REACTIVITY OF [1]BENZOTHIENO[3,2-*b*][1]BENZOTHIOPHENE – ELECTROPHILIC AND METALLATION REACTIONS

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Electrophilic nitration, formylation and acetylation of the title heterocycle **1** were studied. Monosubstitution proceeds preferentially in position 2 and to a lesser extent in position 4. Lowering the reaction temperature substantially increases regioselectivity of nitration and acetylation. Substitution reactions of the 2-substituted derivatives of **1** led to the corresponding 2,7-disubstituted derivatives as major products. Formation of other regioisomers was also observed. Metallation of **1** with butyllithium preferably proceeds in position 1; subsequent reaction with *N*,*N*-dimethylformamide, carbon dioxide or iodine gives rise to corresponding 1-substituted derivatives. Long-chain 2,7-disubstitued derivatives exhibit liquid-crystalline properties.

Keywords: [1]Benzothieno[3,2-*b*][1]benzothiophene; Electrophilic substitution; Nitration; Formylation; Acetylation; Regioselectivity; Metallation; Liquid crystals.

Research on ferroelectric liquid crystals (FLC) is a subject of durable interest[1,2] for their potential technical applications such as in systems for optical processing of information, realization of matrix displays, flat television screens, nonlinear optics, *etc*. FLC usually contain aromatic and heteroaromatic systems in their cores. By introducing heterocyclic compounds, variability of new mesogens increases; heteroatom insertion strongly influences[1,3,4] geometry of the molecules, formation of mesomorphic phases, their polarizability, type of mesophase, transition temperatures, dielectric, optical and other properties. Generally, FLC with heterocyclic cores show frequent appearance of the required SmC* phase in a broader temperature interval than the corresponding carbocyclic systems. In particular, derivatives of pyridine, pyrimidine, and to a lesser extent also 1,3,4-triazine, thiazole, 1,3,4-thiadiazole[5], 1,3-dioxane[6] and other heterocycles have been applied. We introduced[7,8] new structure types of cores for construction of FLC based on thieno[3,2-*b*][1]benzofuran and thieno[3,2-*b*][1]benzothio-

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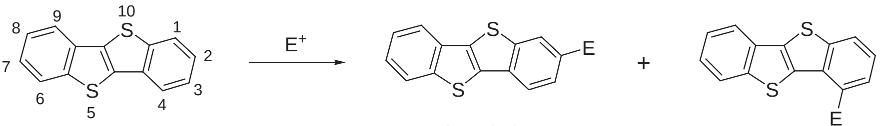
phene systems. We also synthesized[9] a new unsymmetrically substituted tetracyclic [1]benzothieno[3,2-*b*][1]benzofuran as an example of another fused core. Recently it was shown[10,11] that alkyl esters of [1]benzothieno[3,2-*b*][1]benzothiophene-2,7-dicarboxylic acid exhibit liquid-crystalline properties. Syntheses of [1]benzothieno[3,2-*b*][1]benzothiophene (**1**) and its derivatives start with substituted 2,2′-dinitrostilbenes[10–12] or 2,2′-disubstituted diphenylacetylenes[13] and multistep procedures are involved. The parent system **1** was also simply prepared by a one-step high-temperature reaction[14,15]. In this paper we report a new concept of preparation mono- and disubstituted derivatives of **1** based on electrophilic and metallation reactions of **1**. The aim of this study was to elaborate procedures for syntheses of the compounds that could serve as convenient sources of liquid crystal cores derived from **1**.

To obtain heterocycle **1**, the original high-temperature procedure[14] was slightly modified. (Dichloromethyl)benzene was heated with elemental sulfur to 240–250 °C and, after chromatographic purification, **1** was obtained in a moderate but satisfactory yield of 32%.

For prediction of the regioselectivity of electrophilic substitutions in heterocyclic moiety **1**, we used quantum chemical calculations. *Ab initio* calculations were performed with GAMESS (ref.[16]) using the HF//6-31G(d) method for geometry optimization and HF//6-31G(2d,p) for energy and properties calculation. Energy of the HOMO orbital was used to predict relative reactivity of different derivatives and Mulliken population analysis of HOMO was used to determine relative reactivity of different positions in the molecule towards an electrophile (Table I). This approach covers only the kinetic aspect of the reaction and is by its nature static and cannot describe differences between electrophiles involved in the reaction.

