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New mesogenic 1,3,4-oxadiazole derivatives

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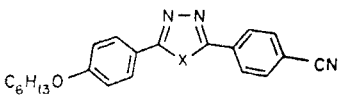
The synthesis of novel liquid-crystalline heteroaromatic compounds incorporating the five membered 1,3,4-oxadiazole ring is described. Due to the bent molecular structure of the oxadiazole ring their mesophase stability is low if the heterocyclic ring occupies a central position, but it is increased if this ring is shifted to a terminal position. Dielectric measurements indicate that the 2-*n*-alkylthio substitutes 1,3,4-oxadiazole derivatives change the sign of the dielectric anisotropy at the phase transition from the nematic to the smectic A phase. This effect is explained by the increase of the antiparallel correlation of the molecules on formation of the smectic layers.

1. Introduction

Heterocyclic compounds like pyridine and pyrimidine derivatives [1] are valuable liquid-crystalline materials for technical applications. It has also been reported that a five membered thiadiazole [2–5] or thiophene ring [6–7] may be incorporated into the principal structure of calamitic mesogens. Contrary to this, compounds with an oxygen atom in an aromatic ring are rare. 1,3,4-Oxadiazole derivatives were first described by Dimitrova and Zaschke [2]. But comparison of these compounds with the analogous thiadiazole derivatives reveals that the replacement of the sulphur atom by oxygen causes a complete loss of liquid-crystalline properties. The probable reason for the lack of mesogenic properties of the oxadiazole derivatives is that this substitution introduces a bend [8] into the molecule which inhibits liquid crystal formation.



X	C		S_A		N		I	Ref.
S	●	146°C	●	258°C	●	264°C	●	[2]
O	●	160°C	—	—	—	—	●	[2]

Nevertheless, mesogenic 2-aminooxadiazole derivatives have been synthesized [9] and recently a patent describing some examples of liquid-crystalline oxadiazole derivatives was published [10].

Here we report the synthesis and investigations of the following types of new liquid-crystalline 1,3,4-oxadiazole derivatives:

* Author for correspondence.

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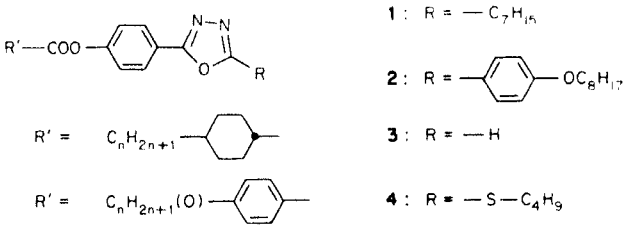
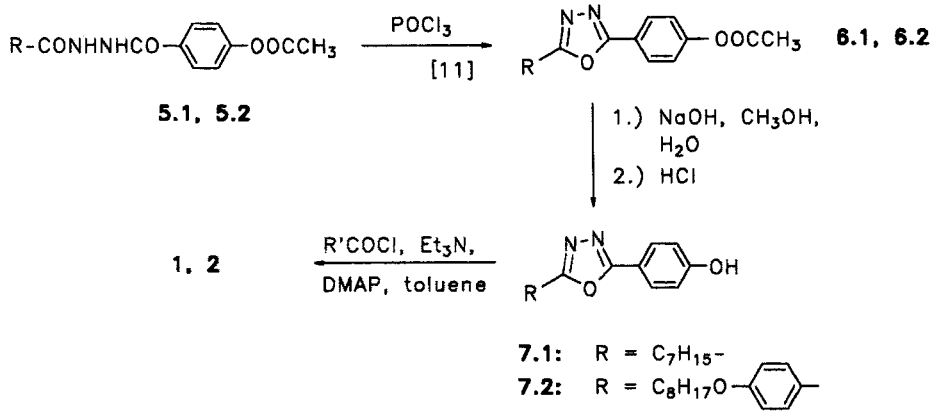


