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Sulphur ligated siamese twin mesogens

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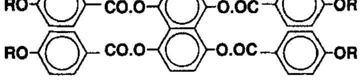
The synthesis of 3,3′-sulphinyl-bis-[alkyl 4-(4-substituted benzoyloxy)-benzoates] and 3,3′-sulphonyl-bis-[alkyl 4-(4-substituent-benzoyloxy)-benzoates] is described. These new nematic compounds are of the ligated siamese twin type. By microscopy and DSC calorimetry the thermal behaviour was investigated. Many of the new compounds transform on quenching to the glassy nematic state with glass temperatures above room temperature. Above the glass temperature the substances behave like highly viscous but ordinary nematics. The substances may be used for the construction of new thermo-electrooptic displays. By means of dielectric and X-ray investigations we were able to show that the two halves of the twin molecules are in an antiparallel orientation in the nematic state. In mixtures of the new compounds with rod-like nematics reentrant nematic behaviour was observed.

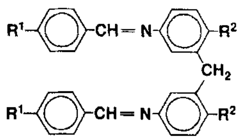
1. Introduction

Long ago Vorländer [1] had already established his rule concerning the elongated shape of mesogenic molecules. This rule has been confirmed in more than 15 000 cases [2, 3] there is, however, a small number of liquid-crystalline substances which does not follow this scheme. Among these non-conventional liquid-crystalline compounds the siamese twins play a special role. Siamese twin mesogens are compounds in which two independently mesogenic parts are joined in a single molecule. Though he did not use the term twin, Vorländer [4] synthesized the first liquid-crystalline twins of the type which is now called the tail-to-tail twins. Malthete *et al.* [5] were the first to use this terminology when reporting their synthesis of nematogenic 1,4,5,8-tetrasubstituted naphthalenes:



(fused twins)

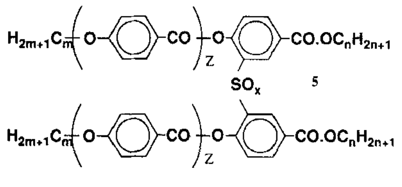
Griffin *et al.* [6–8] synthesized and investigated mesogenic bisazomethines which are ligated by a methylene group:



(ligated twins [9])

The different kinds of twins have been discussed by Griffin *et al.* [9].

Stimulated by these results we have synthesized ligated twins which are joined by sulphur, the sulphinyl or the sulphonyl group

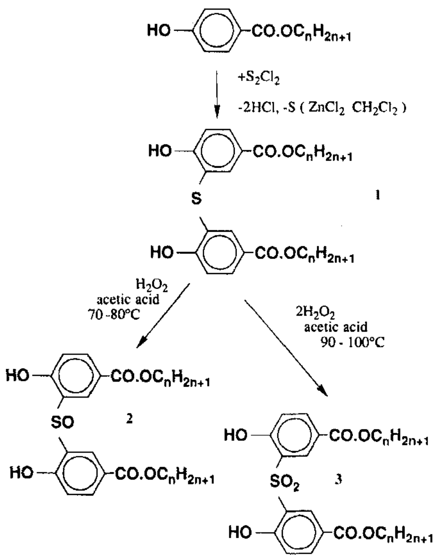


$x = 0, 1, 2$

2. Results

2.1. *Synthesis*

The ligated parent compounds **1**, **2**, **3** were obtained by using the procedure described by Denisova *et al.* [10] for the methyl ester:



We succeeded in applying the method of Denisova *et al.* to other alkyl esters according to the following generalized instruments:

3,3′-Sulphur-bis(alkyl 4-hydroxybenzoates) **1**

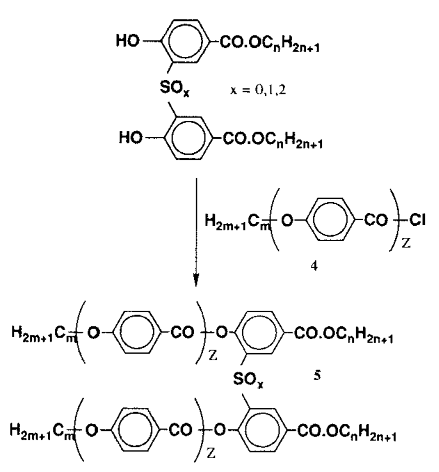
0·4 mol alkyl 4-hydroxybenzoate were suspended with 2·6 g (0·02 mol) $ZnCl_2$ in dry dichloromethane and stirred for 20 min at room temperature. A solution of 16·2 ml (0·2 mol) disulphurdichloride in 20 ml dry dichloromethane was dropped into the refluxed mixture for two hours. The beginning of the reaction is indicated by a rapid generation of HCl gas and a gradual solution of the suspended ester. After three more hours the precipitated sulphide **1** was filtered off, boiled for some minutes in 150 ml water and dried. The crude product was recrystallized from 50 per cent acetic acid. As an example we give some data for the methyl ester: m.p. 184–186°C, yield 80%.