From the results, it can be concluded that the highest electron density in parent system **1** is located in positions 2 and 4 with some preference for the former. Introduction of an electron-withdrawing substituent to position 2 (NO_2, $COCH_3$) results in a general decrease in HOMO orbital energy which indicates lower reactivity of the molecule as a whole. Smaller differences between the most reactive positions (7 and 9) in these derivatives, when compared to unsubstituted heterocycle **1**, could suggest lower regioselectivity in their further electophilic substitutions. A higher calculated selectivity for the 2-ethyl derivative can be ascribed to an increased difference (compared with unsubstituted heterocycle **1**) between electron population in position 7 and positions 4 and 9. The aim of the presented work was to support the results of theoretical calculations by nitration, formylation and acylation experiments with **1** and its monosubstituted derivatives.

It was reported[17] that nitration of **1** with nitric acid in acetic acid at 70 °C afforded a mixture of 2-nitro[1]benzothieno[3,2-*b*][1]benzothiophene (**2**) and 4-nitro[1]benzothieno[3,2-*b*][1]benzothiophene (**3**) in a 3 : 2 ratio. We found that using fuming nitric acid in dichloromethane nitration proceeded at room temperature very easily and compounds **2** and **3** were isolated in an overall yield of 96% in a ratio 4 : 1 (by ^{1}H NMR) (Scheme 1). In addition, regioselectivity of nitration could be substantially influenced by a change of the reaction temperature. Lowering the temperature to –30 °C led to an increase in nitration selectivity to 9 : 1 (overall yield 90%). When the reaction was performed at –50 °C, a mixture of nitro derivatives **2** and **3** (83% yield) was formed in a ratio 13 : 1. Products of dinitration were not detected under these conditions. From the mixture of regioisomers, pure **2** was obtained by a single crystallization from toluene, whereas isomer **3** was obtained from the mother liquor by crystallization from propan-2-ol.



1

2, 4, 6, 8

3, 5, 7

2, **3**, E = NO_2
4, **5**, E = CHO
6, **7**, E = $COCH_3$
8, E = $CO(CH_2)_{10}CH_3$

SCHEME 1

TABLE I
Mulliken atomic population analysis of HOMO (HF/6-31G(2d,p)//HF/6-31G(d)) in **1** and its 2-substituted derivatives

Substituent	E_{HOMO} eV	Position							
		1	2	3	4	5	6	7	8
H	–7.52	0.078	0.175	0.007	0.148	0.078	0.175	0.007	0.148
NO_2	–8.08	0.041	–	0.013	0.135	0.117	0.174	0.011	0.172
$COCH_3$	–7.71	0.066	–	0.010	0.164	0.086	0.161	0.007	0.146
C_2H_5	–7.40	0.090	–	0.011	0.125	0.065	0.178	0.007	0.139

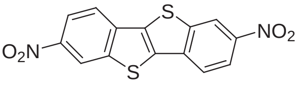
Further we studied formylation of heterocycle **1** under analogous conditions as for the tetracyclic [1]benzothieno[3,2-*b*][1]benzofuran. Reaction of **1** with butyl dichloromethyl ether[18] in the presence of $TiCl_4$ at –60 °C led to the formation of a 2 : 1 mixture of [1]benzothieno[3,2-*b*][1]benzothiophene-2-carbaldehyde (**4**) and [1]benzothieno[3,2-*b*][1]benzothiophene-4-carbaldehyde (**5**) which was separated by crystallization and column chromatography. Change of the reaction temperature (to –30 or –70 °C) did not lead to a change in the product ratio.

Acetylation of **1** with acetyl chloride under aluminium chloride catalysis proceeded analogously. In comparison with nitration, even higher regioselectivity was observed. Reaction at 0 °C afforded a mixture of ([1]benzothieno[3,2-*b*][1]benzothien-2-yl)ethan-1-one (**6**) and ([1]benzothieno[3,2-*b*][1]benzothien-4-yl)ethan-1-one (**7**) in an overall yield of 92% and ratio 8 : 1. Lowering the reaction temperature to –70 °C led to an increase in regioselectivity to 25 : 1. Pure isomer **6** was then obtained by a single crystallization.

