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Electric birefringence of discotic benzene-hexa-*n*-heptanoate in isotropic solution phase

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The electric birefringence of solutions of oblate discogen and prolate nematogen in dioxane has been examined. Discotic benzene-hexa-*n*-heptanoate (BH7) exhibits negative birefringence, while nematic 5CB and MBBA exhibit positive birefringences at low concentrations. Possible modes of solute orientation, compatible with the observed birefringence sign, are discussed. For BH7, it is suggested that the in-plane axes with larger optical polarizabilities align perpendicular to the field direction. The dependence of the specific Kerr constant on the solution concentration is also reported.

Thermotropic nematic liquid crystals are formed typically by prolate rod-like molecules, while discotic columnar phases appear for molecules having an oblate disc-like structure. The shape anisotropy and the associated polarizability anisotropy are generally regarded to be of primary importance in determining the structure and stability of liquid crystals. In recent studies [1–3], Toriumi, Samulski and Janik have discussed the nature of anisotropic intermolecular interactions and the conformational properties of molecules in these two classes of liquid crystals. In this series of studies we wish to expand the above discussion by examining the field-induced orientational behaviour of individual liquid-crystalline molecules dissolved in isotropic solution phases. Some preliminary results of electric birefringence (EB) measurements for discotic benzene-hexa-*n*-heptanoate (BH7) [4, 5], $C_6(OCOC_6H_{13})_6$, are reported below and are compared with those for nematic 4-*n*-pentyl-4′-cyanobiphenyl (5CB) and (*p*-methoxybenzylidene)-*p*-*n*-butylaniline (MBBA). To our knowledge, no experimental EB measurements have so far been reported for discotic molecules.

The sample of BH7 was synthesized from tetrahydroxyquinone and *n*-enanthyl chloride following the published methods [6, 7]. The 5CB sample was obtained from BDH and used without further purification. MBBA from Eastman Kodak was vacuum-distilled before use. Solutions were prepared by dissolving weighed amounts of liquid crystals into freshly distilled 1,4-dioxane. Measurements of EB were carried out using an optical apparatus whose details have been described by Kikuchi [8]. The solution temperature was kept at 25 ± 0·1°C by circulating water and was monitored by a thermistor immersed in solution. The solvent birefringence was measured separately and subtracted from the solution values.

For all three liquid-crystalline materials the transient EB signals were regular and reproducible: they consisted of rise, saturation and decay processes in response to an

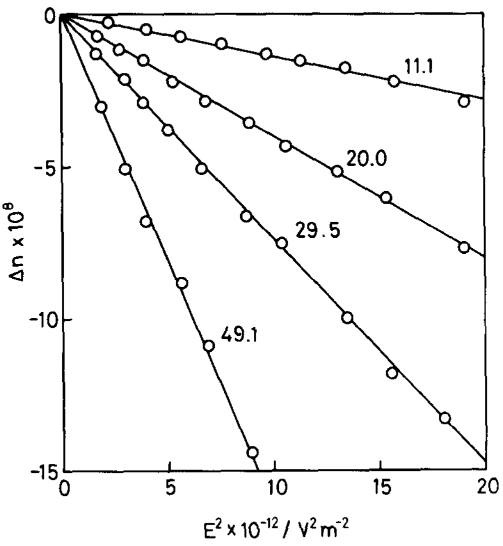

Figure 1. Dependence of Δn on BH7 in dioxane on E^2. The numbers are the solute/solution concentrations in wt %.