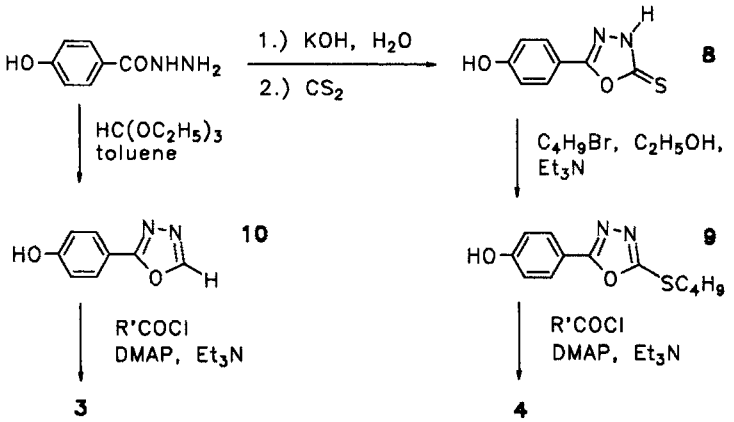
2. Synthesis

The route adopted for the synthesis of the new compounds **1** and **2** is given in scheme 1.



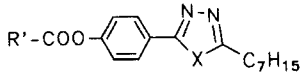
Scheme 1. Synthesis of compounds **1** and **2**.

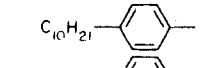
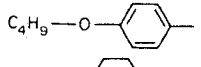
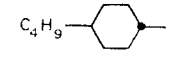
The oxadiazole derivatives **3** and **4** were synthesized, starting with 4-hydroxybenzoic hydrazide. Treatment of this compound with carbon disulphide in the presence of potassium hydroxide yielded the 5-(4-hydroxyphenyl)-1,3,4-oxadiazoline-2-thione **8** [12], from which the 2-butylthio-1,3,4-oxadiazole derivatives **4** were obtained by selective *S* alkylation with *n*-butylbromide in the presence of triethylamine, followed by esterification (see scheme 2) [13]. The reaction of 4-hydroxybenzoic hydrazide with triethyl orthoformate gave the 2-(4-hydroxyphenyl)-1,3,4-oxadiazole **10** [14] from which compounds **3** were available. The final products were purified by repeated recrystallization from ethanol.



Scheme 2. Synthesis of the compounds **3** and **4**.

Table 1. Transition temperatures of the 2-*n*-heptyl-1,3,4-oxadiazole derivatives **1** in comparison with analogous 2-*n*-heptyl-1,3,4-thiadiazole derivatives [5].



		X=O				*X*=S								
Compound	*R'*	C		S_A		I	C		S_C		S_A		N	I
1.1		•	106°C	•	(105°C)	•	•	105°C	•	140°C	•	141°C	• 143°C	•
1.2		•	108°C	•	123°C	•	•	103°C	•	123°C	—	—	• 181°C	•
1.3		•	85°C	•	118°C	•	•	62°CCS_X	•	96°CCS_Y 110°C	•	105°CCS_G 165°C	• 173°C	•

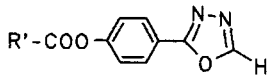
3. Liquid-crystalline properties

Transition temperatures were determined by optical texture observations using a polarizing microscope equipped with a hot stage; they are listed in tables 1–5. Contrary to the oxadiazole derivatives described by Dimitrova and Zaschke in which the oxadiazole ring occupies a central position, the new compounds **1** exhibit smectic A mesophases (see table 1; $X = O$). This can easily be explained if it is assumed that the bend in the molecular shape is reduced to a certain degree if the oxadiazole ring is shifted to the terminal position of the rigid aromatic core. In this position the flexible *n*-alkyl chain allows the partial compensation of the molecular bend. But in comparison to the analogous 1,3,4-thiadiazole derivatives the clearing temperatures are much lower and the polymorphism is less pronounced (see table 1); in particular the S_C phase is largely suppressed. This may be due to the decreased permanent lateral dipole and/or the bend molecular structure.

The mesophase stability could be increased by detaching the alkyl chain next to the oxadiazole ring (see table 2). This is a rather unusual behaviour and is contradictory to that observed for other (rigid) rod-like mesogens. Usually, compounds with only one chain exhibit lower clearing temperatures than those with two chains (see table 3).

The attachment of an alkyl chain to the oxadiazole ring should amplify the bend of the molecule and therefore, the mesophase stability decreases in this special case. Furthermore, the unsubstituted oxadiazole ring may be looked upon as a polar terminal substituent increasing nematic thermal stability.