3,3′-Sulphinyl-bis(alkyl 4-hydroxy-benzoates) **2** *and* *3,3′-Sulphonyl-bis(alkyl 4-hydroxy-benzoates)* **3**

0·045 mol sulphide **1** were suspended in acetic acid. In order to obtain the sulphoxide **2** it was stirred and refluxed at 70–80°C. 5·1 g (0·045 mol) of a 30 per cent solution of H_2O_2 were dropped into the mixture as it became a solution. After stirring at this temperature for two hours, precipitating and cooling the sulphoxide **2** was filtered off and recrystallized from 50 per cent acetic acid. As an example we give some data for the methyl ester: m.p. 222–224°C, yield 60 per cent.

In order to obtain sulphone **3** the suspension of sulphide **1** was stirred and refluxed at 90–100°C. 15 g (0·135 mol) of a 30 per cent solution of H_2O_2 were dropped into the suspension which was rapidly dissolved. After stirring for three hours at this temperature and after cooling the sulphone **3** precipitated and was filtered off. It was recrystallized from methanol. We give as an example some data for the methyl ester: m.p. 210–212°C, yield 64 per cent.

We obtained ligated siamese twin mesogens by esterifying bisphenols **1**, **2** and **3** with 4-substituted benzoyl chlorides **4**



$x = 1, 2;\ z = 1, 2;\ m = 1\text{–}9;\ n = 1\text{–}4.$

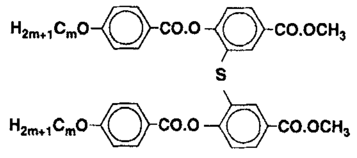
The esterification was performed using a standard procedure [11]. Products **5** were repeatedly recrystallized from methanol or ethanol, **5m,m′** and **5z,z′** from *n*-propanol or acetone (see tables 1, 2 and 3). The yields of the pure product ranged from 45 to 85 per cent.

All of the compounds were subject to elementary analysis and spectral data (e.g. IR spectra) were obtained. The structures of the parent compounds **2** and **3** were ascertained by mass spectroscopy. All results from the characterization are consistent with the proposed structures. A complete set of analytical data is presented for compound **5y**.

3,3′-sulphonyl-bis-[methyl 4-(4-nonyloxy-benzoyloxy)-benzoate]
IR (KBr pellet) cm^{-1}: 3060, 2910, 2840, 1750, 1730, 1334, 1248, 1114
elementary analysis: $C_{48}H_{58}O_{12}S$ (859·1) % calc. C 67·11 H 6·81 S 3·73
% found C 66·81 H 7·21 S 3·90

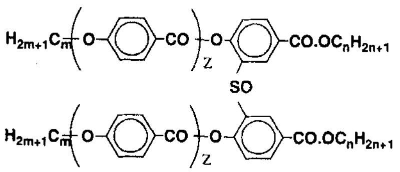
The results of the synthesis are collected in tables 1, 2 and 3.

Table 1. Transitional properties for the 3,3′-sulphur-bis-[methyl 4-(4-*n*-alkyloxy-benzoyloxy)-benzoates].



Compound	m	T_m/°C
5a	6	138
5b	8	142

Table 2. Transitional properties for the 3,3′-sulphinyl-bis-[*n*-alkyl 4-(4-substituted benzoyloxy)-benzoates].



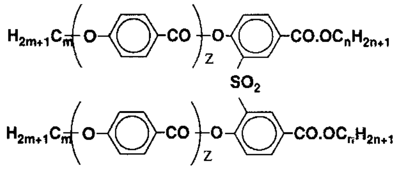
Compound	z	m	n	T_m†/°C	T_{NI}/°C
5c	1	1	1	190	—
5d	1	2	1	210	—
5e	1	3	1	189	(80)
5f	1	4	1	172	(118)
5g	1	5	1	148	(117)
5h	1	6	1	146	(121)
5i	1	7	1	125	(118)
5j	1	8	1	131	(119)
5k	1	8	2	109	(87)
5l	1	8	3	118	(77)
5m	2	8	1	208	218
5m′	2	10	1	185	229

† Melting temperature of the most stable solid crystal modification.
Brackets denote monotropic transitions.

2.2. *Thermal behaviour*

Although the molecular structures of all compounds **5** are very similar, the analogous sulphides, sulphoxides and sulphones have different liquid-crystalline properties. Thus the sulphides ($x = 0, z = 1, n = 1$) **5a** ($m = 6$) and **5b** ($m = 8$) are not mesogenic (see table 1), the analogous sulphoxides ($x = 1$, $z = 1$, $n = 1$) **5h** ($m = 6$) and **5j** ($m = 8$) show nematic phases on supercooling the isotropic phase (see table 2), and the analogous sulphones ($x = 2$, $z = 1$, $n = 1$) **5s** ($m = 6$) and **5n** ($m = 8$) have stable nematic phases (see table 3). Obviously the number of oxygen atoms in the ligating group causes this different thermal behaviour. In figure 1 the N–I transition temperatures of sulphoxides ($x = 1, z = 1$) are compared to those of the analogous sulphones ($x = 2$, $z = 1$). In most cases this transition temperature is about 30 to 50 K higher for the sulphones than for the sulphoxides. We interpret this phenomenon by increasing polarizability of the sulphonyl group as opposed to the

Table 3. Transitional properties for the 3,3′-sulphonyl-bis-[*n*-alkyl 4-(4-substituted benzoyloxy)-benzoates].



