Liquid Crystals

Publication details, including instructions for authors and subscription information:
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To cite this Article Hetzheim, Annemarie , Wasner, Christina , Werner, Johannes , Kresse, Horst and Tschierske, Carsten(1999) 'Liquid crystalline and dielectric properties of homologous series of substituted 1,3,4-oxadiazoles', Liquid Crystals, 26: 6, 885 — 891

To link to this Article: DOI: 10.1080/026782999204570

URL: http://dx.doi.org/10.1080/026782999204570

Liquid Crystals, 1999, Vol. 26, No. 6, 885–891

Liquid crystalline and dielectric properties of homologous series of substituted 1,3,4-oxadiazoles

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(*Received 24 November 1998; accepted 12 January 1999*)

Three homologous series of 2-alkylthio-5-phenyl-1,3,4-oxadiazole derivatives were synthesized [1, 2] and their liquid crystalline and dielectric properties investigated. Depending on the chain length, nematic, smectic A and smectic C phases were observed [1]. Dielectric investigations indicate a cross over of $\varepsilon_{\|o}$ and $\varepsilon_{\perp o}$ at the N/SmA phase transition. This is explained by a transition from a more statistical into an antiparallel correlation of the dipoles, mainly caused by steric effects.

1. Introduction

During the last decades a large number of mesomorphic compounds containing heterocyclic units have been synthesized [3, 4]. Interest in these compounds arises from the fact that inclusion of heteroatoms can cause large changes in the kind of mesophase present or in the physical properties of the phases. The well established classical concept of calamitic mesogens requires a molecular geometry as close to linearity as possible. This linearity is generally obtained by using 1,4-disubstituted six-membered aromatic, heteroaromatic or aliphatic rings as basic units. The incorporation of five membered heterocycles has been less extensively investigated. In particular, liquid crystalline 1,3,4-oxadiazoles were described only in recent years [5–12]. In connection with the considerable theoretical and technological interest in banana shaped achiral molecules [13], substituted 1,3,4-oxadiazoles become more significant. In investigations of liquid crystalline polyesters, it was established [11, 12] that the 1,3,4-oxadiazole unit serves as an angular disruptor in the polymer chain, the deviation from linearity being ~47° ascertained by X-ray analysis [15]. Also a few months ago non-linear mesomorphic liquid crystalline esters of 2,5-bis(4-hydroxyphenyl)-1,3,4-oxadiazoles [14] were reported.

As early as 1991 we were successful in synthesizing not only similarly substituted liquid crystalline esters of 2,5-bis(4-hydroxyphenyl)-1,3,4-oxadiazoles, but also 2-(4-alkylcyclohexyl)- and 2-alkylthio-5-(4-hydroxyphenyl)-1,3,4-oxadiazoles with wide mesomorphic ranges [5]. The structure–property relationships in these materials were studied and it was interesting to find out that the esters of 2-alkylthio-5-(4-hydroxyphenyl)-1,3,4-oxadiazoles show the widest mesomorphic ranges. Furthermore, these compounds exhibit an unusual dielectric behaviour: the sign of the dielectric anisotropy changes at the phase transition from the nematic to the smectic A phase. In addition, it is noted that the present increasing interest in mesomorphic oxadiazole derivatives is due to their photoconducting properties [16].

In continuation of our investigations [5], we have synthesized three homologous series of esters of 2-alkylthio-5-(4-hydroxyphenyl)-1,3,4-oxadiazoles and investigated their mesomorphic and dielectric properties.