Table 2. Transition temperatures of the oxadiazole derivatives **3**.



Compound	*R*	C		N		I
3.1	$C_{10}H_{21}$—	•	99°C	•	121°C	•
3.2	$C_{10}H_{21}$—O—	•	117°C	•	145°C	•
3.3	C_5H_{11}—	•	94°C	•	157°C	•

Table 3. Comparison of the liquid-crystalline phase behaviour of pyrimidine and oxadiazole derivatives with one or two alkyl chains attached to the rigid core.

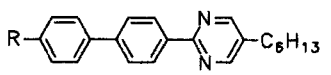
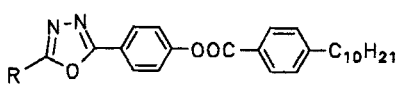
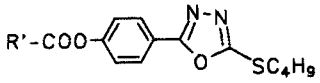
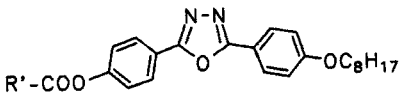
	R	C		S_A		I	Ref.
	H—	•	96°C	•	137°C	•	[15]
	C_6H_{13}—	•	104°C	•	185°C	•	[16]
	H—	•	99°C	N	121°C	•	
	C_7H_{15}—	•	106°C	•	(105°C)	•	

Table 4. Mesomorphic properties of the 2-butylthio-1,3,4-oxadiazole derivatives **4**.



Compound	*R'*	C	S_A	N	I
4.1	$C_{10}H_{21}$—	• 60°C	• 95°C	• 104°C	•
4.2	$C_{10}H_{21}$—O—	• 74°C	• 125°C	• 128°C	•
4.3	C_4H_9—	• 57°C	• 95°C	• 127°C	•

Table 5. Transition temperatures of the 2,5-diphenyl-1,3-4-oxadiazole derivatives **2**.



Compound	*R'*	C	S_B	S_C	S_A	N	I
2.1	$C_{10}H_{21}$—	• 104°C	• 106°C	• 115°C	— —	• 146°C	•
2.2	C_4H_9—O—	• 135°C	— —	— —	— —	• 178°C	•
2.3	C_8H_{17}—O—	• 142°C	— —	— —	— —	• 171°C	•
2.4	C_6H_{13}—CH=CH—	• 138°C	— —	— —	— —	• 187°C	•
2.5	C_4H_9—	• 117°C	— —	— —	• 140°C	• 179°C	•
2.6	C_5H_{11}—	• 120°C	— —	— —	• 158°C	• 186°C	•

The 2-alkylthio-1,3,4-oxadiazole derivatives **4** (see table 4) have clearing temperatures, which are similar to those of the analogous *n*-alkyl derivatives, but the melting temperatures are significantly lower and so these compounds exhibit the broadest mesomorphic ranges.

Finally we tried again to obtain liquid-crystalline phases by variation of the structure given in the Introduction. The idea was to increase the molecular length by incorporating an additional six-membered ring into the rigid core. These four ring 2,5-diphenyl-1,3,4-oxadiazole derivatives **2** (see table 5) exhibit nematic and some of them also smectic liquid-crystalline properties. However the clearing temperatures are only moderate and they are of the same order of magnitude as those of the unsymmetric three ring compounds **1**. We must conclude, therefore, that the 2,5-diphenyl substituted 1,3,4-oxadiazole derivatives **2** (see table 5) exhibit liquid-crystalline properties only if the rigid core contains at least four rings. For the 1,3,4-thiadiazole derivatives only

three or even two such rings are sufficient to obtain liquid-crystalline phases [2–5]; therefore, a significant mesophase destabilization is caused by the replacement of sulphur by oxygen. This should mainly be due to the deviation of the molecular shape from linearity, which is much more significant for 1,3,4-oxadiazoles and is especially strong if the oxadiazole ring occupies a central position.