Compound	*z*	*m*	*n*	T_m†/°C	T_{NI}/°C
5n	1	1	1	226	—
5o	1	2	1	217	—
5p	1	3	1	209	(161)
5q	1	4	1	174	(170)
5r	1	5	1	170	(159)
5s	1	6	1	152	163
5t	1	7	1	144	155
5u	1	8	1	139	151
5v	1	8	2	126	(116)
5w	1	8	3	106	(104)
5x	1	8	4	100	(82)‡
5y	1	9	1	139·5	144·5
5z	2	8	1	220	258
5z′	2	10	1	199	244

† Melting point of the most stable crystal modification.

‡ The melt begins to crystallize at 90°C on cooling, the solid and mesogenic phase exist together until complete crystallization.

sulphinyl or the sulphur group and by the influence of the geometry of the ligating group on the molecular shape. The sulphonyl group has an approximately tetrahedral shape and thus enables the two halves of the molecule to arrange themselves in a parallel or antiparallel conformation and to form a stretched rod. The sulphinyl group and sulphur deviate in their bonding angles from a tetrahedron shape and so the

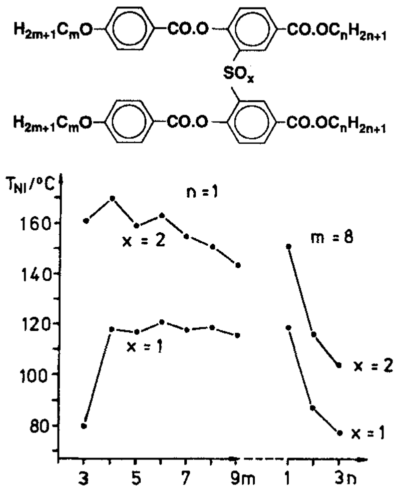
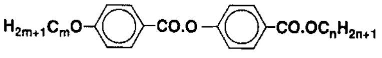


Figure 1. Comparison of the N–I transition temperatures and sulphinyl ligated twins **5** (x = 1) and sulphonyl ligated twins **5** (x = 2).

mobility of the twin halves should increase with decreasing number of oxygen atoms. This increasing mobility makes it more difficult for a stretched molecular shape to emerge and consequently the liquid-crystalline properties deteriorate.

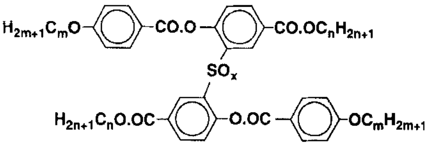
In some cases the half twins



also have nematic properties [3]. The N–I transition temperatures are more than 100 K lower than those of analogous sulphonyl ligated twins. In contrast to the twins the tendency to form stable mesogenic phases increases for the half twins if both terminal groups become longer, e.g.:

$m = 5$	$n = 1$	C	96	I				[3]
$m = 7$	$n = 1$	C	37·2	N	39·5	I		[3]
$m = 6$	$n = 4$	C	63·8	N	67·2	I		[3]
$m = 8$	$n = 3$	C	49	S_A	80	I		

For twins a prolongation of the alkyl ester group results in a decrease of the clearing points and for the sulphones ($x = 2$, $z = 1$) there is a change from enantiotropic nematic properties for the methyl ester **5u** ($m = 8$, $n = 1$) to monotropic nematic properties for the other alkyl esters **5v–x** ($m = 8$; $n = 2, 3, 4$). For this reason we concluded that twins are most likely to exist in the nematic phase in an antiparallel conformation



and that the alkyl ester group acts upon the molecular shape rather like a lateral substituent. Existing in a parallel conformation the elongation of the alkyl ester group should improve the mesogenic properties. This hypothesis was to be proved by dielectric investigations (see §2.3) and X-ray investigations (see §2.4). The thermal behaviour of all siamese twin mesogens **5** shows an additional interesting feature, on quenching (see table 4) the nematic phases can be transformed into a vitreous nematic state.

In order to observe the thermal behaviour in detail, we made calorimetric investigations by means of a DSC-2 (Perkin-Elmer) calorimeter. Preparing the first recording we placed 6 to 10 mg of the crystalline substances into the DSC and heated it to detect the melting and clearing transitions; the heating rate was 10 K min^{-1} in this case. The second run began with cooling the isotropic liquid; we used cooling rates of 20 K min^{-1}. In the third run we heated the compounds to their melting temperatures; we used a heating rate of 10 K min^{-1} again. The results of the D.S.C. measurements are listed in table 4. We investigated the thermal behaviour of seven compounds of the sulphoxide and of seven compounds of the sulphone series. The general sequence of thermal effects, detected by DSC, is shown in figure 2. The first heating of crystalline substances yields melting peaks with transition enthalpies between 40 and 70 kJ mol^{-1}. Solid–solid transitions were observed in some cases. On cooling samples in the D.S.C., we found N–I transitions for substances **5e**, **f**, **g**, **k**, **m′**,

Table 4. Transitional properties.