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Journal of Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online ©1999 Taylor & Francis Ltd
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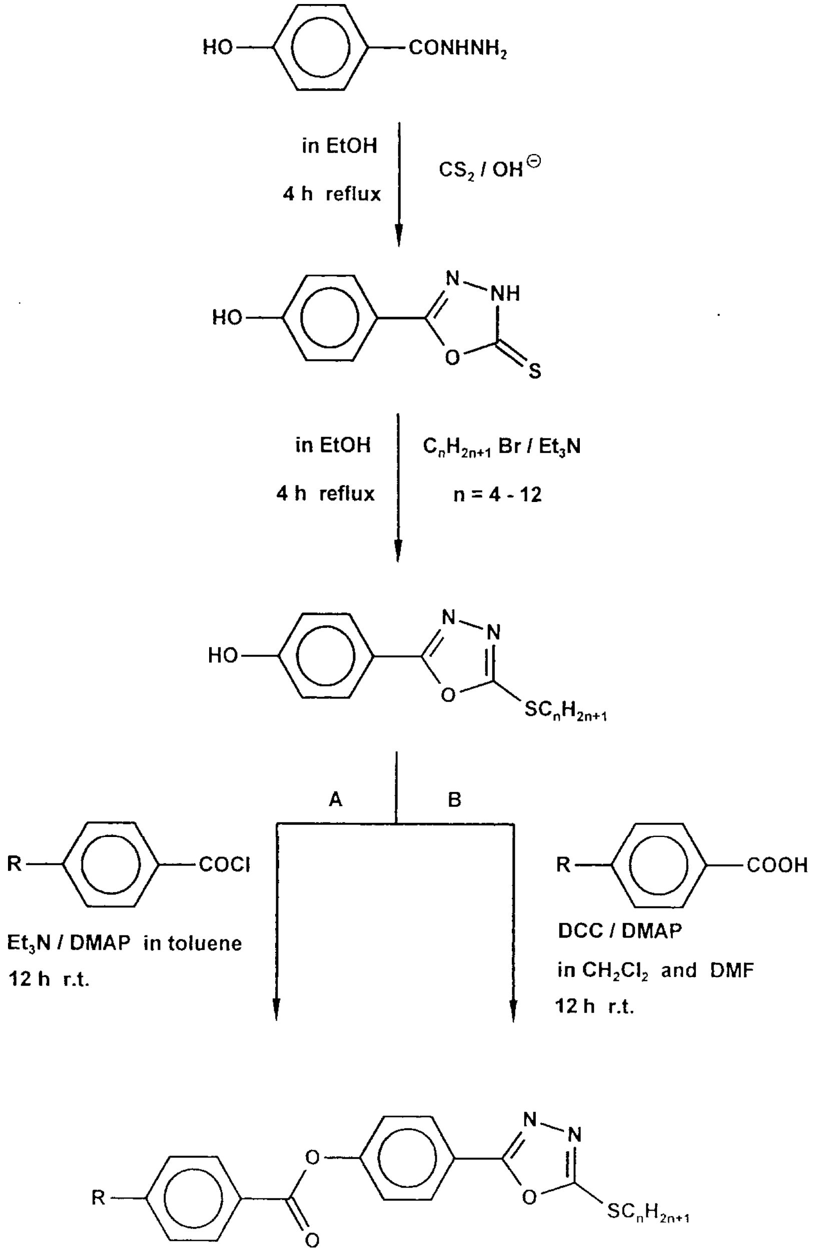
2. Results and discussion

2.1. *Synthesis*

The synthesis of the new compounds **1–3** was carried out as shown in the scheme according to procedures in our recent papers [1, 2, 5].

2.2. *Liquid crystalline properties*

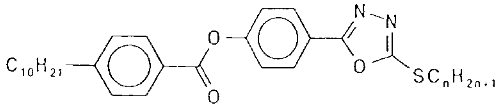
The transition temperatures of the members of these three homologous series are summarized in tables 1–3. All compounds synthesized display broad enantiotropic mesophase regions. The dependence of the clearing temperatures on the chain length is surprisingly low, without a significant odd–even effect. Therefore the individual compounds within each homologous series have nearly identical clearing temperatures. The short chain derivatives ($n = 4$–7) of series **1** and **2** exhibit SmA–N dimorphism. Further increasing the S-terminal alkyl chain gives rise to compounds with enantiotropic



1.1 - 1.9 R = $C_{10}H_{21}$-
2.1 - 2.9 R = $C_{10}H_{21}$-O-
3.1 - 3.9 R = CH_2=CH-$(CH_2)_9$-O-

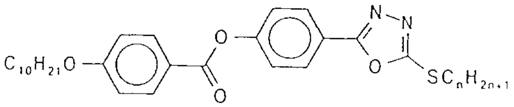
Scheme.

