

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

### Supermolecular self organization via molecular aggregation II. Electro-optical studies on structure formation processes in associated liquid-crystalline diols

R. Festag<sup>a</sup>; R. Kleppinger<sup>a</sup>; M. Soliman<sup>a</sup>; J. H. Wendorff<sup>a</sup>; G. Lattermann<sup>b</sup>; G. Stauffer<sup>b</sup>

<sup>a</sup> Deutsches Kunststoff-Institut, Darmstadt, Germany <sup>b</sup> Institut für Makromolekulare Chemie, Universität Bayreuth, Bayreuth, Germany

**To cite this Article** Festag, R. , Kleppinger, R. , Soliman, M. , Wendorff, J. H. , Lattermann, G. and Stauffer, G.(1992) 'Supermolecular self organization via molecular aggregation II. Electro-optical studies on structure formation processes in associated liquid-crystalline diols', *Liquid Crystals*, 11: 5, 699 – 710

**To link to this Article:** DOI: 10.1080/02678299208029021

**URL:** <http://dx.doi.org/10.1080/02678299208029021>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Supramolecular self organization via molecular aggregation

### II. Electro-optical studies on structure formation processes in associated liquid-crystalline diols

by R. FESTAG†, R. KLEPPINGER†, M. SOLIMAN†,  
J. H. WENDORFF†\*, G. LATTERMANN‡ and G. STAUFER‡

† Deutsches Kunststoff-Institut, Schlossgartenstrasse 6,  
6100 Darmstadt, Germany

‡ Institut für Makromolekulare Chemie, Universität Bayreuth,  
Bayreuth, Germany

*(Received 9 September 1991; accepted 6 November 1991)*

Orientational correlations are investigated in the isotropic phase for mesogens formed by diols which exhibit a columnar discotic or smectic phase at lower temperatures. These compounds consist of a central part to which either three or only one aliphatic chains of various length ( $n = 4-14$ ) are attached at one end and two hydroxy groups at the other. The electro-optical studies reveal that associations are formed in the isotropic phase due to hydrogen bonding and that the stability is controlled by the collective association of a number of molecules giving rise to disc-like or layer-like aggregates. It seems that these aggregates are responsible for the formation of the columnar phase which is stable at a lower temperature as far as the three chain diols with long aliphatic chains are concerned. The same situation holds for the formation of a smectic phase for the single chain diols. Structure formation in this new class of compounds is thus a function of the shape of the aggregates rather than of the shapes of the individual molecules.

#### 1. Introduction

The anisotropy of the shape of rigid molecules or molecular groups provides a strong driving force towards the formation of liquid-crystalline phases; the range of the thermodynamic stability is controlled by the strength of the anisotropic attractive interactions [1-4]. More recently it has become apparent that the tendency of molecules of appropriate chemical composition to form molecular associations also constitutes a driving force towards liquid-crystalline phase formation even if the individual molecules, as judged, for instance, from their shape or from the corresponding strength of the attractive interaction, are not mesogenic. An example of this behaviour is provided by compounds exhibiting charge transfer interactions where complexing leads to the stabilization or even to the induction of smectic or columnar phases and where complex formation is found to be the primary process governing structure formation [5].

This paper is concerned with structure formation in diols via aggregation. These diols consist of a central part to which three aliphatic chains, of various length, are attached at one end and two hydroxy groups at the other [6, 7]. In addition diols were studied containing a single aliphatic chain at one end. Molecular modelling studies

\* Author for correspondence.

showed for the case of three chain diols that the individual molecules do not possess a shape which lends itself to the induction of liquid-crystalline phases [7]. The three aliphatic chains are free to move and to adopt a large number of conformations. However, based on calorimetric, density and X-ray studies on the three chain diols we were forced to conclude that this class of compound forms planar associations which in turn self-assemble to form a two dimensional hexagonal lattice at lower temperatures [7]. This structure strongly resembles that of the hexagonal disordered columnar phase. Our conclusion was that the tendency of the diols to form a columnar phase was a consequence of the formation of associations well within the isotropic fluid phase. The association is driven by hydrogen bonding and leads in the case of three chain diols to disc-like units [7].

The previous paper [7] concerned with structure formation in associated liquid crystals concentrated primarily on the analysis of the liquid-crystalline state and it did not consider in any detail the primary structure formation process, i.e. the formation of associations. This paper is concerned just with this primary structure formation process and the experimental method of choice to gain information on this process involves electro-optical studies.

## 2. Experimental

The diols studied have the general structure shown in figure 1. The synthesis of these materials has already been published [6]. The electro-optical (Kerr effect) studies consist in applying an electric field to the isotropic phase. The optically and dielectrically anisotropic molecules reorient in the external field, causing a birefringence  $\Delta n$ , which increases linearly as a function of the square of the applied field  $E$

$$\Delta n = \lambda B E^2, \quad (1)$$

where  $B$  is the Kerr constant and  $\lambda$  the wavelength of the light. The electro-optical results (Kerr results) were obtained with the experimental arrangement described previously [8]. The induced optical birefringence was monitored as a function of temperature and the magnitude of the applied electric field.

