

Full Paper

Effect of Lateral Nitro Groups on the Properties of Sulfur-Ligated Twin Mesogens

Amália Uamusse, Heinz Dehne, and Helmut Reinke

Rostock, Department of Chemistry, University

Jörgen Dobbertin, and Christoph Schick

Rostock, Department of Physics, University

Siegmar Diele

Halle/Saale, Institute of Physical Chemistry, Martin Luther University

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Abstract. The syntheses and the properties of new sulfur-ligated liquid crystalline sulfones, containing biphenyl units, as well as the influence of lateral nitro groups on their phase behaviour are described. Differential scanning calorimetry, optical polarizing microscopy and X-ray diffraction measurements reveal liquid crystalline properties for most of the synthesized bis(4-alkoxy-biphenyl-3-yl)sulfones (**4**). The

mesomorphic behaviour of these compounds is compared with that of the corresponding nitro compounds **6**. The bis(4-alkoxy-6-nitrobiphenyl-3-yl)sulfones (**6**) are not mesogenic. The results demonstrate that lateral nitro groups introduced into the biphenyl unit, changing the length–breadth relation, depress the thermal stability and lead to the loss of the mesomorphic properties.

Siamese twin mesogens of benzene derivatives in which two independent mesogenic parts are joined by sulfur were first reported in 1989 [1, 2]. According to these reports only the structures connected by a sulfinyl or a sulfonyl group exhibit liquid crystalline properties whereas the corresponding sulfides do not form mesophases.

In this study we were interested in the synthesis and properties of new sulfur-ligated liquid crystals with a large core in which the two halves of the molecule themselves are not mesogenic [3]. The influence of the length of terminal alkyl chains on the phase behaviour of liquid crystals has been reported in some papers and is still of great interest. Increase of length of the alkyl tail may affect the nature and stability of the mesophase [4]. Therefore we also describe the influence of the alkyl chain length on the phase behaviour of the obtained compounds.

Generally lateral substituents alter the molecular length–breadth relation because they broaden the molecule, reduce lateral attractions and lower nematic and smectic phase stability. Smectic A phase stability depends on dipole–dipole interactions and induced interactions as well as dispersion forces. Thus, the effect of a

lateral substituent on the smectic phase stability is influenced both by its size and polarity. The most polar lateral groups tend to favour smectic phases due to increased dipole–dipole interactions until the substituent pushes the molecules too far apart for this to be effective, in that case liquid crystal thermal stability is reduced. Some investigations of the influence of lateral substituents on liquid crystalline behaviour predict that lateral substituents depending on several parameters such as the phase type, the substituent type and the substituent position can decrease the thermal stability of the mesophase and may even lead to a complete loss of the liquid crystalline properties [5, 6].

The main goal of this work was to study the influence of lateral nitro groups at the aromatic system on the mesomorphic behaviour of the new sulfur-ligated siamese twin mesogens with biphenyl structure.

Results and Discussion

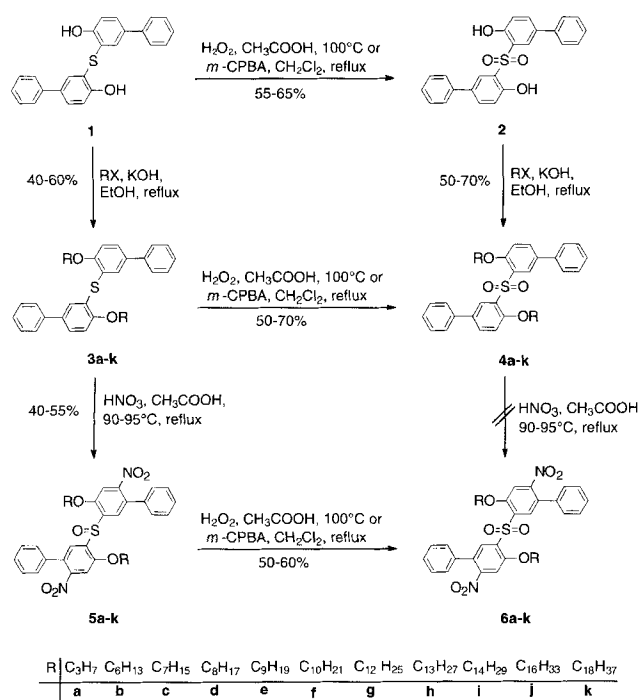
Synthesis and Structures

The synthetic route used for the preparation of the new title compounds is outlined in scheme 1. Bis(4-hydroxy-