Table 1. Transition temperatures (°C) for the numbers of homologous series **1**.



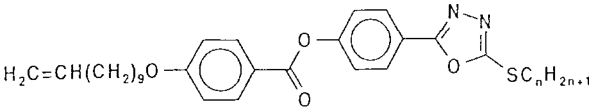
Compound	*n*	Cr		SmC		SmA		N		I
1.1	4	•	60	—	—	•	95	•	103	•
1.2	5	•	52	—	—	•	95	•	101	•
1.3	6	•	65	—	—	•	98	•	102	•
1.4	7	•	55	—	—	•	100	•	102	•
1.5	8	•	73	•	80	•	100	•	102	•
1.6	9	•	50	•	92	•	102	•	102.5	•
1.7	10	•	58	•	98.5	•	104.5	—	—	•
1.8	11	•	61	•	99	•	103.5	—	—	•
1.9	12	•	62	•	99.5	•	104	—	—	•

Table 2. Transition temperatures (°C) for the members of homologous series **2**.



Compound	*n*	Cr		SmC		SmA		N		I
2.1	4	•	74	—	—	•	125	•	128	•
2.2	5	•	85	—	—	•	125	•	127	•
2.3	6	•	88	—	—	•	125	•	127	•
2.4	7	•	81	—	—	•	126	•	126.5	•
2.5	8	•	75	•	95	•	125.3	—	—	•
2.6	9	•	71	•	115	•	127	—	—	•
2.7	10	•	85	•	110	•	123	—	—	•
2.8	11	•	81	•	117	•	126	—	—	•
2.9	12	•	85	•	116	•	125	—	—	•

Table 3. Transition temperatures (°C) for the members of homologous series **3**.



Compound	*n*	Cr		SmA		N		I
3.1	4	•	76	•	126	•	128	•
3.2	5	•	69	•	125	•	126	•
3.3	6	•	74	•	127	—	—	•
3.4	7	•	67	•	124	—	—	•
3.5	8	•	73	•	128	—	—	•
3.6	9	•	67	•	124	—	—	•
3.7	10	•	66	•	125	—	—	•
3.8	11	•	75	•	124	—	—	•
3.9	12	•	67	•	119	—	—	•

smectic C phases. In series **3**, the first two members ($n = 4$ and 5) exhibit SmA–N dimorphism; the remaining members studied are purely SmA in character.

2.3. *Dielectric investigations*

Comparative dielectric investigations were carried out on the 2-alkylthio-1,3,4-oxadiazoles **1.2**–**1.9**†. It was important to investigate the change of the dielectric data in a homologous series in order to make sure that the recently found abnormal dielectric behaviour [5] is connected with the special structure of these compounds. It was also important to test the quality of the orientation by precise dielectric measurements using the new equipment. The measured absorption on curves of the 5-substituted 2-pentylthio-1,3,4-oxadiazole **1.2** are presented in figure 1 at 84.6°C for the two main directions.

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† The measurements were carried out on samples in a microcapacitor ($d = 0.2$ mm, $A = 1\,\mathrm{cm}^2$). Capacities and resistances were measured with an HP 4192A impedance analyser. The samples were oriented in an external magnetic field of 0.6 T. The good orientation necessary for the calculation of the static dielectric constants, $\varepsilon_{\parallel\mathrm{o}}$ and $\varepsilon_{\perp\mathrm{o}}$, could be obtained in the nematic phase.