To estimate molecular electronic and geometric properties of the diols we have employed the semi-empirical quantum mechanical method AM1 [9, 10].

## 3. Results of electro-optical studies on the three chain diols

### 3.1. Analysis of the magnitude of the Kerr constant

Figure 2 gives an example of a Kerr experiment performed on a diol with  $n=4$  within the isotropic phase showing the linear dependence of the induced birefringence on the square of the electric field. The Kerr constant turns out to be negative and to be of the order of  $10^{-13} \text{ m/V}^2$ . The value of the Kerr constant can, as will be shown, be

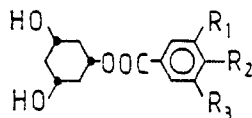


Figure 1. Molecular structure of the single and three chain diols investigated. Chain diol:  $R_1, R_3 = \text{H}, R_2 = \text{OC}_n\text{H}_{2n+1}$ ;  $n = 14$ . Three chain diols:  $R_1, R_2, R_3 = \text{OC}_n\text{H}_{2n+1}$ ;  $n = 4-10$ .

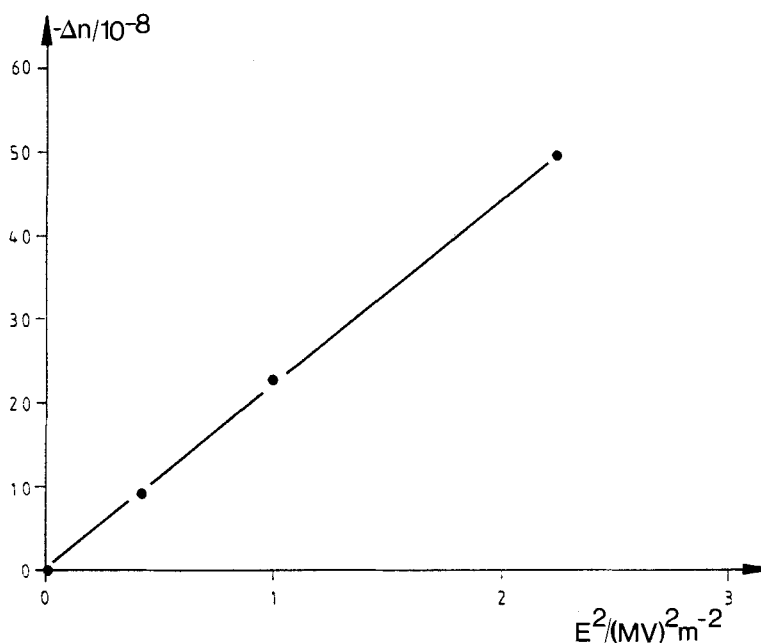


Figure 2. Plot of the birefringence  $\Delta n$  versus the square of the electric field  $E^2$  for three chain diols with  $n=4$ .

used to obtain information on the degree of aggregation in terms of the orientational order parameter  $g_2$ , defined as

$$g_2 = 1 + 1/2 \sum_i \langle 3 \cos^2 \phi_{ij} - 1 \rangle_j \quad (2)$$

here  $\phi_{ij}$  is the angle between the symmetry axes of molecules  $i$  and  $j$ . Using a statistical mechanical approach [11] we may express the Kerr constant in terms of molecular parameters, such as the anisotropy of the polarizability and the dipole moment, on the one side and in terms of orientational correlations resulting from associations within the condensed state, in terms of orientational order parameters  $g_2$ , on the other hand as follows:

$$B = \Delta n_s / 15 \lambda k T ((\bar{\epsilon} + 2)/3)^2 \{ \Delta \alpha + f_c \mu^2 / k T \} g_2, \quad (3)$$

where  $\Delta n_s = (\Delta \alpha / 2 \epsilon_0 \bar{n})(\bar{n}^2 + 2/3)^2 N$ ,  $N$  is the particle number density,  $\bar{\epsilon}$  is the mean dielectric constant,  $\bar{n}$  is the mean refractive index,  $\Delta \alpha$  is the anisotropy of polarizability, and  $\mu$  is the dipole moment. The factor  $f_c$  is defined by

$$f_c = (3 \cos^2 \beta - 1)/2,$$

where  $\beta$  is the angle between the main axis of the polarizability tensor  $\alpha$  and the dipole moment. This equation is valid provided the dipolar correlation is weak, which is usually the case in liquid crystals containing no strong longitudinal dipole moments.