In an attempt to prepare intermediates for liquid crystals, we also tried to introduce a longer-chain moiety to heterocyclic moiety **1**. Using dodecanoyl chloride instead of acetyl chloride did not influence the course and regioselectivity of acylation. Reaction at –70 °C led selectively to ([1]benzothieno[3,2-*b*][1]benzothien-2-yl)dodecan-1-one (**8**) (yield 80%).

Aryl bromides also belong to common intermediates in organic synthesis. However, bromination of **1** failed when using a solution of bromine in dichloromethane in the presence of iron. The reaction led to formation of inseparable mixtures of mono- and higher brominated products. By no means we were able to isolate and characterize components of the product in pure form. Not even lowering the reaction temperature to –60 °C led to a substantial improvement of the bromination selectivity.

It is remarkable that introduction of a nitro group into one benzene ring of **1** strongly influences the reactivity of the other benzene ring through the four-ring system of **1**. Attempted dinitration of **1** proceeded slowly even with large excess of 100% nitric acid and sulfuric acid in dichloromethane solution at room temperature. Under these conditions, formation of a mixture of nitrated products along with some sulfur-oxidized by-products[17] was observed. 2,7-Dinitro derivative **9** was identified as a minor component of the product mixture and its separation appeared to be very difficult. We found that dinitration was more convenient as performed in a two-step procedure: 2-nitro derivative **2** was nitrated with fuming nitric acid in the presence of sulfuric acid in nitromethane solution. The use of nitromethane made it possible to decrease reaction temperature to 0 °C and accelerate the reaction. A 3 : 1 mixture of 2,7-dinitro[1]benzothieno[3,2-*b*][1]benzothiophene (**9**) and 2,9-dinitro[1]benzothieno[3,2-*b*][1]benzothiophene (**10**) was obtained in 92% overall yield.



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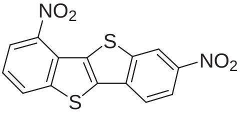

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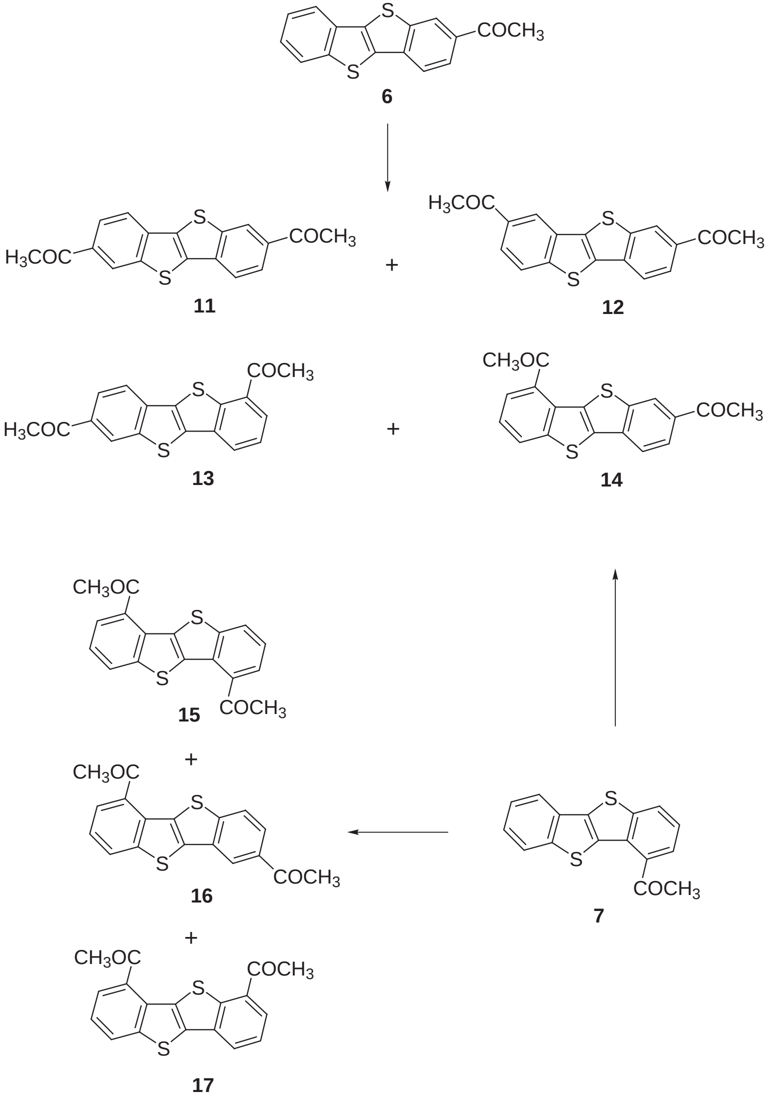
No oxidation product was detected under these conditions. Due to very low solubilities of both isomers, their separation by crystallization was very difficult and pure compound **9** could be isolated only in 17% yield. The results of nitration are in agreement with our theoretical calculations of the preferred positions for electrophilic attack in heterocyclic moiety **1**.