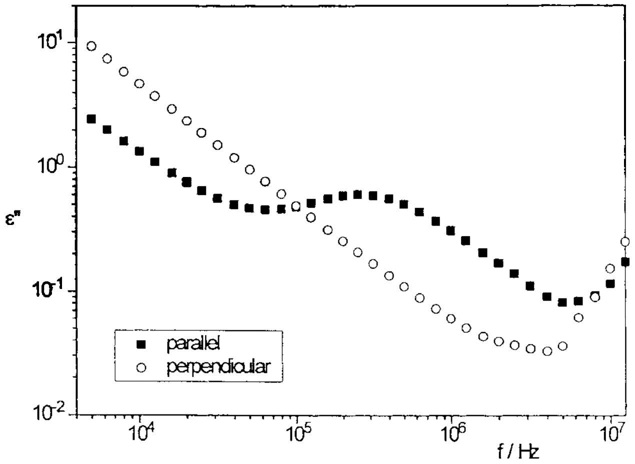


Figure 1. Absorption curves of compound **1.2** oriented parallel and perpendicular to the electric field at 84.6°C.

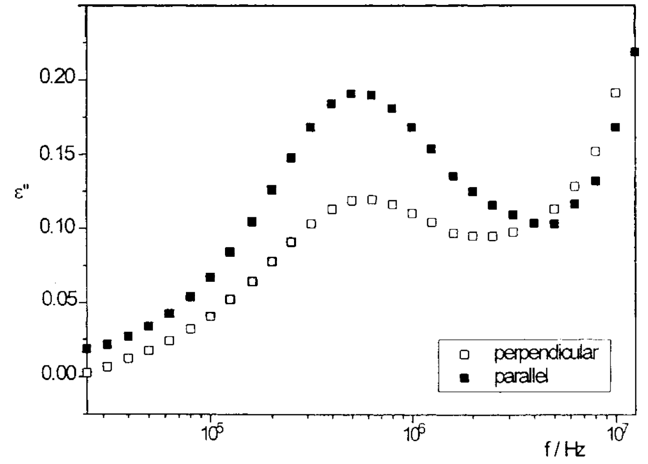


Figure 2. Absorption curves of compound **1.9** oriented parallel and perpendicular to the electrical field at 99.2°C.

An increase of ε'' at low frequencies is connected with the conductivity. Only in the parallel direction was a dielectric absorption detected at about 4×10^5 Hz. This indicates a well oriented sample. The absorption curves were fitted to the Debye equation [17] taking into consideration the conductivity Af^{-n} and the increase of ε'' at high frequencies Bf^m which arises from induction effects of the measuring equipment.

$$\varepsilon'' = \frac{\Delta_\parallel}{1+(f/f_R)^2} f/f_R + Af^{-n} + Bf^m. \qquad (1)$$

In this way the dielectric increments $\Delta_\parallel$ and the relaxation frequencies f_R of the samples could be calculated. An attempt to fit the data to the Cole–Cole equation [17] results in such small distribution parameters that the description by a Debye absorption is sufficient. The experimental fact that the absorption can be seen only in the parallel direction explains the molecular mechanism, namely reorientation around the molecular short axis hindered by the nematic potential [18]. For the compound **1.9** a dielectric absorption in both directions was measured (figure 2).

In order to eliminate the conductivity, the term Af^{-n} of equation (1) was subtracted from the measured values. From figure 2 it is evident that the relaxation frequencies measured in both directions are the same. Due to the incomplete orientation, one can see the reorientation around the molecular short axis in both directions given by the external magnetic field. Experimentally obtained absorption data after substraction of the terms $Af^{-n} + Bf^m$ are shown in figure 3 for compound **1.5**.

The decreasing absorption intensity of $\varepsilon''(\max) = \Delta_\parallel$ with decreasing temperature is the main feature of this experiment. For normal liquid crystals the opposite behaviour is expected [19]. For comparison, the $\Delta_\parallel$ data for four well oriented samples are plotted in figure 4 versus the temperature.