First, we comment on the origin of the negative sign of the Kerr constant. The reason for the negative sign has to be that the angle between the direction of the dipole moment and the principal axis of the optical polarizability is larger than  $54^\circ$  for the particles controlling the electro-optical response, since the quantity  $f_c$  is negative in this

case. Next we consider the absolute value of the Kerr constant. Two routes can be chosen to obtain the magnitude of  $g_2$  and thus information on the degree of association  $g_2$  from the experimental value of  $B$ . One consists in determining the Kerr constant for single molecules ( $g_2 = 1$ ) experimentally, the other is based on theoretical estimates on the optical anisotropy as well as on the density and the dipole moment of an individual molecule using a bond increment method or a molecular theory. The first route involves experiments on dilute solutions and an extrapolation to infinite solution. This approach failed for the diols since we found that they tend to aggregate even for very dilute concentrations in solvents such as  $\text{CCl}_4$ . The occurrence of aggregation effects even at low concentrations is a rather frequent observation [12]. So we had to take the second route based on theoretical estimates. In principle, we might use bond increment methods. However this results, for the case considered here, in large errors since the geometry factor  $f_c$  depends very sensitively on the angle between the main axis of the polarizability tensor  $\alpha$  and the direction of the dipole moment  $\mu$  and thus the conformation which is not adequately taken into account by the bond increment approach. The best approach which is currently available to estimate the electronic and geometric properties of rather large molecules with a given chemical structure involves semi-empirical quantum mechanical calculations of the MNDO or AM1-type [9, 10]. Such a method has been found to lead to quite accurate predictions (only some per cent deviations) for example on geometry, dipole moment and polarizabilities. Based on MNDO calculations on the geometry, the dipole moment and the anisotropy of the polarizability for individual diols (see figure 3) we obtained a value for the Kerr constant of uncorrelated molecules in the condensed state of  $-2.91 \times 10^{-15} \text{ m/V}^2$ . So

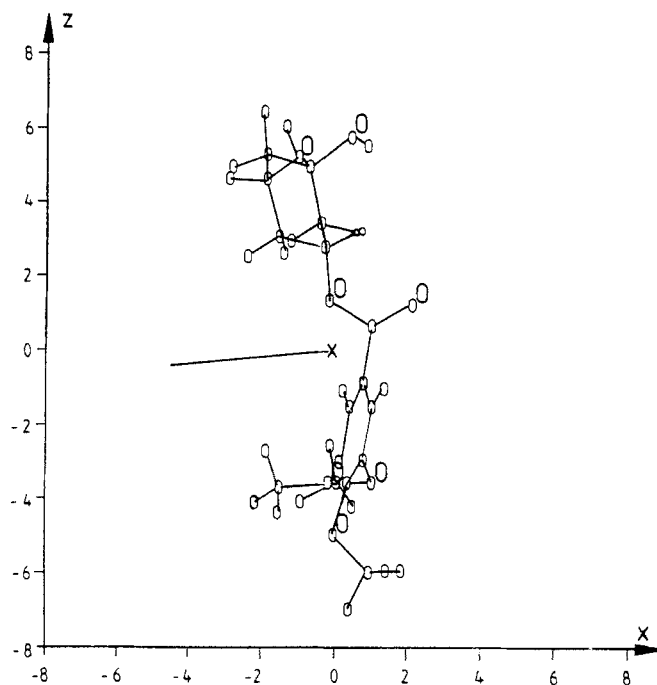


Figure 3. Result of semi-empirical quantum mechanical calculations. Configuration of a single diol molecule (three chain diol) and resulting dipole moment displayed in a coordinate system defined by the principal axes of polarizability; calculated by MOPAC 5.0, a QCPE program on a GRAPHICS IRIS 4D workstation.

the sign is in agreement with experimental observation. The absolute value is, however, much smaller than observed experimentally, well outside the limit of error. So we have to conclude that associations already occur in the isotropic state. Based on the value of the Kerr constant obtained by these calculations we estimated  $g_2$  to be of the order of 10. Additional information on the association behaviour is available from results on the temperature dependence of the Kerr constant.

### 3.2. Analysis of the temperature dependence of the Kerr constant

The temperature dependence of  $B$  is shown in figure 4. It is obvious that the Kerr constant increases in this case quite strongly with decreasing temperature. This increase is much stronger than expected on the basis of equation (3) ( $1/T$  or  $1/T^2$ ). We attribute this variation to the presence of orientational correlations in the isotropic fluid state and their partial destruction with increasing temperature. A well-known example of such orientational correlations are those resulting from the particular weakness of the first order nematic isotropic phase transition [1, 11]. The correlation parameter  $g_2$  and thus the value of  $B$  increases in this case with decreasing temperature and diverges as

$$g_2 \sim (T - T^*)^{-1}, \quad B \sim (T - T^*)^{-1}, \quad (4)$$

at a temperature  $T^*$  which is close to but below the first order phase transition into the nematic phase [11]. Figure 5 shows a plot of  $1/B$  versus  $T$  for one of the diols studied here, the obvious result is that the correlations do not diverge in the neighbourhood of the phase transition. Furthermore no linear relation exists between the inverse of the Kerr constant and the temperature. These results are not surprising since the isotropic columnar phase transition is a conventional first order phase transition [13, 14]. So it is evident beyond any doubt that the strong temperature dependence of the Kerr