An attempt to prepare dialdehydes by subsequent formylation of aldehyde **4** with butyl dichloromethyl ether was unsuccessful even on long-term refluxing the reaction mixture in dichloromethane.

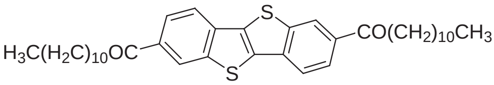
We also intended to accomplish a consecutive acetylation of 2-acetyl derivative **6**. To perform the reaction with a satisfactory rate, it was necessary to increase the reaction temperature to room temperature. The major product was the corresponding 2,7-diacetyl derivative **11** (45% yield) accompanied by other regioisomers (Scheme 2). From the mother liquor after crystallization of **11**, the following acyl derivatives were obtained by column chromatography and preparative thin layer chromatography: 2,8-diacetyl **12** (8% yield), 1,7-diacetyl **13** (3% yield) and 2,9-diacetyl **14** (1% yield). Isolation of a large variety of by-products confirms the predicted decrease in substitution selectivity. It is, however, interesting that second substitution on the same aromatic ring has never been observed, even if the calculations indicate relatively high reactivity of position 4. Also the presence of **12** and **13** in amounts larger than that of **14** does not correspond with the calculated results. It is possible that the reaction, that proceeds several days at room temperature, is influenced not only by kinetic factors. Because it was impossible to distinguish unambiguously between isomers **13** and **14** on the basis of their NMR spectra, we took advantage of the regioselectivity of electrophilic substitution reactions. When preserving the mode of 2 and 7 substitution, acetylation of 4-acetyl derivative **7** should lead to the formation of 2,9-diacetyl derivative **14** as the major product. Indeed, the reaction of **7** under analogous conditions afforded a mixture of four diacetyl derivatives. Their separation was successful with preparative thin layer chromatography. 2,9-Diacetyl derivative **14** (yield 45%) was isolated along with other regioisomers: 4,9-diacetyl **15** (yield 9%), 3,9-diacetyl **16** (yield 20%) and 1,9-diacetyl **17** (yield 9%).

Because alkyl esters of [1]benzothieno[3,2-*b*][1]benzothiophene-2,7-dicarboxylic acid showed liquid crystalline properties[10,11], structurally related diacyl derivatives could behave similarly. We found that diacylation



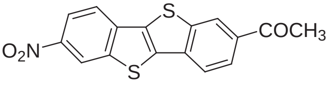
Scheme 2

of **1** can be easily accomplished using an excess of dodecanoyl chloride at room temperature and the corresponding 2,7-didodecanoyl derivative **18** was obtained in 46% yield. The same result was achieved in a two-stage procedure, where acylation of **8** afforded **18** in 45% yield. Other regioisomers, which were formed in minor amounts, were not isolated and identified. Compound **18** exhibited a relatively broad SmA phase (Cr-134-SmX-187-SmA-227-Iso) under polarizing microscope.