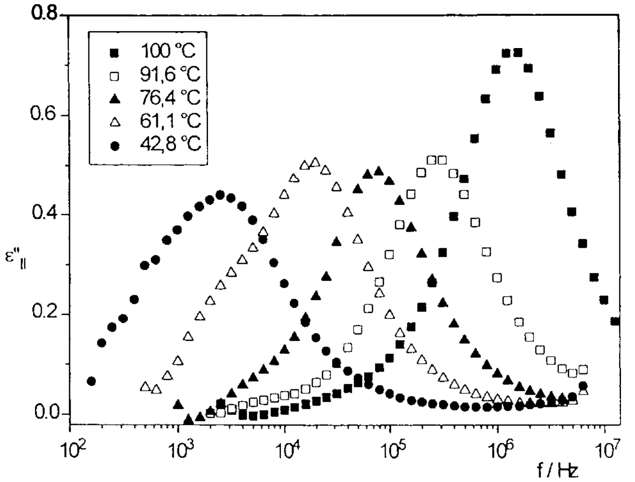


Figure 3. Corrected absorption curves for compound **1.5** at different temperatures.

Generally, a decrease of the dielectric increment with increasing chain length of the S-alkyl groups is observed. The abnormal behaviour of the dielectric absorption curves should be seen in the static dielectric constants too. In this case, it was necessary to fit the measured values to a dielectric dispersion curve to which a term Cf^{-n} was added in order to allow for the beginning of the formation of an electrical double layer:

$$\varepsilon_{\parallel 0} = \varepsilon_{\parallel\infty} \frac{\Delta_\parallel}{1+(f/f_R)^2} + Cf^{-n}. \qquad (2)$$

The data obtained for the dielectric increments $\Delta_\parallel$ and the relaxation frequencies f_R agree well with those from the independent fit of the absorption measurements according to equation (1). The results are presented for compounds **1.2** and **1.5** in figures 5 and 6, respectively.

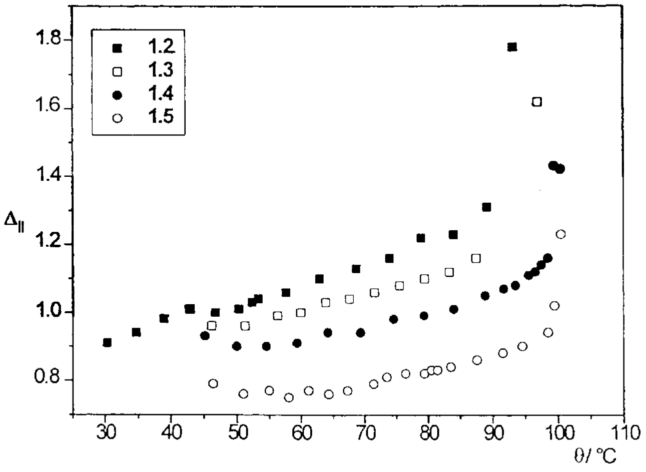


Figure 4. Temperature dependence of the dielectric increment of the compounds **1.2** to **1.5**.

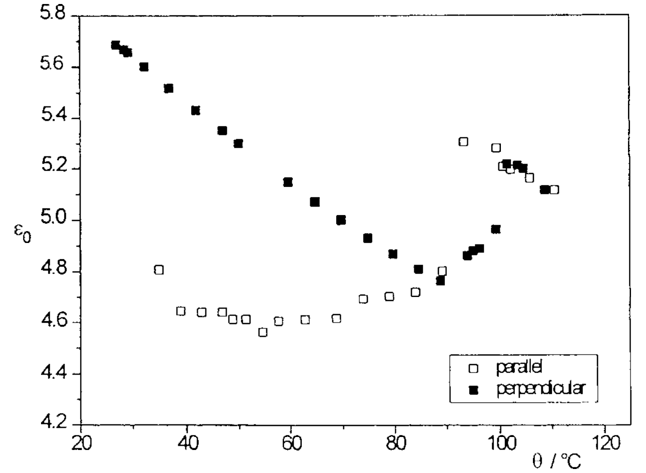


Figure 5. Temperature dependence of the static dielectric constant ε_0, measured parallel and perpendicular to the electrical field for sample **1.2**.