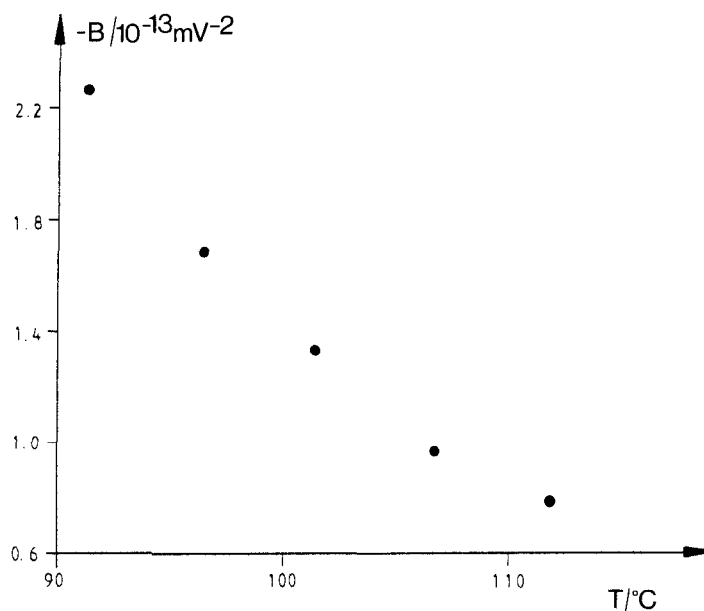


Figure 4. Variation of the Kerr constant with temperature (three chain diol,  $n=8$ ).

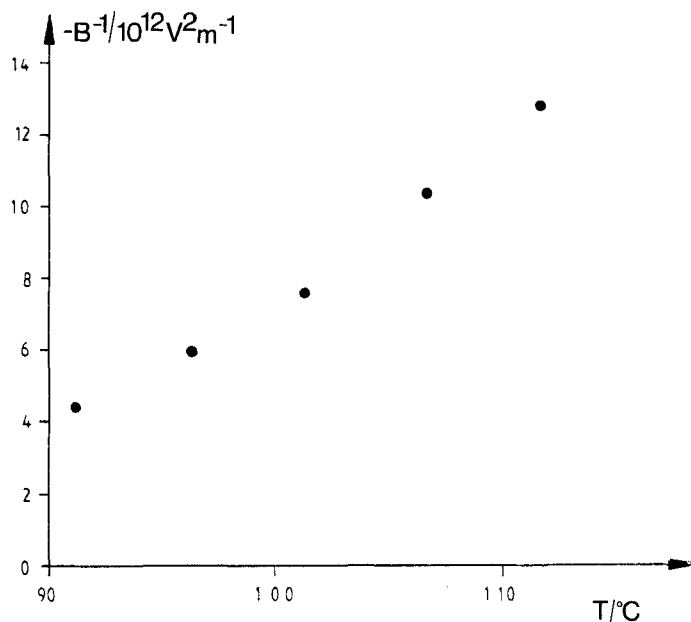
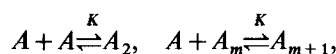


Figure 5. Variation of the inverse of the Kerr constant with temperature (three chain diols,  $n=8$ ).

constant and the curvature shown in figure 5 are special features of the diol systems: the effects are obviously connected with the occurrence of associations controlled by hydrogen bond formation.

In order to describe the relation between the size of the associated regions and the magnitude of the Kerr constant we follow the route taken by Dannhaeuser and Flueckinger [15] to relate associations and dielectric properties in hydrogen bonding fluids. The association is assumed to be governed by an equilibrium constant  $K$  which is independent of the number of molecules already present in the association



where

$$K = C_{m+1}/C_1 \times C_m,$$

and  $C_m$  is the concentration of  $m$ -mer. A cluster containing  $m$  orientationally correlated molecules is proportional to  $g_2$

$$g_2 \sim m.$$

The average enhancement factor  $g$  is determined by the distribution of the sizes of the clusters