4. Dielectric properties

It should be proved by dielectric measurements, whether the special geometry of the 1,3,4-oxadiazoles will influence the short range order. The dielectric measurements were carried out in the frequency range from 100 Hz to 100 kHz in a double plate capacitor ($A \approx 2\,\text{cm}^2$, $d = 0{\cdot}02\,\text{cm}$). Because of the relatively high conductivity the dielectric constants parallel $\varepsilon'_{\parallel}$ and perpendicular $\varepsilon'_{\perp}$ to the director were measured at 10 kHz. The samples were magnetically oriented ($H \approx 0{\cdot}7\,\text{T}$). The static ($\varepsilon_{\perp 0}$, $\varepsilon_{\parallel 01}$) and quasistatic ($\varepsilon_{\parallel 02}$) dielectric constants of sample **4.1** are presented in figure 1. Here $\varepsilon_{\parallel 02}$ is the dielectric constant after the first relaxation process is finished, i.e. the reorientation around the short molecular axis. We note that $\varepsilon_{\parallel 01}$ decreases at the transition from the nematic to the smectic A phase which results in a change of sign of $\Delta\varepsilon = \varepsilon_{\parallel 01} - \varepsilon_{\perp 0}$ of samples **4.1** and **4.2**. Dielectric absorption curves of sample **4.1** are given in figure 2. They have been used to estimate the low ($\varepsilon_{\parallel 01}$) and high frequency limits ($\varepsilon_{\parallel 02}$) of $\varepsilon_{\parallel}$. Sample **4.3** has such a high conductivity at high temperatures that electrical double layers falsify the ε values. The maxima of dielectric absorption $\varepsilon''_{\parallel}$(max)

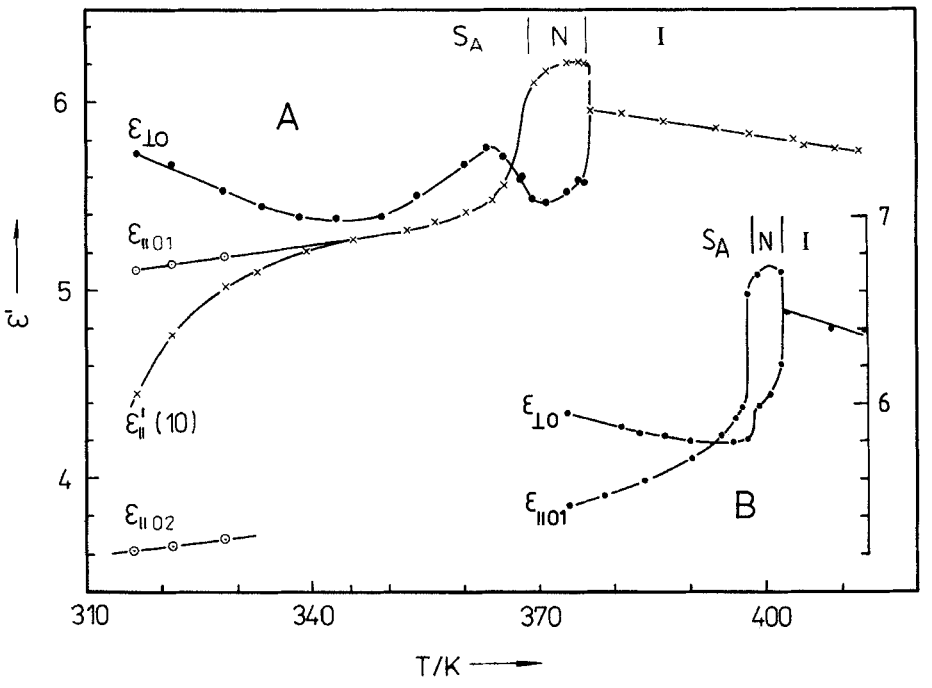


Figure 1. Static ($\varepsilon_{\perp 0}$, $\varepsilon_{\parallel 01}$) and quasistatic ($\varepsilon_{\parallel 02}$) dielectric constants at 10 kHz ($\varepsilon'_{\parallel}$ (10)) of sample **4.1** (A) and **4.2** (B) at different temperatures. The ε' scale of sample B is on the right hand side of the figure.