Compounds **5**	x	z	m	n	ΔH_m/kJ mol^{-1}	ΔH_{NI}/kJ mol^{-1}	T_g/°C	ΔC_p/J K^{-1} mol^{-1}
c	1	1	1	1	61·1 (prim.) 40·1 (sec.)	—	58	273
d	1	1	2	1	65·0 (prim.) 29·8 (sec.)	—	49	310
e	1	1	3	1	56·4 (prim.) 52·6 (sec.)	1·8	44	282
f	1	1	4	1	63·8 (prim.) 61·1 (sec.)	2·7	41	210
g	1	1	5	1	50·4 (prim.) 47·3 (sec.)	2·4	33	297
k	1	1	8	2	44·6 (sec.)	2·1	10	140
m′	1	2	10	1	57·6 (prim.) 50·8 (sec.)	3·2	37	414
n	2	1	1	1	53·3 (prim.) 24·2 (sec.)	—	65	207
o	2	1	2	1	66·9 (prim.) 51·3 (sec.)	—	55	165
p	2	1	3	1	56·4 (prim.) 49·0 (sec.)	1·0	49	167
q	2	1	4	1	51·3 (prim.) 44·2 (sec.)	2·0	43	280
r	2	1	5	1	50·3 (prim.) 17·1 (sec.)	1·4	34	201
v	2	1	8	2	44·6 (sec.)	1·3	12	190
z′	2	2	10	1	58·2 (prim.) 48·5 (sec.)	?	39	284

p, **q**, **r**, **v** and **z′**. The enthalpies of these transitions have values between 1 and 4 kJ mol^{-1}. On further cooling, at certain temperatures the observation of glass-transitions was possible. The output of the D.S.C. shows a step in this temperature region. The thermal interval of the glass transition had a width of about 8 K, on average. We obtained isotropic glasses for substances **5c**, **d**, **n** and **o** and nematic glasses for the other compounds (figure 2). The temperatures for the start of the softening process on heating the glassy materials are given in table 4. In the method of determining T_g we have followed earlier publications [12, 13]. We also made an attempt to determine the jump in the heat capacity, ΔC_p, from the steps. We found values in the range between 140 and 414 J K^{-1} mol^{-1} (see table 4), which is in good agreement with literature results [12, 14] obtained for liquid crystals with different chemical structure.

Comparing the T_g values with the molecular structure, we may point out, that due to the bulky molecular shape, these compounds have relatively high glass transition temperatures [29]. Moreover, there is a regular connection between T_g and the length of the alkyl or alkyloxy groups on both ends of the molecules. This relationship is shown in figures 3 and 4. With growing length of the alkyl and/or alkyloxy chains the T_g values decrease. This becomes clear, if we consider, that the degree of flexibility of the peripheral parts of the molecules increases with increasing chain length. In this way the alkyloxy chains carry out a softening effect on the glassy phase.

Further heating leads to exothermal effects, corresponding to the crystallization of the metastable liquid. Additional endothermal effects are also possible. They may

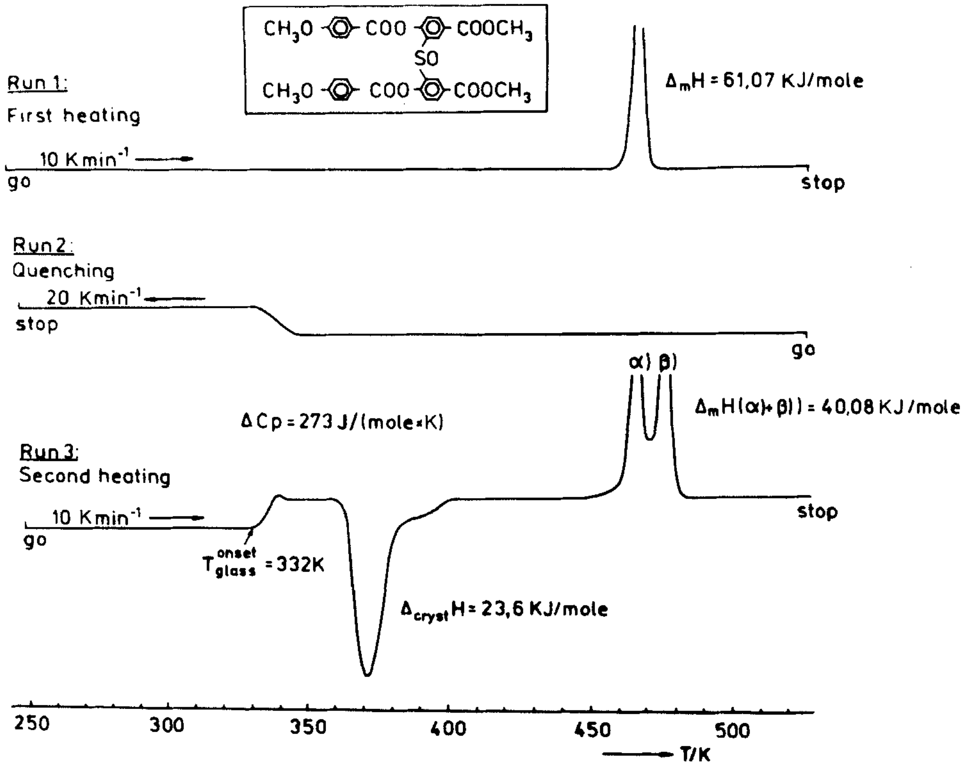


Figure 2. D.S.C. plot for a glass transition obtained by quenching an isotropic melt. No liquid-crystalline phase occurs. Width of softening interval: 8 K. The enthalpy relaxation peak in run 3 at the end of the softening interval is a characteristic feature for the transformation glass to liquid.