$$C_0 = \sum_m m C_m, \quad g = \frac{\sum_m m^2 C_m}{\sum_m m C_m},$$

which may be expressed as

$$(g^2 - 1)/4C_0 = K,$$

and by replacing  $g_2$  by the Kerr constant  $B$

$$B^2 \sim K, \quad K = K_0 \exp(-\Delta H/kT), \quad \ln B^2 = -\Delta H/kT.$$

The prediction thus is that a plot of  $\ln B^2$  versus  $1/T$  should be a straight line, the slope of which is given by the activation energy  $\Delta H$ . Figure 6 shows such a plot of different diols. It is apparent that linear plots result and that the slopes are close to each other in all cases. The activation energy turns out to be about  $96 \text{ kJ mol}^{-1}$  in all cases. This value is surprisingly large. It is known from dielectric studies on liquids associating via hydrogen bonding that the activation energy should be of the order of 14 to  $20 \text{ kJ mol}^{-1}$  [15, 16]. The value observed is larger by a factor of the order of 6. This seems to suggest that the formation and the destruction of the aggregates is not controlled by aggregation of individual molecules, as in the case of linear chain-like aggregation [15, 16], but rather by the collective aggregation of several molecules. It is tempting to speculate that the value 6 originates from six molecules forming, by cyclic association, disc-like aggregates, already in the isotropic phase. These may serve as precursors for a similar structure within the low temperature columnar phase as apparent from X-ray studies [7]. In that case, however, we would expect, because of the two OH groups per diol, that the activation energy should amount to about  $200 \text{ kJ mol}^{-1}$ . This is, however, not necessarily the case.

Studies on water absorption by the three chain diols have revealed that water uptake is fast up to a concentration of one water molecule per diol and that the transition temperature of the columnar phase is influenced by the water uptake [17]. The water uptake becomes slow above this concentration and the additional uptake does not have any further influence on the phase stability. These findings suggest that only half of the hydrogen bonds are effective in stabilizing the aggregates whereas the other half are not able to enter into contact with other molecules, possibly because of steric hindrances. This would explain the observed value of the activation energy. The result of molecular modelling calculations are actually in agreement with this model since they show that every other OH group is turned out of the plane of that flat aggregate for steric reasons [7].

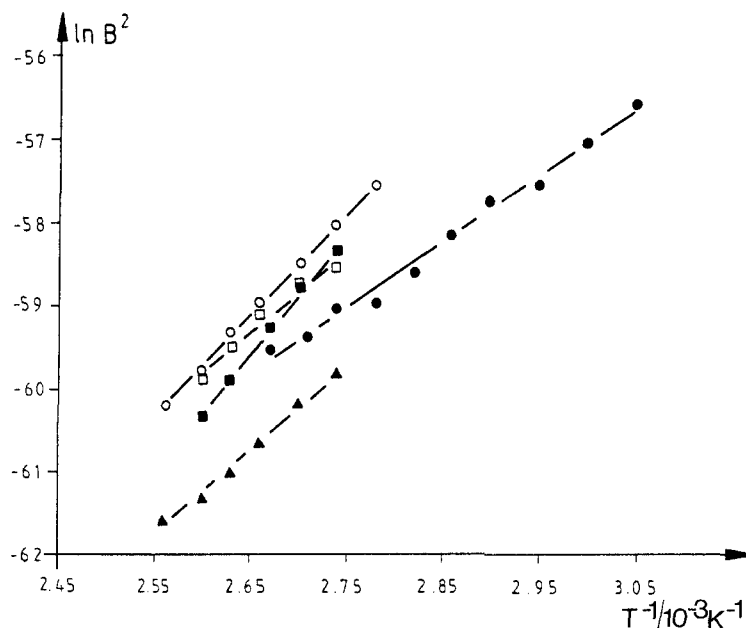


Figure 6. Plot of  $\ln B^2$  versus  $1/T$  (three chain diols). ●,  $n=6$ ; ○,  $n=7$ ; ■,  $n=8$ ; □,  $n=9$ ; ▲,  $n=10$ .



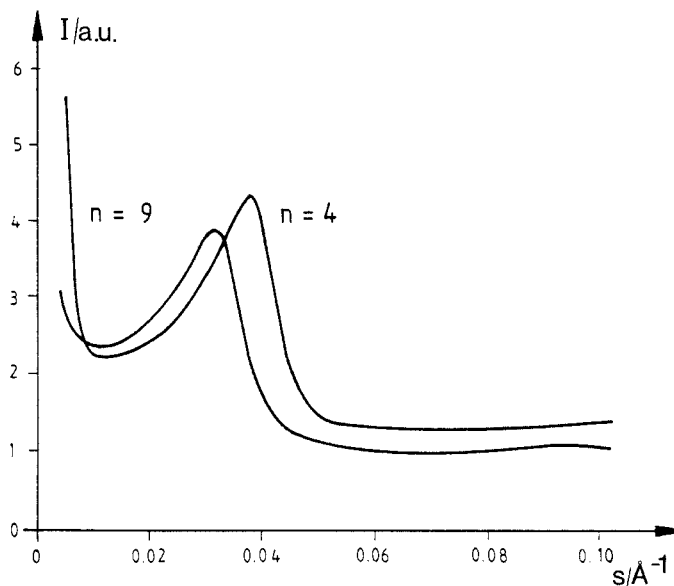


Figure 7. Small angle X-ray data on the isotropic phase of three chain diols with  $n = 4$  and  $n = 9$ .