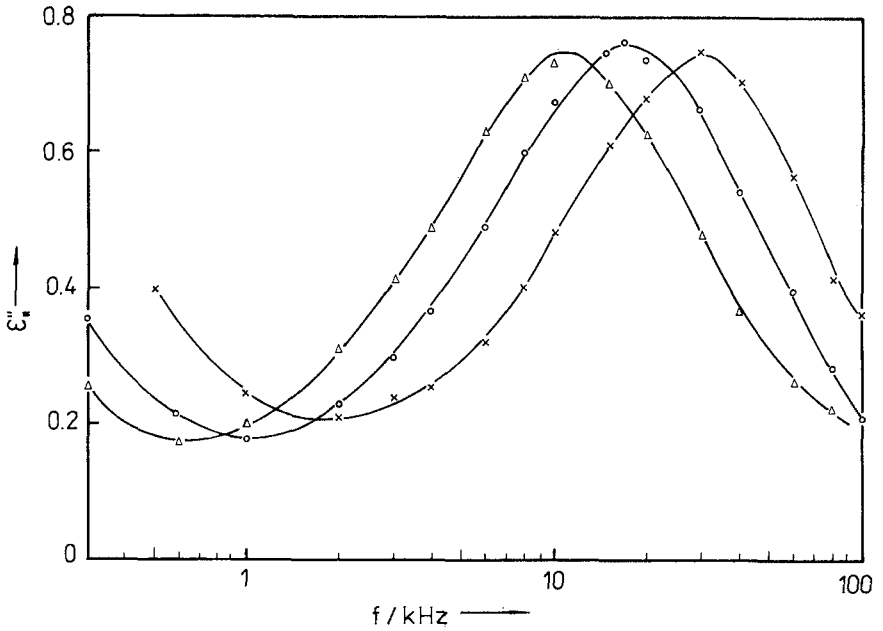


Figure 2. Dielectric absorption curves for $\varepsilon''_{\parallel}$ of sample **4.1** at 316·7 K (△), 321·5 K (○) and 328·5 K (×).

Table 6. Dielectric absorption intensity and jump in $\varepsilon_{\parallel 01}$ at T_{S_AN}.

Sample	$\varepsilon''_{\parallel(max)}$	$\Delta\varepsilon(N\text{–}S_A)$
4.1	0·75	0·55
4.2	0·75	0·85
4.3	0·28	0·2

50 K below the clearing temperatures and the steps of $\varepsilon_{\parallel 01}$ at the N–S_A transition, estimated according to

$$\Delta\varepsilon(N\text{–}S_A)=\varepsilon_{\parallel 01}(T_{S_AN}+2/K)-\varepsilon_{\parallel 01}(T_{S_AN}-2/K)$$

are given in table 6.

Figure 3 shows the relaxation frequencies of the three substances as a function of the reciprocal temperature; the activation energy is about 72 kJ mol^{-1}.

The following experimental results should be briefly discussed.

(i) The higher absorption intensity of the benzoates (**4.1**; **4.2**) in relation to that of the cyclohexanecarboxylate (**4.3**) is caused by the increase of the longitudinal dipole due to mesomeric effects. The expected higher value of sample **4.2** which should result from the alkyloxy group is diminished at the transition from the nematic into the smectic A phase.

(ii) The unexpected large decrease of $\varepsilon_{\parallel 01}$ at the N→S_A transition is connected with a non-equilibrium distribution of the longitudinal dipole. The molecular reason for such an effect can be a strong dipole–dipole correlation [17] or a preferred orientation of the molecules at short range caused by attractive

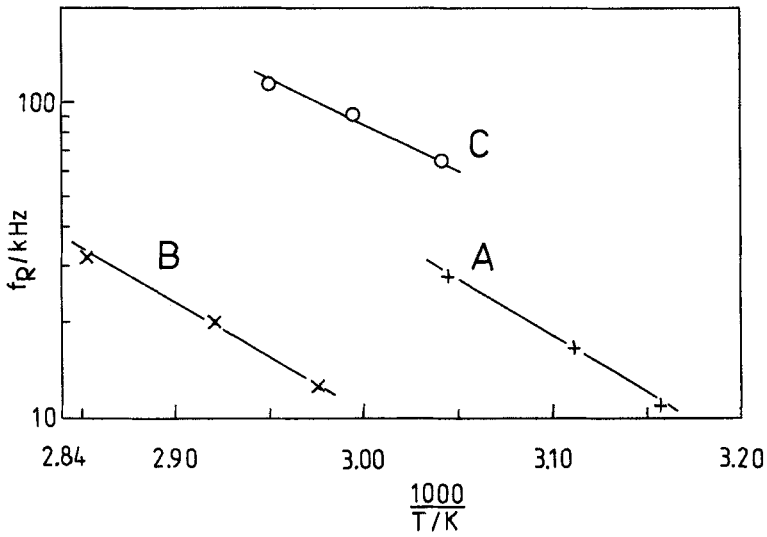


Figure 3. Arrhenius plot of the relaxation frequencies of samples **4.1** (A), **4.2** (B) and **4.3** (C).