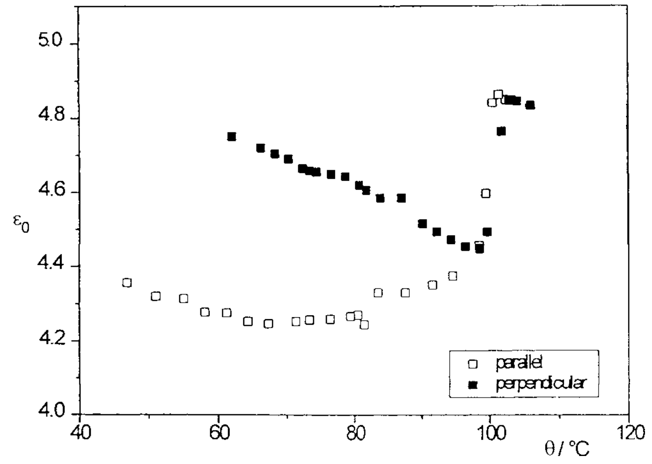
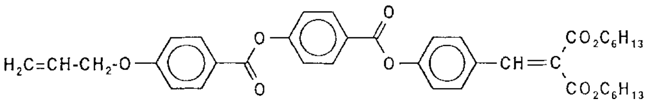


Figure 6. Temperature dependence of the static dielectric constant of compound **1.5**.

The unexpected result here is the cross over of $\varepsilon_{\|\mathrm{o}}$ and $\varepsilon_{\perp\mathrm{o}}$ which reflects a strong decrease of the effective dipole moment in the direction of the molecular long axis. This decrease occurs in the nematic phase and in the range of the N/SmA phase transition. For compound **1.5** with a nematic temperature range of about 1 K, $\varepsilon_{\|\mathrm{o}}$ immediately decreases after the phase transition I/N. The lack of a low frequency dielectric absorption in $\varepsilon_{\perp\mathrm{o}}$ and the cross over of $\varepsilon_{\|\mathrm{o}}$ and $\varepsilon_{\perp\mathrm{o}}$ clearly show that the observed effects are not related to incomplete orientation. Rather one has to think about dipolar correlation effects induced by the angular shape of the 1,3,4-oxadiazole derivatives as was also done in our earlier publication [5]. Here it was demonstrated that it is very difficult to destroy the antiparallel dipolar correlation by addition of rod-like molecules. Now we have done the opposite experiment, adding the swallow-tailed compound **4** to compound **1.5**.



4

Cr 50 SmC 87 N 110 I (°C)

For swallow-tailed compounds, the same tendency to an antiparallel ordering of the molecules in the short range with respect to the long axis is known [20, 21]. The phase diagram in figure 7 was obtained by the contact method and studies of the equimolar mixture. This indicates complete miscibility for the nematic and SmC phases. Static dielectric constants of **4** and the equimolar mixture (**Mi**) are presented in figure 8.

From these data it is obvious that there is a stronger compensation of the longitudinal dipoles in the mixture than in the pure compound **4**. Therefore the dielectric relaxation times of the 1,3,4-oxadiazole derivatives **1** were

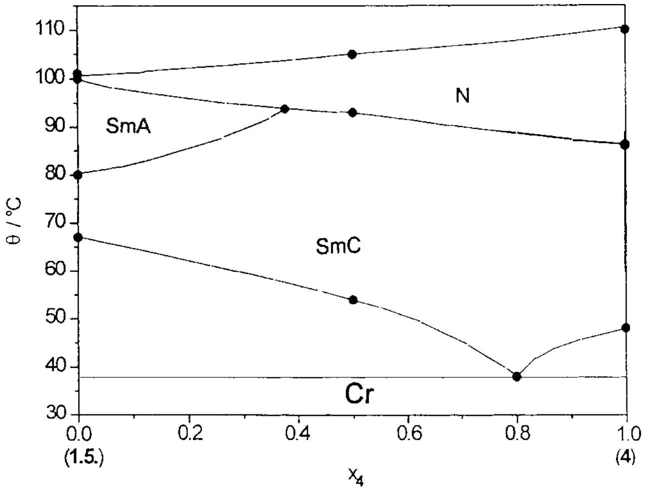


Figure 7. Phase diagram for binary mixtures of compounds **1.5** and **4**.