Additional results supporting the formation of associations in the isotropic melt come from the X-ray scattering data obtained for the isotropic melt. The result is that all of the compounds display two halos, one in the small and one in the wide angle region. The small angle halo (see figure 7) shifts linearly to smaller scattering angles with increasing chain length. This linear dependence allows the extrapolation of the characteristic distance within the isotropic phase for the pure central part, for example  $n = 0$ . The distance derived by this way is about 2.6 nm which fits the size of the disc and which agrees quite well with the value obtained from the extrapolation within the columnar phase.

Finally, the dependence of the sizes of the associations on the chain length will be discussed. The observation is that the associations are larger for shorter lengths of the flexible aliphatic chains whereas the stability of the columnar phase increases with increasing chain length at least for shorter chains. This indicates that the driving force for the associations within the isotropic phase comes from hydrogen bonding and not primarily from a microphase separation of aliphatic and aromatic regions. Associations within the isotropic phase are expected to grow as the length of the aliphatic chains approaches zero while at the same time the columnar phase is strongly destabilized. Microphase separation is apparently the main driving force for the formation of the columnar structures, in agreement with theory [18, 19].

#### 4. Results on single chain diols

The single chain diols display electro-optical properties within the isotropic melt which resemble those of the three chain diols discussed previously. This is evident from the results displayed in figure 8. The Kerr constant turns out to increase strongly with decreasing temperature. The analysis of this temperature dependence leads to the conclusion that again an association of the molecules takes place in the isotropic phase, that these associations are formed due to hydrogen bonding and that the temperature

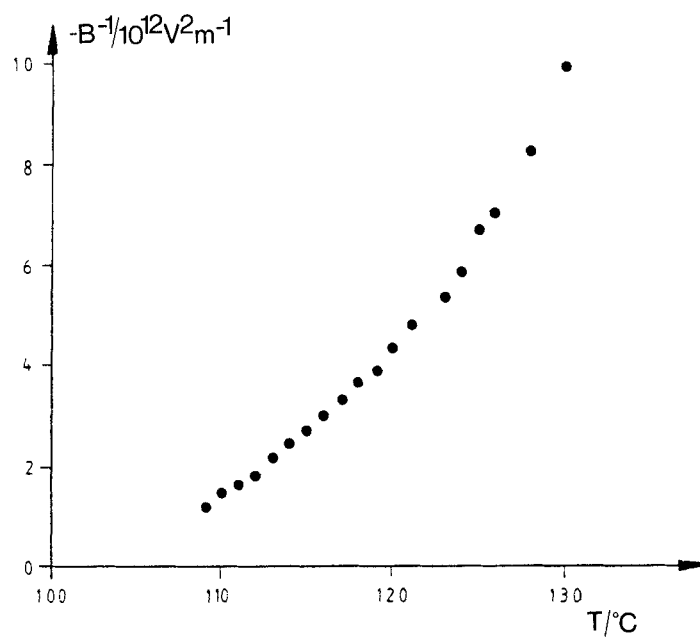


Figure 8. Variation of the inverse of the Kerr constant with temperature (single chain diol,  $n=14$ ).

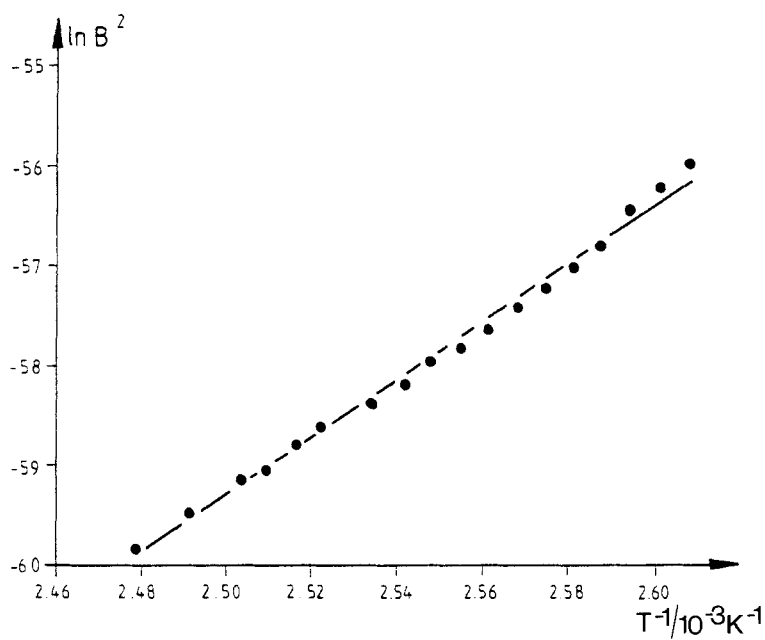


Figure 9. Plot of  $\ln B^2$  versus  $1/T$  (single chain diol,  $n=14$ ).

dependence of the association can be described by the scheme described earlier. Figure 9 shows the activation plot, i.e. a plot of  $\ln B^2$  versus  $1/T$ ; a nearly straight line results and the activation energies derived from this plot are in the range of  $200 \text{ kJ mol}^{-1}$ .