forces [18]. In contrast to swallow-tailed molecules [19] where $\varepsilon_{\parallel 01}$ also decreases strongly in the S_A phase [18], here the main effect arises if the molecules are ordered in layers. Perhaps this is connected with the non-rod-like shape of the molecules, which forces them to be more antiparallel ordered in the S_A layers.

(iii) A comparison of the relaxation frequencies of samples **4.2** and **4.3**, which exhibit nearly the same clearing temperatures, shows that the cyclohexane derivative has a ten-fold higher mobility for the reorientation of the molecules around the short molecular axis then that of the respective benzene derivative **4.2**.

Based on this model we wanted to destroy the antiparallel order of the molecules of **4.2** by the addition of rod-like molecules. Therefore, a mixture of 35·5 mole% of **4.2** and 64·5 mole% of 4-*n*-heptyloxyphenyl-4′-*n*-hexyloxy benzoate (C 55°C N 87°C I) was investigated. The phase sequence of the mixture (C 43–46°C S_A 84–85°C N 99–100·5°C I) indicates the dominance of a molecular interaction, which forms a higher ordered smectic A phase. From the dielectric measurements given in figure 4 it could be shown that $\varepsilon_{\parallel 01}$ decreases in the nematic phase with decreasing temperature. The decrease of $\varepsilon_{\parallel 01}$ at the N→S_A transition is not so pronounced as for **4.2** but it can be observed. Generally it can be concluded that the decrease of $\varepsilon_{\parallel 01}$ arises from compound **4.2** and cannot be observed in the pure phenyl benzoate derivative (see figure 4 E). In comparison with swallow-tailed molecules which show the same effect [18] we explain the decrease of $\varepsilon_{\parallel 01}$ by the bent molecular structure which leads in the S_A phase to aggregates in which the molecules are more antiparallel oriented. Due to the statistical distribution of the positions of the molecules in the nematic phase, here the antiparallel correlation is not so strong but nevertheless $\varepsilon_{\parallel 01} < \varepsilon_{\parallel 01}$ (cal) (see dotted line in figure 4, curve D, $\varepsilon_{\parallel 01}$ (cal)), a value which was calculated from $\varepsilon_{\perp 0}$ and ε_1 according to the Maier–Meier theory [20].