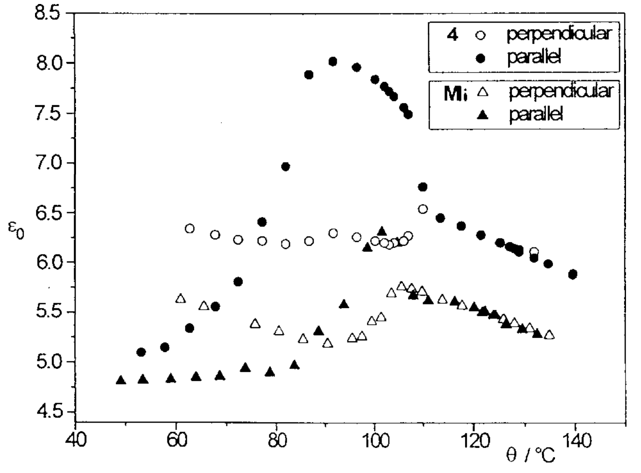


Figure 8. Static dielectric constants of compound **4** and an equimolar mixture (**Mi**).

compared, and figure 9 shows the systematic decrease of f_R with lengthening of the alkyl chain.

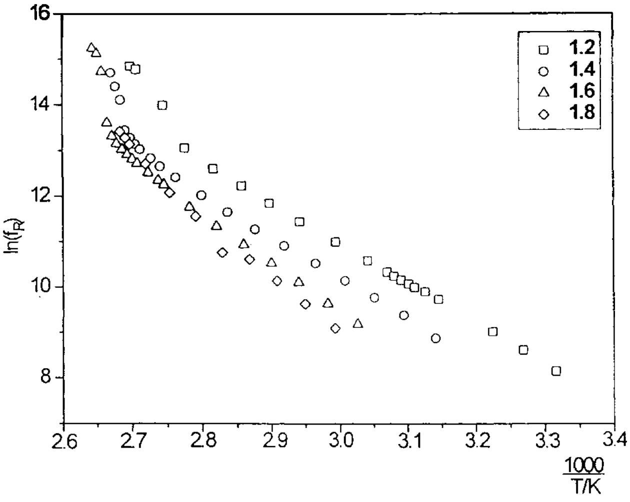
In some cases the f_R values in the isotropic state and the step in f_R at the N/I transition were also measured. Due to the small nematic phase range, activation energies E_A according to the Arrhenius equation were calculated only for the SmA and SmC phases.

$$\ln f_R = -\frac{E_A}{RT} + D \tag{3}$$

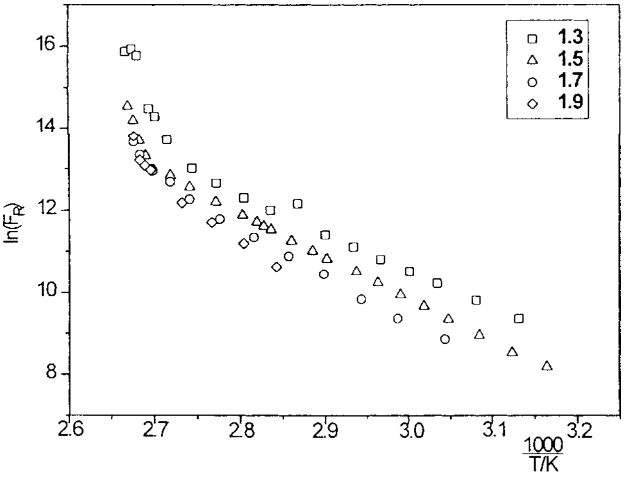
The data shown in figure 10 show a systematic increase of E_A with increase of the alkyl chain length.