biphenyl-3-yl)sulfide (**1**) was prepared only in moderate yields at first by reaction of commercially available 4-hydroxybiphenyl with disulfur dichloride in dichloromethane according to Denisova *et al.* [7]. The use of sulfur dichloride in petroleum ether as described by Gump and Vitucci [8] afforded also low yields. An approach of the reaction conditions of both pathways using sulfur dichloride in dichloromethane led to a suitable method for preparation of the new sulfide **1** in high yield and purity. The following oxidation of **1** to **2** was performed with hydrogen peroxide in acetic acid [7] as well as with *m*-chloroperbenzoic acid in dichloromethane [9].

The alkylation of **1** and **2** resulted in the bis(4-alkoxybiphenyl-3-yl)sulfides (**3**) and the bis(4-alkoxybiphenyl-3-yl)sulfones (**4**), respectively. Compounds **4** were also obtained by subsequent oxidation of **3**.

Nitric acid has been employed some years ago to oxidize sulfides to sulfoxides [10, 11] or as a nitrating agent [12, 13]. In our aim to introduce lateral nitro groups into the aromatic system we achieved the chemoselective oxidation of the sulfur and at the same time the regioselective nitration of **3** by fuming nitric acid in acetic acid only providing the bis(4-alkoxy-6-nitrophenyl-3-yl)sulfoxides (**5**). The consecutive oxidation of the compounds **5** using the same conditions as above mentioned for **1** resulted in the bis(4-alkoxy-6-nitrophenyl-3-yl)sulfones (**6**). These compounds could not be prepared by nitration of the sulfones **4**.



Scheme 1

All compounds were characterized by elemental analysis, ¹H NMR, ¹³C NMR, IR and mass spectrometry. The structures of **3**, **4**, **5** and **6** were additionally verified by X-ray crystallographic analysis.

Thermal Behaviour

The phase behaviour was investigated by polarizing microscopy, differential scanning calorimetry (DSC) and X-ray diffraction.

While the sulfides **3** in analogy to previously synthesized compounds [1, 2] are not mesogenic the stronger polar sulfones **4** exhibit liquid crystalline properties. The phase transition temperatures are listed in table 1.

Table 1 Phase transition temperatures of the sulfones **4**

4	R	Transition temperatures ^{a)} (°C)
a	C ₃ H ₇	Cr 210 I
b	C ₆ H ₁₃	Cr 168 I
c	C ₇ H ₁₅	Cr 166 I
d	C ₈ H ₁₇	Cr 154 (S _A 132) I
e	C ₉ H ₁₉	Cr 148 (S _A 134) I
f	C ₁₀ H ₂₁	Cr 147 (S _A 137) I
g	C ₁₂ H ₂₅	Cr 138 S _A 144 I
h	C ₁₃ H ₂₇	Cr 127 S _A 145 I
i	C ₁₄ H ₂₉	Cr 124 S _A 145 I
j	C ₁₆ H ₃₃	Cr 116 S _A 142 I
k	C ₁₈ H ₃₇	Cr 110 S _A 140 I

^{a)} Cr = crystalline, S_A = smectic A phase, I = isotropic phase

The members with short and middle alkyl chain are not mesogenic. Generally, we observe a decrease of the melting points and a tendency of increasing of the clearing temperatures when the alkyl chain is lengthened. A maximum of the mesophase stability is at **4h/i**. The liquid crystalline properties start with the octyloxy derivative **4d**, and the compounds display monotropic smectic A phases up to the decyloxy derivative **4f**. The higher homologues have enantiotropic smectic A phases. Furthermore the mesophase range increases from 6 °C for the dodecyloxy **4g** to 30 °C in the octadecyloxy derivative **4k**. Figure 1 displays representatively the smectic A texture exhibited by the octadecyloxy derivative **4k**. Its DSC thermogram is presented in figure 2.