correspond to the formation of other solid phases or to the intermediate formation of disordered crystals. At the end of the second heating we found melting peaks in the vicinity of the observed primary melting peaks. The melting temperatures and the melting enthalpies in run 3 are lower than in run 1 in most cases. This may be due, partly, to incomplete crystallization or also to the appearance of metastable solid phases. Similar behaviour frequently occurs in organic compounds and has been considered in detail in [15]. Griffin *et al.* [6] report that a metastable solid phase is exhibited by their methylene bridged compounds. The sluggish crystallisations which occur in these compounds [8] may indicate a very high viscosity of the melt, as is characteristic for regions near to a glass transition. This shows that these twins are behaving very similarly to the sulphur bridged compounds.

2.3. *Dielectric investigations*

In the new twin compounds, in principle, two conformations should be possible in the nematic state; parallel (model A, figure 5) or antiparallel (model B, figure 5) arrangement of the two molecular halves. In order to obtain some information about the conformation we carried out dielectric measurements in magnetically oriented samples ($B = 0{\cdot}6\,T$) in a microcapacitor ($d = 0{\cdot}02\,\mathrm{cm}$, $A = 1\,\mathrm{cm}^2$) made from silver.

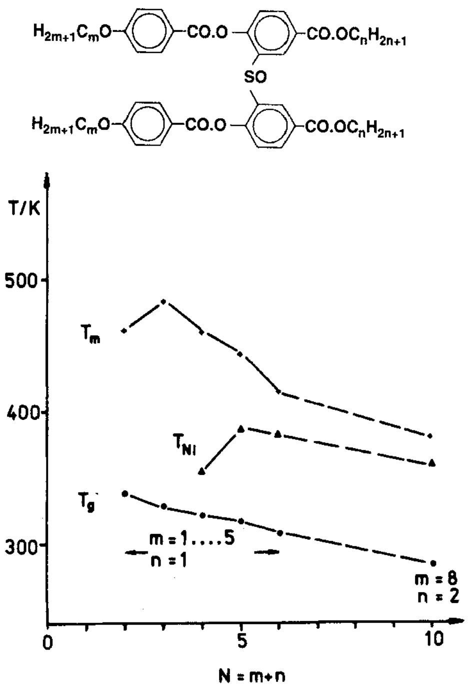


Figure 3. Transition temperatures in the series of the 3,3′-sulphinyl-bis-[alkyl 4-(4-substituted benzoyloxy)-benzoates].

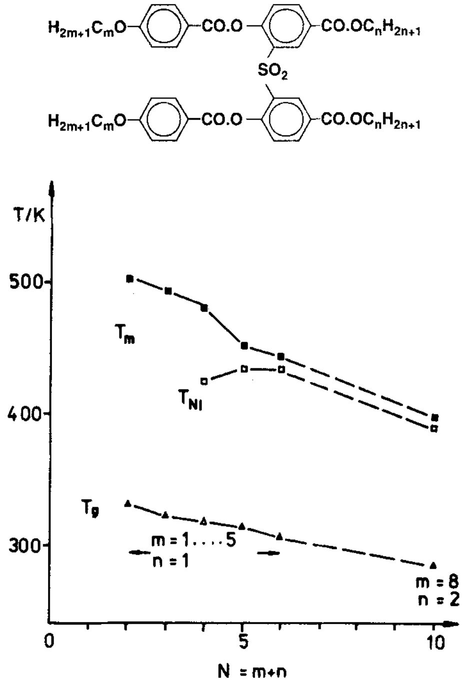


Figure 4. Transition temperatures in the series of the 3,3′-sulphonyl-bis-[alkyl 4-(4-substituted benzoyloxy)-benzoates].

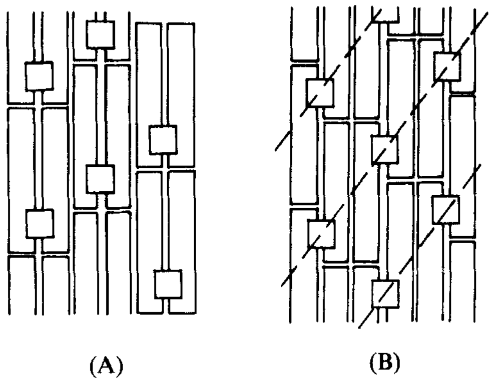
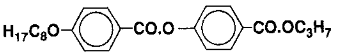


Figure 5. Models of the parallel (A) and antiparallel (B) orientation of the molecular halves of the ligated twins; *d* is the X-ray periodicity.