The absolute number differs from those reported for the three chain diols. This has to be taken as an indication that the internal structure of the associations and the internal interactions differ in each case and are thus controlled by the number of aliphatic chains per diol molecule. X-ray studies have revealed that the single chain diols build up layered structures [20]. X-ray investigations showed that similar structures might occur in the isotropic state, for instance as fluctuating associations.

So the conclusion is, as in the case of three chain diols, that hydrogen bonding leads to associations in the isotropic phase neighbouring a liquid-crystalline phase and that these associations couple strongly to the electro-optical properties of the diols. Next we address the problem of the absolute value of the activation energy.

### 5. Results of infrared spectroscopic studies

Further information about the aggregational behaviour results from infrared studies since the formation of hydrogen bonds leads to several absorption peaks in the IR spectrum. These peaks originate from different intermolecular bridging conformations (see figure 10). Besides groups which are only H bridged (see figure 10, case 1), O bridged (case 3) and O + H bridged (case 2) arrangements exist [21, 22]. These influence the OH vibration, resulting in three different peaks located at  $3420 \text{ cm}^{-1}$  (case 1),  $3325 \text{ cm}^{-1}$  (case 2) and  $3490 \text{ cm}^{-1}$  (case 3), respectively, whereas the vibration of the free OH group gives rise to a peak at  $3520 \text{ cm}^{-1}$ . It is possible, therefore, to deduce additional information on the local association and its variation with temperature from infrared studies. At room temperature the absorption bands can easily be resolved (see figure 11, case 1) whereas an increase in temperature (up to  $100^\circ\text{C}$ ) leads to a very broad single peak (see figure 11, case 2). A further increase of the temperature causes finally a change in the shape of the peak because of the different intensities of the individual peaks connected with the different kinds of hydrogen bonding (see figure 11, cases 3 and 4). In a first step the single peaks can be approximated by a lorentzian curve. Thus, the frequencies, widths and intensities of the single peaks can be determined at various temperatures. The experimental result is that the magnitude of the peak connected with O + H bridging is clearly decreased by increasing the temperature (see figure 12). Simultaneously the intensity of the band attributed to the free OH group is enhanced. Thus, a study of the slope of the intensity versus temperature yields information on the temperature dependence of the equilibrium constant and the activation energy. The analysis leads to values for the activation energy of the order of  $40 \text{ kJ mol}^{-1}$  in contrast to the value of  $200 \text{ kJ mol}^{-1}$  obtained from the temperature dependence of the Kerr constant. This leads to the conclusion that the association behaviour in the isotropic phase, although being strongly influenced by the effect of hydrogen bonding, is

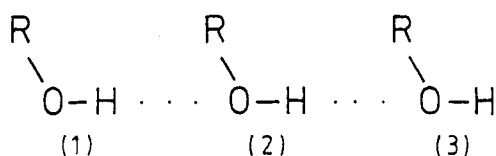


Figure 10. Possible ways of hydrogen bonding. Case 1, H bridged; case 2, O + H bridged; case 3, O bridged.

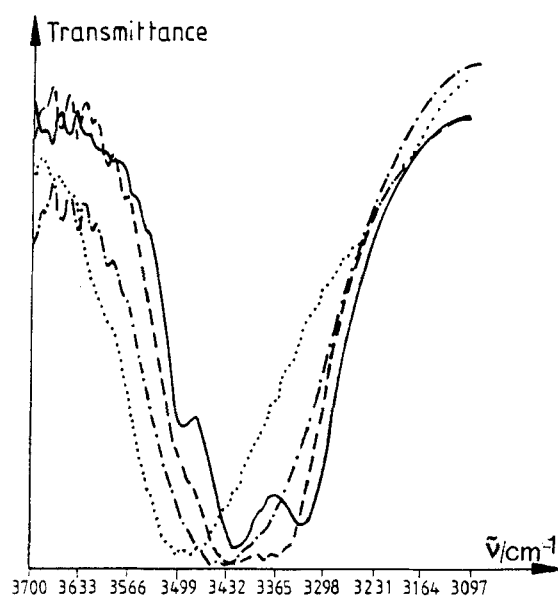


Figure 11. IR spectroscopic investigations. —, Room temperature; crystalline phase; ---, 100°C; mesophase; - · - · -, 125°C; isotropic phase; ···, 170°C; isotropic phase.