Compared with other compounds [19], the dynamical behaviour of the 1,3,4-oxadiazoles **1** is not unusual. On the other hand the static dielectric constants in the parallel direction and $\Delta_{\|}$ decrease with decreasing temperature. This phenomenon can be explained by a transition from a more statistical into an antiparallel correlation of the dipoles in the short range as sketched in figure 11.

This results in a decrease of the effective dipole moment in the direction of the molecular long axis. The dipoles in the perpendicular direction are of course still statistically oriented. Another question is related to the driving force for this effect. Here one has to think first about the longitudinal dipole itself as a molecular reason [22]. However, if we look at the structure of the compounds **1** (given at the top of table 1), it is not possible to see big differences with respect to the dipolar components compared with those of the 4-methoxyphenyl 4-*n*-alkoxybenzoates [22] which show a normal dielectric behaviour according to the Maier–Meier model [23]. Therefore, we conclude that the angular shape of the molecules is responsible for this effect. Indeed, a mixture with the swallow-tailed compound **4** shows a systematic change in the dipolar correlation from the weaker one of **4** to the stronger one of **1.5**. The molecules of **1.5** are probably packed in the smectic layers like other swallow-tailed molecules, but here the experiment showing that rod-like molecules [5] and especially laterally branched [21, 24] molecules destroy the antiparallel correlation should be remembered. These arguments and the considerably strong change of $\varepsilon_{\|o}$ in comparison with the small longitudinal dipole moment (see for example [23]) lead to the conclusion that the observed dipolar correlation is mainly driven by steric factors.



(*a*)



(*b*)

Figure 9. (*a*) Arrhenius plot for compounds **1.2**, **1.4**, **1.6** and **1.8**; (*b*) Arrhenius plot for compounds **1.3**, **1.5**, **1.7** and **1.9**.

We are grateful for the financial support of the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft.

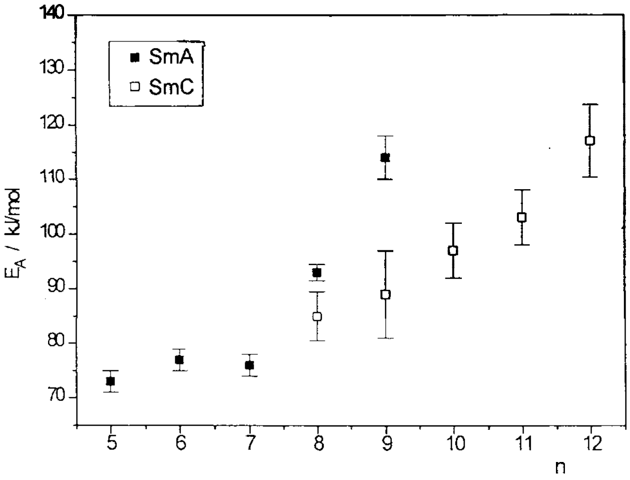


Figure 10. Activation energies for the reorientation around the molecular short axis of the compounds **1.2–1.9** (cf. table 1) as a function of the length of the alkyl chain. The error bars characterize a confidence level of 95%.

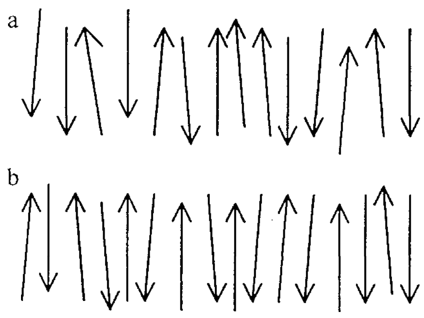


Figure 11. Model of a statistical (*a*) and an antiparallel correlated (*b*) arrangement of dipoles.

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