The basic molecule *B*



C 49°C S_A 80°C I

may be considered as the half of the twin **5w**. Since this compound is smectic we have made comparative investigations by mixing it with the basic mixture. The basic mixture BM [16] is nematic at room temperature and it consists of the chemically very stable compounds

27 mol-%	4-*n*-octyloxyphenyle	4-*n*-pentyloxybenzoate
24 mol-%	4-*n*-hexyloxyphenyle	4-methoxybenzoate
12 mol-%	4-*n*-heptyloxyphenyle	4-*n*-hexyloxybenzoate
37 mol-%	4-*n*-butyloxyphenyle	4-*n*-hexylbenzoate

The static dielectric constants (f = 1 kHz) are given in table 5 for $T_{NI}-T = 20\,K$. The dielectric anisotropy of the dissolved compound $\Delta\varepsilon'_B$ has been calculated with the assumption of a linear relationship between the dielectric anisotropies [18]

$$\Delta\varepsilon'_B = [\Delta\varepsilon' - X_{BM}\cdot\Delta\varepsilon'_{BM}]/X_B,$$

where $\Delta\varepsilon'$ is the dielectric anisotropy of the mixture, and X_B, X_{BM} are the mole fractions of the dissolved molecules and the basic mixture, respectively.

Table 5. Dielectric properties of the mixtures

Mixture	T_{NI}/°C	$\varepsilon'_\parallel$	$\Delta\varepsilon$	X_B	$\Delta\varepsilon'_B$
BM	70	4·61	−0·314	0	—
BM + B	70	5·45	+0·072	0·167	2·0

Dielectric data for **5w** are presented in figure 6. From a comparison of the static dielectric constants $\varepsilon'_\parallel$ of the basic mixture and of the basic molecule B we can deduce that the dielectric constant $\varepsilon'_\parallel(B) \approx 9{\cdot}6$ (T_{NI}-T = 20 K). If two molecules of B are connected via an SO_2 bridge the model A should give an increase of $\varepsilon'_\parallel$ because the parallel components of the dipole moments are pointing in the same direction. The dielectric constant $\varepsilon'_\parallel \approx 5$ (see figure 6) found experimentally can be explained only

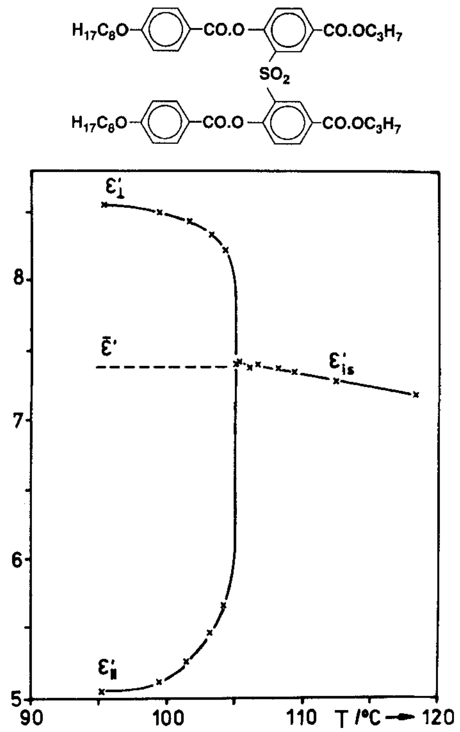


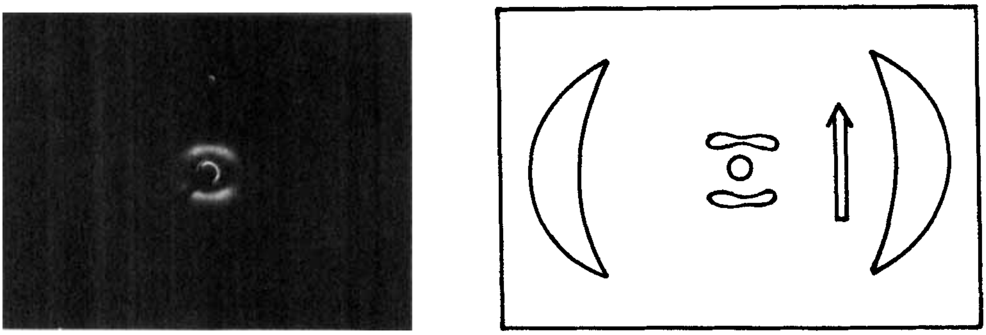
Figure 6. Dielectric constants of compound **5w** measured at a frequency of 1 kHz.

if the two parts of the twin molecule are oriented antiparallel. The longitudinal component of the SO_2 electric dipole moment should enhance $\varepsilon'_\parallel$ further in comparison to compound B so that the small experimental value strongly favours the antiparallel orientation of the halves. The SO_2 bridge exhibits a dipole component perpendicular to the molecular long axis, therefore $\varepsilon'_\perp$ increases from 7·5 (extrapolated from the mixture with BM) of the basic molecule to about 8·5 for the twin.

The second explanation for a strong decrease of $\varepsilon'_\parallel$ for the twin in relation to B can be a strong antiparallel order of the twins with respect to one another. In this case the mean dielectric constant $\bar{\varepsilon}' = (\varepsilon'_\parallel + 2\varepsilon'_\perp)/3$ should decrease rapidly at the phase transition from the isotropic into the nematic phase [14]. Such effect could not be detected (see figure 6). The curves in figure 6 correspond to the typical behaviour of uniaxial crystals in the static case with the condition $\varepsilon'_\parallel + \bar{\varepsilon}' = 2(\varepsilon'_\perp - \bar{\varepsilon}')$ [19]. The measurements are clearly made in the static regime since we have found the following data at 82·2°C, $\varepsilon'_\parallel$, 5·80, 5·78, 5·52, at frequencies of 1, 10, 100 kHz respectively.

