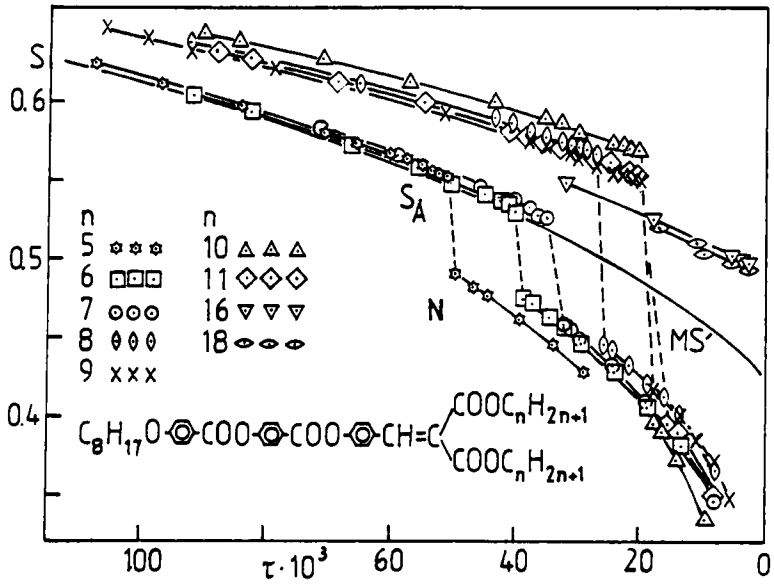


FIGURE 4 The order parameter vs. the reduced temperature.

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