application of the d.c. rectangular pulse. The dependence of the steady-state birefringence (Δn) on the squared strength of the applied electric field (E) is depicted for BH7 in figure 1, where we can see that the Kerr law ($\Delta n \propto E^2$) holds for the entire E range and the slope with *negative* sign increases with the solute concentration. A negative birefringence would arise when the axis of maximum optical polarizability of the molecule lies perpendicular to its dipole moments, and hence to the direction of the external field interacting with the dipoles. (Note that the orientation of the maximum polarizability axis to the dipole moment is either parallel or perpendicular in an axially symmetric BH7 molecule.) For benzene, with a polarizability anisotropy $\alpha_1 = \alpha_2 > \alpha_3$, the EB sign is reported to be positive [9]. This indicates that its in-plane axis (1 or 2 axis) is oriented predominantly parallel to the field direction. Since polarizability anisotropies of benzene derivatives are mainly due to π-electron displacements, the relation $\alpha_1 = \alpha_2 > \alpha_3$ should also hold for BH7. Hence, the orientation of BH7, compatible with its negative birefringence, must be exactly opposite to the case of benzene, i.e. the in-plane axes (or the molecular plane) are perpendicular to the field and the normal axis lies in the field direction. Any dipole moments (permanent or induced) responsible for the field-induced orientation should be along this normal axis. The sign inversion in birefringence from benzene to BH7 can thus be attributed to a shift of the dipole moment caused by an introduction of alkanoate chains to the periphery of the benzene ring.

The specific Kerr constant B_{sp} can be calculated from the slope of the linear Δn versus E^2 plot as

$$B_{sp} = \Delta n/\lambda C E^2, \quad (1)$$

where $\lambda = 632{\cdot}8$ nm is the wavelength of the He–Ne laser. The concentration C in equation (1) has to be given in the volume concentration, however, since the density value of BH7 is not available, all calculations had to be made by using the weight concentration. This approximation does not influence significantly the B_{sp}

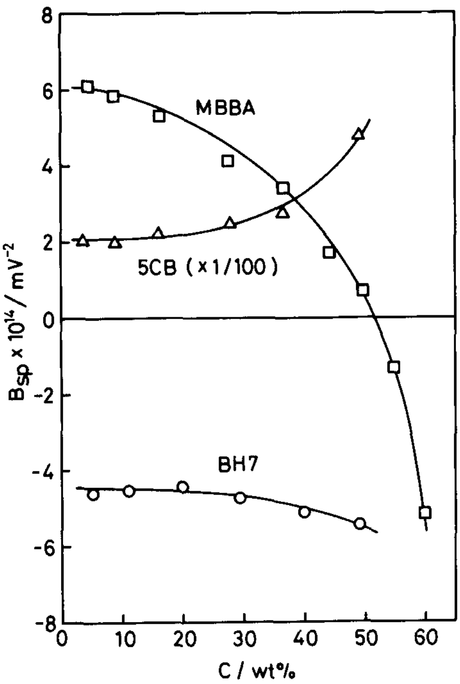

Figure 2. Concentration dependence of the specific Kerr constants of BH7 (○), 5CB (△) and MBBA (□) in dioxane.

values of two nematogens as their densities are close to that of the solvent dioxane (ϱ = 1·023 g cm^{-3} for 5CB at 25°C [10], 1·025 for MBBA at 46·1°C [11] and 1·028 for dioxane at 25°C [12]). The B_{sp} values thus calculated are summarized in figure 2.

The intense, positive birefringence observed for 5CB is consistent with its chemical structure in which the axis of maximum polarizability and that of permanent dipole moment are coincident in the direction of the long molecular axis [13]. The birefringence of MBBA, being positive in dilute solutions, reverses to negative as concentration increases. This phenomenon, first reported by Coles and Jennings [13], was interpreted in terms of solute–solute associations. At low concentrations the field-induced orientation of MBBA is mainly driven by the induced dipole moment oriented along the long molecular axis. With increasing solute concentration, side-by-side type associations take place thereby enhancing the transverse permanent dipole moment, and when the contribution of this transverse moment exceeds that of the longitudinal dipole the birefringence sign changes. The B_{sp} values of 5CB and BH7 show no indications of sign inversion, but tend to increase at higher concentrations. This latter observation suggests again certain molecular associations.

The three liquid-crystalline materials examined above are different from each other in the chemical and geometrical structure. The birefringence data sensitively reflects their structural characteristics and exhibits substantially different B_{sp} versus C curves as shown in figure 2. The results of EB measurements can be analysed further if orientations of polar groups within a molecule are determined from independent measurements. For example, knowledge concerning the local conformation of the pendant ester groups is of critical importance in discussing the origin of the EB sign inversion from benzene to BH7. The structure of aggregates must also be known in order to analyse the concentration effects on B_{sp}. These problems will be discussed in subsequent studies.

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