The compounds **5** and **6** bearing lateral nitro substituents are not mesogenic, even the compounds **6d–6k** for which the corresponding sulfones **4d–4k** are liquid crystalline, lose these properties. Obviously incorporating lateral nitro groups into the mesogenic core leads to a different molecular packing arrangement. Indeed comparing the X-ray crystallographic structures of **4a** and **6d** it can be seen that in the last compound (Fig. 3) the two alkoxy chains are crossed and their orientation is not antiparallel as in **4a**. The molecular packing in the crystalline state could be quite different from the

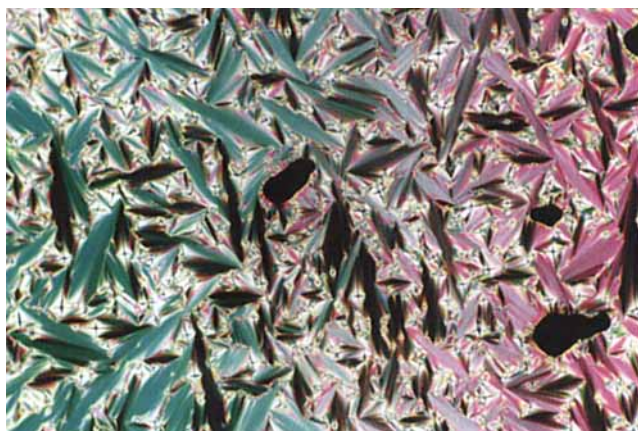


Fig. 1 Smectic A texture of bis-(4-octadecyloxybiphenyl-3-yl)sulfone (**4k**)

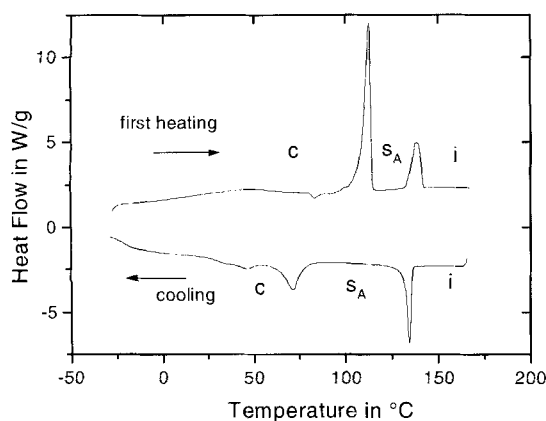


Fig. 2 DSC plot of the sulfone **4k**

molecular packing in the liquid crystalline state, so that the different molecular arrangements represent only one of the possible explanations of the observed behaviour (the loss of the mesomorphy of the compounds **6**).

Table 2 Data of the compounds **3**, **5** and **6**

R	3		5		6	
	<i>m.p.</i> (°C)	yield (%)	<i>m.p.</i> (°C)	yield (%)	<i>m.p.</i> (°C)	yield (%)
a C ₃ H ₇	134–135	60	165–166	55	198–199	58
b C ₆ H ₁₃	106–108	50	144–146	52	169–171	60
c C ₇ H ₁₅	95–97	59	139–140	55	189–190	55
d C ₈ H ₁₇	88–89	56	130–132	45	149–151	56
e C ₉ H ₁₉	99–100	50	121–122	50	164–165	59
f C ₁₀ H ₂₁	86–87	60	107–109	48	158–160	55
g C ₁₂ H ₂₅	88–89	52	102–103	45	144–145	60
h C ₁₃ H ₂₇	96–97	40	97–98	42	129–130	50
i C ₁₄ H ₂₉	88–89	41	94–96	40	138–140	52
j C ₁₆ H ₃₃	89–91	45	66–68	45	115–117	54
k C ₁₈ H ₃₇	94–95	40	58–59	43	91–93	50

Some of the compounds **6** were analysed by quenching the isotropic melt, and a glass transition could be observed (see **6d** in “Experimental”).