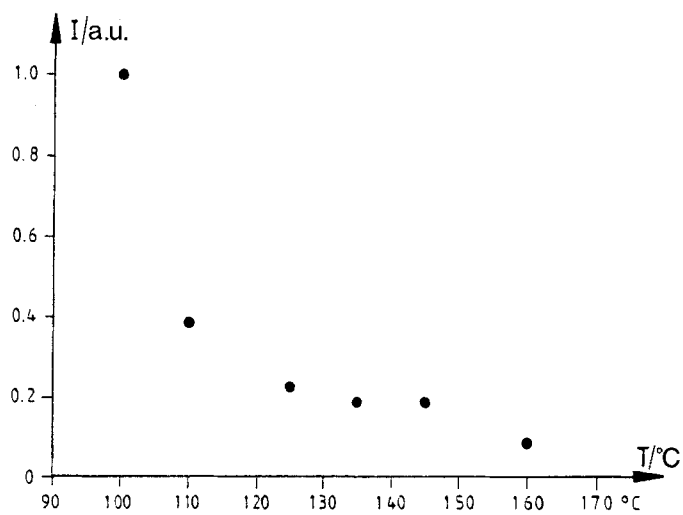


Figure 12. Relative intensity of the IR peak corresponding to O+H bonding (case 2).

subjected to additional aggregation phenomena. We suggest that this effect may arise from a critical Landau-de Gennes behaviour connected with a second order phase transition located at  $T^*$ . This gives rise to an additional temperature dependence of  $g_2$  in the form  $g_2 \sim (T - T^*)^{-1}$  and thus

$$g_2^{\text{total}} = g_2^{\text{hydrogen}} \times g_2^{\text{pretrans}}.$$

It is the superposition of these two phenomena which controls, evidently, structure formation in the diols considered here. The relative magnitude of the two phenomena seems to be a function of the number of aliphatic chains and thus also of the low temperature liquid-crystalline phase.

So the conclusion is that hydrogen bonding causes the occurrence of orientational correlations for three and single chain diols already in the isotropic phase. The orientational correlations seem to be controlled predominantly by hydrogen bonding for the three chain diols, whereas orientational correlations connected with a weak first order phase transition are superimposed for the single chain diols.

We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft (DFG) and the Fonds der Chemischen Industrie. We would like to thank P. Merz for performing the IR studies.

### References

- [1] DE GENNES, P. G., 1974, *The Physics of Liquid Crystals* (Clarendon Press).
- [2] FLORY, P. J., 1984, *Adv. Polym. Sci.*, **59**, 1.
- [3] MAIER, W., and SAUPE, S., 1959, *Z. Naturf. A*, **14a**, 882; 1960, **15a**, 287.
- [4] McMILLAN, W. L., 1971, *Phys. Rev. A*, **4**, 1238.
- [5] DE JEU, W. H., LONGA, L., and DEMUS, D., 1986, *J. chem. Phys.*, **84**, 6410.
- [6] LATTERMANN, G., STAUFER, G., and RENNER, G., 1988, *12th International Liquid Crystal Conference*, Freiburg.
- [7] EBERT, M., KLEPPINGER, R., LATTERMANN, G., SOLIMAN, M., STAUFER, G., WENDORFF, J. H., and WOLF, M., 1990, *Liq. Crystals*, **7**, 553.
- [8] EICH, M., ULLRICH, K. H., and WENDORFF, J. H., 1985, *Polymer*, **25**, 1271.
- [9] STEWART, J. J. P., 1990, *J. Comp. molec. Des.*, **4**, 1.
- [10] THIEL, W., 1988, *Tetrahedron*, **44** (24), 7393.
- [11] DUNMUR, D. A., 1981, *Molecular Electro-Optics*, edited by S. Krause (Plenum Press), p. 435.
- [12] DUNMUR, D. A., and TORIYAMA, K., 1986, *Molec. Crystals liq. Crystals*, **139**, 132.
- [13] CHANDRASEKHAR, S., 1983, *Phil. Trans. R. Soc. A*, **309**, 93.
- [14] KATS, E. I., and MONASTYRSKY, M. I., 1984, *J. Phys., Paris*, **45**, 709.
- [15] DANNHAUSER, W., and FLUECKINGER, A. F., 1963, *J. chem. Phys.*, **38**, 69.
- [16] BÖTTCHER, C. J. F., 1973, *Theory of Electric Polarization*, Vol. 1 (Elsevier Sci. Publ. Co.), chap. VI, §40.
- [17] LATTERMANN, G., and STAUFER, G., 1990, *Proceedings of the Liquid Crystal Workshop*, Freiburg.
- [18] SHARMA, N. K., PELZL, G., DEMUS, D., and WEISFLOG, W., 1980, *Z. phys. Chem. (Leipzig)*, **261**, 579.
- [19] KOLBE, A., PELZL, G., and WEISFLOG, W., 1982, *Adv. molec. relax. Interact. Processes*, **24**, 251.
- [20] EBERT, M., 1990, Ph.D. Thesis, TH Darmstadt.
- [21] SMITH, E. A., and CREITZ, E. C., 1951, *J. Res. natn. Bur. Stand.*, **46**, 145.
- [22] COBURN, W. C., and GRÜNWARD, E., 1958, *J. Am. chem. Soc.*, **80**, 1318.