2.4. *X-ray investigations*

Oriented samples of substances **5y**, **5t** and **5s** have been investigated in the nematic state by means of X-ray diffraction experiments. The orientation of the nematic has been achieved by a magnetic field of about 1·2 T. The patterns (see figure 7) exhibit the common feature for nematic phases: an inner diffuse crescent-like scattering at Bragg angles of about 2° and perpendicular to this, on the equator of the pattern, the crescent-like diffuse outer scattering. The inner scattering shows a weak dumbell-like character indicating a tendency to form cybotactic groups. The tilt angle between the



(A) (B)

Figure 7. X-ray investigation of compound **5s**: (A) X-ray pattern of the aligned sample, (B) schematic representation of the pattern.

normal of the groups and the averaged long axes of their building units is about 32° ± 2°. The period d of the density wave in the direction of the long axes has been estimated to be 2·2 nm and 2·4 nm for the substances **5s** and **5t**, respectively. In both cases the length L of the molecules in the parallel conformation has been found to be 0·3 nm greater assuming fully stretched alkyl chains. Two different structural models

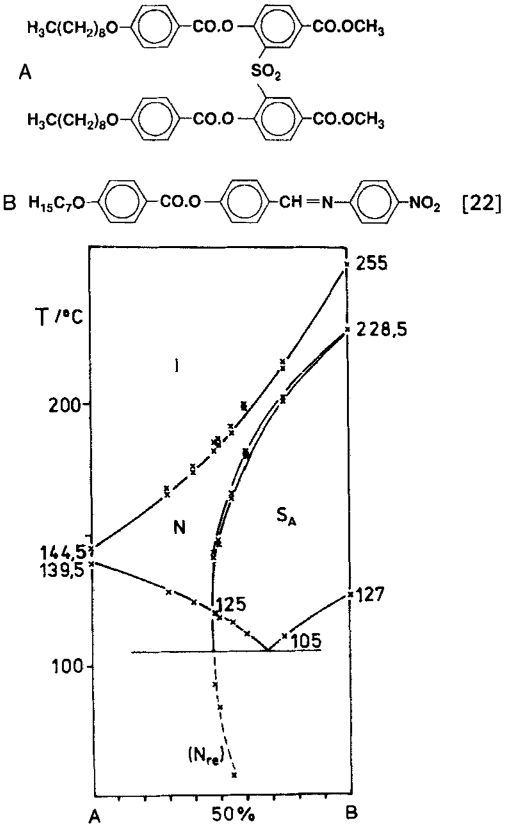


Figure 8. Phase diagram of a binary system of a twin and a rod-like compound.

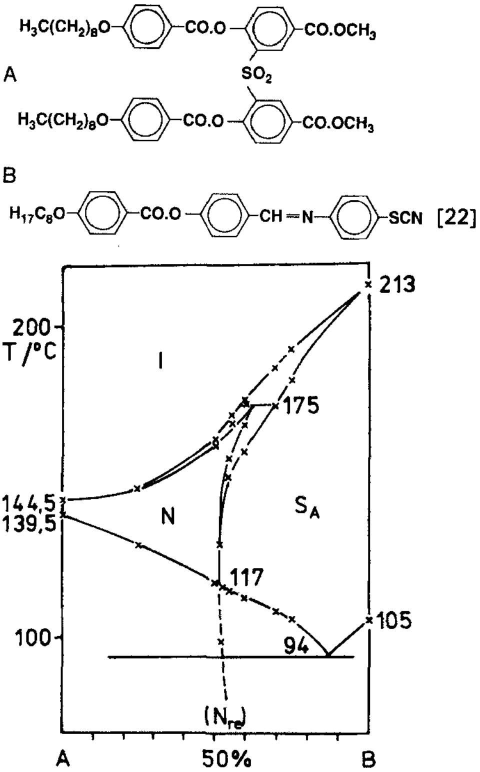


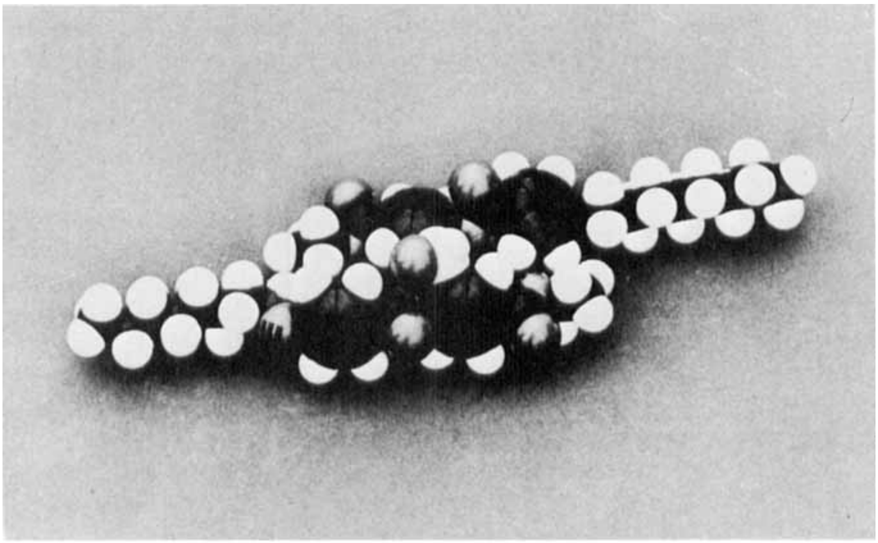
Figure 9. Phase diagram of a binary system of a twin and a rod-like compound.