The melting points and yields of the compounds **3**, **5** and **6** are given in table 2.

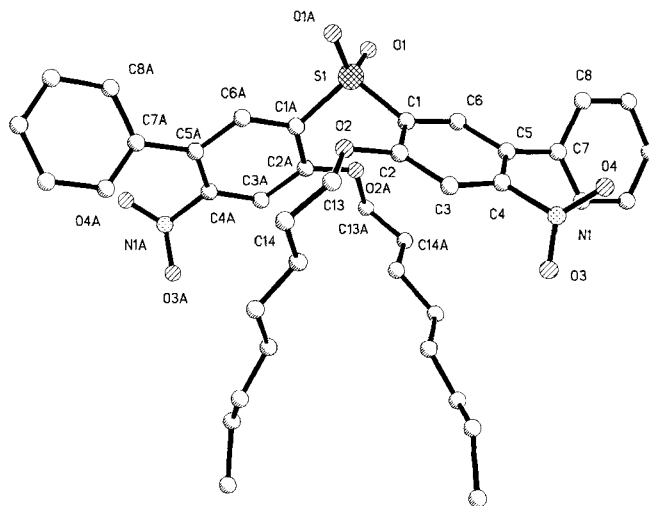


Fig. 3 Molecular structure (hydrogens omitted for clearness) of bis-(6-nitro-4-octyloxybiphenyl-3-yl)sulfone (**6d**)

Further experimental results indicate that incorporating a lateral bromo substituent into the mesogenic core also leads to the loss of the liquid crystalline properties.

X-ray Diffraction

The X-ray investigations of the S_A phase were performed using a Guinier goniometer (Fa. Huber Diffraktionstechnik, Germany) equipped with a heating stage. The X-ray diagrams of **4k** display the typical feature of smectic phase without order in the layer. The strong inner reflection corresponds to a layer thickness of $d = 2.49$ nm. This value is in good agreement with the length of the molecule $L = 2.55$ nm, as determined by CPK-models. This confirms the results obtained by polarizing microscopy measurements, which shows smectic A phases.

Through the chemical structure of the SO₂-ligated twin halves parallel or antiparallel arrangement of the compounds **4** can be discussed. The performed X-ray studies are not able to distinguish between both types, because the electron density period of parallel and antiparallel orientation is $d \cong L$. Roger *et al.* reported on the antiparallel orientation of the molecule halves of their ligated twins [1].

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Experimental

A LEITZ Laborlux 12 Pol polarizing microscope equipped with a Mettler heating stage FP 90 was used to observe the thermal transitions and to analyse the anisotropic textures. DSC measurements were performed using a differential scanning calorimeter (Perkin-Elmer DSC-2) by heating and cooling rates of 10 K/min. ^1H NMR and ^{13}C NMR were carried out with a Bruker AC 250 spectrometer using TMS as internal reference. Mass spectra were recorded on an AMD 402-3 spectrometer (Intectra GmbH) and IR spectra on a 205 FT-IR spectrometer. Elemental analyses were determined by a CHNS-932 LECO analyser. The found analytical data of all compounds correspond to the theoretical values.

The spectra of the homologous series **3** and **4** as **5** and **6** are quite similar, therefore only two selected representatives of each series are detailed described. We chose the derivatives **d** (C_8H_{17}) and **i** ($\text{C}_{14}\text{H}_{29}$) of the compounds **3–6**.