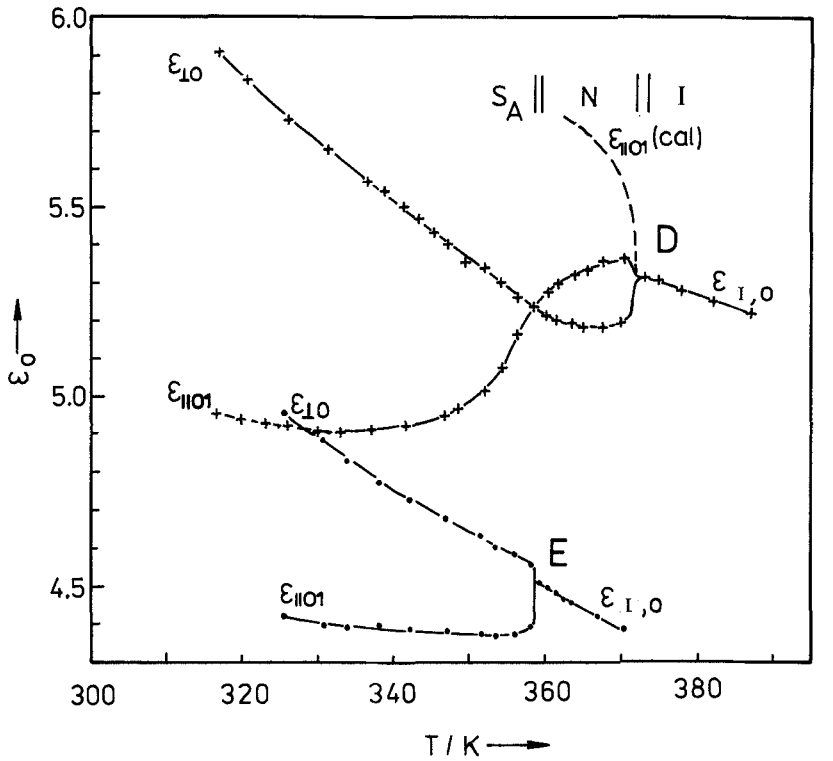


Figure 4. Static dielectric constants of the mixture **4.2** + 4-*n*-heptyloxyphenyl-4′-*n*-hexyloxy benzoate (D) and pure 4-*n*-heptyloxyphenyl-4′-*n*-hexyloxy benzoate (E) as functions of the frequency. The $\varepsilon_{\parallel 01}$ (cal) values are expected data if the strong antiparallel correlation is neglected.

5. Experimental

Melting points and transition temperatures were determined using a Boetius polarizing microscope. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WP 200 spectrometer. All new compounds have satisfactory IR, ^{1}H and ^{13}C NMR spectra and elemental analysis.

5.1. *2-(4-Hydroxyphenyl)-5-(4-octyloxyphenyl)-1,3,4-oxadiazole* **7.2**

The diacylhydrazine derivatives **5** were prepared according to the procedure given in [2]. 0·01 mol (4·26 g) of **5.2** was added to 0·05 mol (7·7 g) $POCl_3$ and heated to reflux temperature for 1 h. The excess of $POCl_3$ was evaporated under reduced pressure at 70°C. After cooling to room temperature, the oily residue was treated with 50 ml ice-water and the precipitate formed (comp. **6.2**) was filtered off and washed three times with 50 ml of cold water. The crude product obtained was dissolved in 100 ml of methanol. After addition of a solution of 0·025 mol (0·14 g) KOH in 0·5 ml of water the mixture was refluxed for 15 min. Afterwards the solvent was evaporated using a rotatory evaporator, and the resulting residue was dissolved in 50 ml of water. The cold solution was acidified by careful addition of dilute hydrochloric acid. A white precipitate was formed, which was filtered off and recrystallized from ethanol to yield 0·8 g of **7.2** (0·0034 mol, 34%; mp: 167°C). Compound **7.1** was obtained in an analogous manner (yield 52 per cent; mp: 123°C).

5.2. *5-(4-Hydroxyphenyl)-1,3,4-oxadiazole-2-thione* **8**

A solution of 5·5 g of KOH in 50 ml of water was added dropwise to a stirred suspension of 0·1 mol (15 g) of 4-hydroxybenzoic hydrazide in 300 ml of ethanol at 20–25°C. After all of the hydrazide had dissolved, 8 ml carbon disulphide was carefully added at the same temperature. The solution was refluxed for 4 h and afterwards the solvent was evaporated in vacuum using a rotatory evaporator. The residue was poured into a mixture of 200 g ice and 50 ml concentrated hydrochloric acid. The precipitate formed was filtered off and recrystallized from ethanol/water (4 : 1) to yield 13·9 g of **8** (72·5 per cent; mp: 214°C).

5.3. *2-(4-Hydroxyphenyl)-5-butylthio-1,3,4-oxadiazole* **9**

0·01 mol (1 g) of triethylamine and 0·01 mol (1·4 g) of *n*-butyl bromide were successively added dropwise to a stirred solution of 0·01 mol (1·94 g) of 8 in 20 ml of dry ethanol. After heating the mixture for 4 h the solvent was evaporated on a rotatory evaporator. 50 ml of water was added and the resulting precipitate was collected and recrystallized from ethanol/water (1 : 1). 2·4 g (96%) of **9** were obtained in this way. mp: 130–132°C.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7·86 (d, $J = 8{\cdot}7$ Hz, 2H, CH-arom.), 7·12 (s, broad, 1H, –OH), 6·92 (d, $J = 8{\cdot}7$ Hz, 2H, CH–arom.), 3·27 (t, $J = 7{\cdot}2$ Hz, 2H, $-CH_2-S-$), 1·79 (m, 2H, $-CH_2-$), 1·47 (m, 2 H, $-CH_2$), 0·94 (t, $J = 7{\cdot}3$ Hz, 3 H, $-CH_3$).