sketched in figure 5 can be discussed on the basis of the different conformers. The approximate agreement between *d* and *L* seems to favour the model A. The interaction between the aromatic systems in the paired moieties could suggest the model A, too. However, the dielectric measurements yield a low value of $\varepsilon'_{\parallel}$, which demands an antiparallel arrangement of the two parts, i.e. model B.

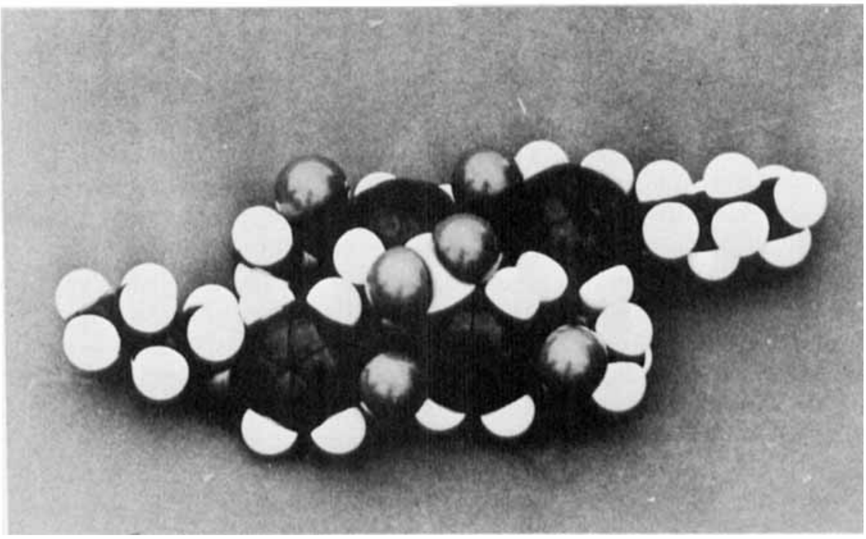
In addition the appearance of cybotactic groups is more easy to understand on the basis of the packing in model B. The experimentally observed density wave in the direction of the preferred axes can also be explained on the basis of model B (see figure 5) despite the greater molecule length in antiparallel conformation. Therefore the antiparallel arrangement of the two halves of the twin molecules should be favoured. Griffin *et al.* [16] observed in a ligated twin molecule both the parallel and antiparallel orientation of the two halves depending on the thermal history of the sample.

2.5. *Reentrant behaviour in mixtures*

The reentrant nematic phenomenon has been found frequently in systems containing one or several compounds with highly polar substituents [20–23]. In rarer cases, however, it also occurs in systems with non-polar components [23–26]. Consideration of the chemical structure of the components in these cases suggests that the molecules should possess a certain flexibility which allows a temperature dependent change of the conformation of alkyl chains or other parts of the molecules. With respect to this suggestion the higher homologues of the new series seem to be suitable candidates for



(A)



(B)

Figure 10. Space filling model of compound **5** (A) with $x = 1$, $z = 1$, $m = 8$, $n = 2$, (B) with $x = 2$, $z = 1$, $m = 4$, $n = 1$.

finding reentrant nematic phases. Figures 8 and 9 show the phase diagrams of compound **5y** (component A) in binary systems with two different substances. In figure 8 we have used a substance with a highly polar substituent which can be assumed to associate thus yielding S_{Ad} phases. The occurrence of reentrant behaviour in this system could be explained by the effect of the polar component. However, in the system shown in figure 9 we have used a thiocyanate substituted compound which do not usually exhibit association effects [27]. Nevertheless, there is distinct reentrant nematic behaviour. This is an additional example in the relative small list of reentrant phenomena in non-polar non-associating systems.

3. Concluding remark

With the 3,3′-sulphinyl and sulphonyl-bis-[alkyl 4-(4-substituted benzoyloxy)-benzoates] we present two new liquid-crystalline classes which are of the ligated twin type. The physical investigations indicate an antiparallel orientation of the two molecule halves corresponding to the space-filling model shown in figure 10.

Due to the sulphur containing bridges the molecules possess a dieder like shape. Many of the new compounds transform to the glassy nematic state on rapid quenching of the nematic phases. In several compounds the glass transition temperatures occur above room temperature. These substances may be used for the construction of new thermo-electrooptic displays [11, 28] in which the information can be written in and erased by the combined action of heat and an electric field, the information is stored for a long time in the glassy state. The unconventional properties of the new compounds are also indicated by the occurrence of reentrant nematic phases in binary systems.

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