Bis(4-hydroxybiphenyl-3-yl)sulfide (1)

To a suspension of 4-hydroxybiphenyl (10.5 g, 0.06 mol) in 30 ml of dry dichloromethane, ZnCl_2 (0.4 g, 0.003 mol) was added and stirred for 20 min at r. t. The reaction mixture was heated under reflux. Sulfur dichloride (1.9 ml, 0.03 mol) in 5 ml of dry dichloromethane was added dropwise for 2 h. Afterwards stirring was continued for more than 3 h. After cooling to r. t. the product was filtered off, boiled for few min with water, filtered again and dried. The sulfide was recrystallized from 50% acetic acid to afford a pale yellow solid. Yield 8.4 g (74%); *m.p.* 152–154 °C. – ^1H NMR (300 MHz, acetone- d_6): δ/ppm = 9.0 (s, OH), 7.89 (d, 2H, arom., $^4J_{3,5}$ = 2.2 Hz), 7.74 (m, 4H, arom.), 7.73 (dd, 2H, arom., $^4J_{3,5}$ = 2.2 Hz, $^3J_{5,6}$ = 8.4 Hz), 7.59 (m, 4H, arom.), 7.48 (m, 2H, arom.), 7.29 (d, 2H, arom., $^3J_{5,6}$ = 8.4 Hz). – ^{13}C NMR (75.5 MHz, acetone- d_6): δ/ppm = 157.01, 140.93, 134.54, 132.90, 129.62, 129.17, 127.61, 127.15, 121.55, 116.85. – IR (KBr): ν/cm^{-1} = 3374 (OH).

$\text{C}_{24}\text{H}_{18}\text{O}_2\text{S}$ calcd.: C 77.8 H 4.9 S 8.7
(370.46/370) found: C 77.2 H 4.9 S 8.8.

Bis(4-hydroxybiphenyl-3-yl)sulfone (2)

This compound was prepared in 55% yield using H_2O_2 in acetic acid as mentioned in literature [7] as well as described here.

A solution of 85% *m*-chloroperbenzoic acid (1.98 g, 0.01 mol) in 50 ml dichloromethane was added dropwise to a stirred solution of **1** (3.7 g, 0.01 mol) in 50 ml dichloromethane and refluxed for 2h. After cooling the solvent was evaporated under reduced pressure and the product recrystallized from ethanol. Yield 2.6 g (65%); *m.p.* 218–220 °C. – ^1H NMR (300 MHz, acetone- d_6): δ/ppm = 10.0 (s, OH), 8.1 (d, 2H, arom., $^4J_{3,5}$ = 2.1 Hz), 8.04 (m, 4H, arom.), 7.82 (dd, 2H, arom., $^4J_{3,5}$ = 2.1 Hz, $^3J_{5,6}$ = 8.5 Hz), 7.65 (m, 4H, arom.), 7.56 (m, 2H, arom.), 7.32 (d, 2H, arom., $^3J_{5,6}$ = 8.5 Hz). – ^{13}C NMR (75.5 MHz, acetone- d_6): δ/ppm = 156.65, 139.94, 134.98, 133.71, 129.82, 128.37, 127.33, 126.88, 119.31, 119.23. – IR (KBr): ν/cm^{-1} = 3330 (OH), 1310, 1126 (SO_2).

$\text{C}_{24}\text{H}_{18}\text{O}_4\text{S}$ calcd.: C 71.6 H 4.5 S 8.0
(402.46/402) found: C 71.4 H 4.6 S 8.1.

Bis(4-alkoxybiphenyl-3-yl)sulfides (3a – k)

To a stirred mixture of **1** (1.85 g, 0.005 mol), KOH (1.12 g, 0.02 mol) in 5 ml H_2O and 20 ml EtOH, 0.016 mol of the corresponding alkyl halide was added dropwise and refluxed for 15 h. After addition of KOH (0.01 mol), solved in 5 ml H_2O and 10 ml EtOH, refluxing was continued for further 2 h. The mixture was allowed to cool to r. t., the precipitate washed with enough water and collected by filtration. The products were recrystallized from ethanol.