5.4. *2-(4-Hydroxyphenyl)-1,3,4-oxadiazole* **10**

A mixture consisting of 0·1 mol (15 g) of 4-hydroxybenzoic hydrazide, 0·19 mol (28 g) of triethyl orthoformate and 100 ml of toluene was heated to 100°C and the ethanol formed during the reaction was distilled off continuously. After the formation of ethanol had ceased, the solution was cooled down to −20°C. The crystals formed were filtered off and recrystallized from ethanol/water (3 : 7) to yield 14·3 g of **10**. 88 per cent; mp: 256–257°C.

5.5. *Esterification*

To a solution of 1 mmol of one of the compounds **7.1, 7.2, 9** or **10**, 10 mg 4-dimethylaminopyridine (DMAP) and 1·5 mmol (0·15 g) of triethylamine in 10 ml of dry toluene was added 1·1 mmol of the appropriate acid chloride. The mixture was stirred overnight at room temperature. After dilution with 50 ml of diethyl ether and 50 ml of water, the organic layer was separated, washed twice with 50 ml of water and once with 20 ml of brine. Drying over sodium sulphate and evaporation of the solvent gave the crude esters **1**–**4**, which were purified by repeated recrystallization from methanol or ethanol. Representative examples of the ^{1}H and ^{13}CNMR spectra are:

1.2: ^{1}H NMR (200 MHz, $CDCl_3$): δ 8·12 (d, $J = 8{\cdot}9$ Hz, 2 H, CH–arom.), 8·07 (d, $J = 8{\cdot}5$ Hz, 2 H, CH–arom.), 7·34 (d, $J = 8{\cdot}7$ Hz, 2 H, CH–arom.), 6·96 (d, $J = 8{\cdot}9$ Hz, 2 H, CH–arom.), 4·04 (t, $J = 6{\cdot}4$ Hz, 2 H, $-CH_2-O$), 2·91 (t, $J = 7{\cdot}6$ Hz, 2H, $-CH_2-$ oxadiaz.), 0·83–1·87 (m, 20 H, $-CH_2-$, $-CH_3$),

^{13}C NMR (50 MHz, $CDCl_3$): 167·1, 164·4, 164·1, 163·8, 132·9 (2C), 128·1 (2C), 122·6 (2C), 121·6, 121·0, 114·4 (2C), 68·1, 31·6, 31·1, 29·0, 28·8, 26·6, 25·5, 22·6, 19·2, 14·0, 13·8;

3.2: ^{1}H NMR (200 MHz, $CDCl_3$): δ 8·45 (s, 1 H, H-oxadiaz.), 8·12 (d, $J = 7{\cdot}9$ Hz, 2 H, CH–arom.), 8·11 (d, $J = 8{\cdot}8$ Hz, 2 H, CH–arom.), 7·36 (d, $J = 8{\cdot}7$, 2 H, CH–arom.), 6·95 (d, $J = 6{\cdot}5$ Hz, 2 H, CH–arom.), 4·02 (t, $J = 6{\cdot}5$ Hz, 2 H, $-CH_2-O-$), 0·82–1·87 (m, 19 H $-CH_2-$, $-CH_3$),

^{13}C NMR (50 MHz, $CDCl_3$): 164·3, 164·1, 163·8, 153·9, 152·6, 132·3 (2C), 128·4 (2C), 122·7 (2C), 120·8, 114·4 (2C), 68·3, 31·8, 29·5 (3C), 29·3 (2C), 29·0, 25·9, 22·6, 14·0;

4.2: ^{1}H NMR (200 MHz, $CDCl_3$): δ 8·12 (d, $J = 8·8$ Hz, 2 H, CH–arom.), 8·05 (d, $J = 8·7$ Hz, 2 H, CH–arom.), 7·34 (d, $J = 8·7$ Hz, 2 H, CH–arom.), 6·96 (d, $J = 8·9$ Hz, 2 H, CH–arom.), 4·03 (t, $J = 6·5$ Hz, $-CH_2-O-$), 3·29 (t, $J = 7·2$ Hz, 2 H, $-CH_2-S-$), 0·84–1·90 (26 H, $-CH_2-$, $-CH_3$).

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