3d: – ^1H NMR (300 MHz, CDCl_3): δ/ppm = 7.56–7.76 (m, 8H, arom.), 7.52 (m, 4H, arom.), 7.41 (m, 2H, arom.), 7.11 (d, 2H, arom., $^3J_{5,6}$ = 8.7 Hz), 4.24 (t, 4H, $\text{CH}_2\text{-O-}$, 3J = 6.3 Hz), 1.30–1.61 (m, 24H, CH_2), 0.93 (t, 6H, CH_3 , 3J = 6.5 Hz). – ^{13}C NMR (75.5 MHz, CDCl_3): δ/ppm = 157.40, 140.83, 134.36, 131.02, 129.07, 127.22, 127.10, 127.00, 124.12, 112.56. – IR (KBr): ν/cm^{-1} = 2850 (C–O–C).

$\text{C}_{40}\text{H}_{50}\text{O}_2\text{S}$ calcd.: C 80.8 H 8.5 S 5.4
(594.89/594) found: C 80.6 H 8.4 S 5.6.

3i: – ^1H NMR (300 MHz, CDCl_3): δ/ppm = 7.33–7.43 (m, 8H, arom.), 7.27 (m, 4H, arom.), 7.18 (m, 2H, arom.), 6.87 (d, 2H, arom., $^3J_{5,6}$ = 9.0 Hz), 3.95 (t, 4H, $\text{CH}_2\text{-O-}$, 3J = 6.5 Hz), 1.09–1.64 (m, 48H, CH_2), 0.81 (t, 6H, CH_3 , 3J = 7.0 Hz). – ^{13}C NMR (75.5 MHz, CDCl_3): δ/ppm = 157.36, 140.82, 134.35, 131.02, 129.06, 127.20, 127.08, 127.00, 124.11, 112.55. – IR (KBr): ν/cm^{-1} = 2851 (C–O–C).

$\text{C}_{52}\text{H}_{74}\text{O}_2\text{S}$ calcd.: C 81.8 H 9.8 S 4.2
(763.21/762) found: C 81.2 H 9.9 S 4.4.

Bis(4-alkoxybiphenyl-3-yl)sulfones (4a – k)

The compounds **4** were synthesized by alkylation of **2** (in a procedure like for **3**), as well as by the oxidation of **3** (as described for **2**). The crude products were recrystallized from isopropanol. Yields 50–70%.

4d: – ^1H NMR (300 MHz, CDCl_3): δ/ppm = 8.27 (d, 2H, arom., $^4J_{3,5}$ = 2.1 Hz), 7.63 (dd, 2H, arom., $^3J_{5,6}$ = 8.7 Hz, $^4J_{3,5}$ = 2.1 Hz), 7.56 (m, 4H, arom.), 7.31 (m, 4H, arom.), 7.25 (m, 2H, arom.), 6.84 (d, 2H, arom., $^3J_{5,6}$ = 8.7 Hz), 3.71 (t, 4H, $\text{CH}_2\text{-O-}$, 3J = 6.3 Hz), 0.88–1.24 (m, 24H, CH_2), 0.72 (t, 6H, CH_3 , 3J = 7.0 Hz). – ^{13}C NMR (75.5 MHz, CDCl_3): δ/ppm = 156.33, 139.66, 133.39, 133.18, 130.01, 129.73, 129.28, 127.72, 127.02, 113.39. – IR (KBr): ν/cm^{-1} = 1315, 1146 (SO_2), 2854 (C–O–C).

$\text{C}_{40}\text{H}_{50}\text{O}_4\text{S}$ calcd.: C 76.6 H 8.0 S 5.1
(626.89/626) found: C 76.3 H 8.0 S 4.9.

4i: – ^1H NMR (300 MHz, CDCl_3): δ/ppm = 8.47 (d, 2H, arom., $^4J_{3,5}$ = 2.2 Hz), 7.72 (dd, 2H, arom., $^3J_{5,6}$ = 8.9 Hz, $^4J_{3,5}$ = 2.2 Hz), 7.62 (m, 4H, arom.), 7.44 (m, 4H, arom.), 7.35 (m, 2H, arom.), 6.92 (d, 2H, arom., $^3J_{5,6}$ = 8.9 Hz), 3.83 (t, 4H, $\text{CH}_2\text{-O-}$, 3J = 6.5 Hz), 0.95–1.44 (m, 48H, CH_2), 0.89 (t, 6H, CH_3 , 3J = 7.0 Hz). – ^{13}C NMR (75.5 MHz, CDCl_3): δ/ppm = 156.33, 139.67, 133.39, 133.17, 130.02, 129.74, 129.28, 127.72, 127.02, 113.38. – IR (KBr): ν/cm^{-1} = 1320, 1148 (SO_2), 2851 (C–O–C).

$\text{C}_{52}\text{H}_{74}\text{O}_4\text{S}$ calcd.: C 78.5 H 9.4 S 4.0
(795.21/794) found: C 78.2 H 9.3 S 4.2.

Bis(4-alkoxy-6-nitrobiphenyl-3-yl)sulfoxides (5a – k)

A suspension of the corresponding sulfide **3** (0.002 mol) in

10 ml acetic acid was heated at 90–95 °C until the solid was dissolved. A mixture of fuming nitric acid (0.012 mol, 0.5 ml) in 1 ml acetic acid was added slowly. The mixture was maintained at 90–95 °C for 1 h and then refluxed for 30 min. After cooling to r.t. the solution was poured on ice, the yellow precipitate was filtered off and recrystallized from ethanol.

5d: ^1H NMR (300 MHz, acetone- d_6): δ/ppm = 7.66 (s, 2H, arom.), 7.43 (s, 2H, arom.), 7.12–7.37 (m, 10H, arom.), 4.02 (t, 4H, $\text{CH}_2\text{-O-}$, 3J = 6.3 Hz), 0.93–1.28 (m, 24H, CH_2), 0.77 (t, 6H, CH_3 , 3J = 6.5 Hz). ^{13}C NMR (75.5 MHz, acetone- d_6): δ/ppm = 155.06, 151.16, 135.67, 134.80, 130.75, 130.05, 128.10, 127.60, 107.54. – IR (KBr): ν/cm^{-1} = 1048 (SO), 1526, 1355 (NO_2), 2848 (C–O–C).

$\text{C}_{40}\text{H}_{48}\text{N}_2\text{O}_7\text{S}$ calcd.: C 68.5 H 6.9 N 4.0 S 4.6
(700.89/700) found: C 68.2 H 6.8 N 4.2 S 4.4.

5i: ^1H NMR (300 MHz, acetone- d_6): δ/ppm = 7.72 (s, 2H, arom.), 7.5 (s, 2H, arom.), 7.2–7.4 (m, 10H, arom.), 4.05 (t, 4H, $\text{CH}_2\text{-O-}$, 3J = 6.5 Hz), 1.2–1.82 (m, 48H, CH_2), 0.79 (t, 6H, CH_3 , 3J = 6.8 Hz). ^{13}C NMR (75.5 MHz, acetone- d_6): δ/ppm = 154.84, 150.94, 135.44, 134.64, 129.77, 127.88, 127.04, 126.92, 123.19, 107.31. – IR (KBr): ν/cm^{-1} = 1050 (SO), 1526, 1345 (NO_2), 2851 (C–O–C).

$\text{C}_{52}\text{H}_{72}\text{N}_2\text{O}_7\text{S}$ calcd.: C 71.9 H 8.3 N 3.2 S 3.7
(869.21/868) found: C 71.6 H 8.3 N 3.5 S 3.6.

Bis(4-alkoxy-6-nitrobiphenyl-3-yl)sulfones (6a–k)

Compounds **6** were prepared from compounds **5** using an analogous procedure as for **2**. The crude products were recrystallized from acetic acid.

6d: ^1H NMR (300 MHz, acetone- d_6): δ/ppm = 8.12 (s, 2H, arom.), 7.55 (s, 2H, arom.), 7.22–7.38 (m, 10H, arom.), 3.97 (t, 4H, $\text{CH}_2\text{-O-}$, 3J = 6.5 Hz), 0.98–1.35 (m, 24H, CH_2), 0.72 (t, 6H, CH_3 , 3J = 6.5 Hz). ^{13}C NMR (75.5 MHz, acetone- d_6): δ/ppm = 157.37, 154.45, 136.64, 134.73, 131.90, 129.94, 129.44, 128.96, 127.99, 109.38. – IR (KBr): ν/cm^{-1} = 1328, 1149 (SO_2), 1529, 1346 (NO_2), 2854 (C–O–C). Glass transition temperature (T_g) = 19.1 °C.

$\text{C}_{40}\text{H}_{48}\text{N}_2\text{O}_8\text{S}$ calcd.: C 67.0 H 6.7 N 3.9 S 4.5
(716.88/716) found: C 66.8 H 6.7 N 3.7 S 4.7.

6i: ^1H NMR (300 MHz, acetone- d_6): δ/ppm = 8.23 (s, 2H, arom.), 7.69 (s, 2H, arom.), 7.42–7.57 (m, 10H, arom.), 4.14 (t, 4H, $\text{CH}_2\text{-O-}$, 3J = 6.5 Hz), 1.00–1.54 (m, 48H, CH_2), 0.89 (t, 6H, CH_3 , 3J = 7.0 Hz). ^{13}C NMR (75.5 MHz, acetone- d_6): δ/ppm = 157.15, 154.23, 136.81, 134.51, 132.29, 129.90, 129.53, 128.92, 127.77, 110.01. – IR (KBr): ν/cm^{-1} = 1330, 1150 (SO_2), 1530, 1349 (NO_2), 2848 (C–O–C).

$\text{C}_{52}\text{H}_{72}\text{N}_2\text{O}_8\text{S}$ calcd.: C 70.6 H 8.2 N 3.2 S 3.6
(885.21/884) found: C 70.2 H 8.2 N 3.2 S 3.5.

Crystal Structure Determination

4a: The compound crystallizes in $\text{P}2_1/c$ with $a = 9.138(2)$, $b = 19.754(4)$, $c = 14.162(3)$ Å, $\beta = 94.45(3)^\circ$, $V = 2548.7(9)$ Å³, $D = 1.268$, $Z = 4$. The data collection for compound **4a** was done on a STOE-IPDS (laser scanned imaging plate) at room temperature. The structure was solved by direct methods (SHELXS-86, G. M. Sheldrick, Universität Göttingen, 1986) and refined with 3880 reflections. Due to the very weak scattering of the crystals the structure could be refined to

$R1 = 0.0949$ for the 1498 observed reflections only (observation criterion $I > 2\sigma(I)$).

6d: The compound crystallizes in $\text{C}2/c$ with $a = 23.400(3)$, $b = 16.571(3)$, $c = 10.566(2)$ Å, $\beta = 111.630(10)^\circ$, $V = 3808.6(11)$ Å³, $D = 1.250$, $Z = 4$. After the first data collection for **6d** it was noticed that there is considerable disorder of the alkyl chain in the solid state. That is why in a second attempt the data collection was done at 213 K on a Siemens P4 four-circle diffractometer in routine ω -scan. However, there was only little improvement in the final results. The structure was solved by direct methods. The calculations performed had to be done including several restraints, both of distance and distant ones. 2167 reflections were included. The structure was refined to $R1 = 0.0898$ for the observed reflections. However, due to the observation criterion $I > 2\sigma(I)$ only 961 reflections could be classified as observed.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101204. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code +(1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Address for correspondence:

Prof. Dr. Heinz Dehne
Fachbereich Chemie, Universität Rostock
Buchbinderstr. 9
D-18051 Rostock
e-mail: heinz.dehne@chemie.uni-rostock.de
Fax: +49-(381)-498-1763