18

Because unsymmetrical 2,7-disubstituted derivatives of **1** could serve as useful starting compounds for preparation of further intermediates, nitration of ketone **8** was also studied. The reaction in nitromethane proceeded selectively to form a 3 : 1 mixture of 7-nitro ketone **19** and 9-nitro ketone **20** in overall yield of 94%. The major product **19** was separated by crystallization and column chromatography. We were not able to obtain the isomeric compound **20** in analytical purity but its structure was established by ^1H NMR.



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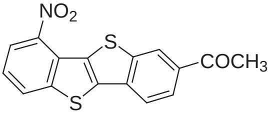
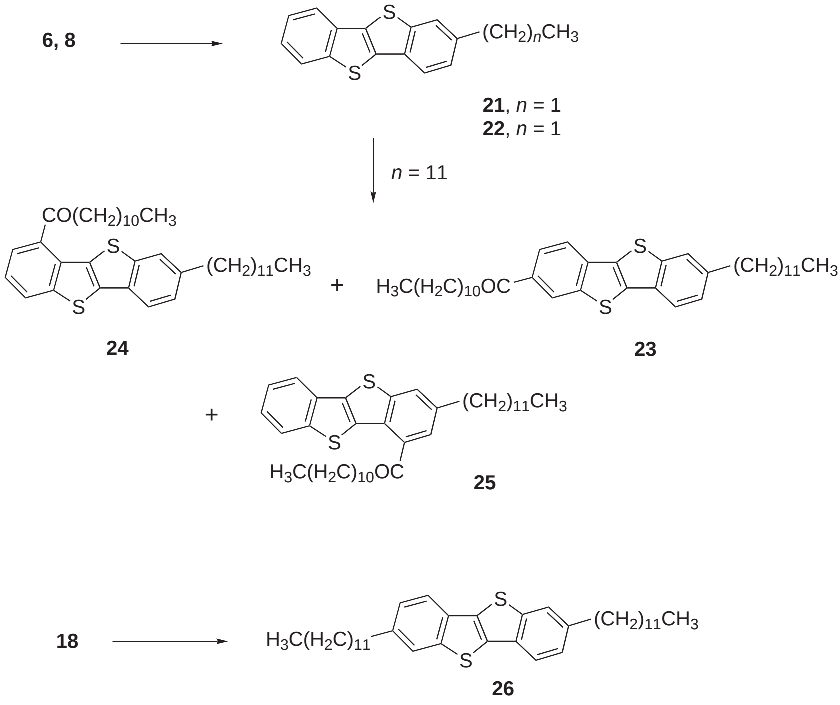


20

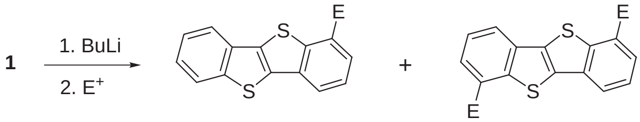
Reduction of ketones **6** and **8** by a Huang–Minlon procedure led easily to the corresponding alkyl derivatives of **1**: 2-ethyl[1]benzothieno[3,2-*b*]-[1]benzothiophene (**21**) and 2-dodecyl[1]benzothieno[3,2-*b*][1]benzothiophene (**22**), respectively (Scheme 3). It is interesting to note that the presence of a weak electron-donating alkyl group did not influence the general trend of selectivity of electrophilic substitution reactions: acylation of dodecyl derivative **22** with dodecanoyl chloride afforded selectively (7-dodecyl[1]benzothieno[3,2-*b*][1]benzothien-2-yl)dodecan-1-one (**23**) along with trace amounts of (7-dodecyl[1]benzothieno[3,2-*b*][1]benzothien-4-yl)dodecan-1-one (**24**) and (2-dodecyl[1]benzothieno[3,2-*b*][1]-benzothien-4-yl)dodecan-1-one (**25**). The 2,7-disubstitued derivative **23** showed also mesomorphic properties and SmC and SmA phases (Cr-130-SmC-150-SmA-174-Iso) were observed. 2,7-Didodecylbenzothieno-

[3,2-*b*][1]benzothiophene (**26**), which was easily obtained by reduction of **18**, exhibited formation of the SmA phase in a narrow temperature range (Cr-105-SmA-117-Iso).



SCHEME 3

Various directing groups can control regioselectivity and rate of lithiation reactions. For sulfur-containing heterocycles[19], the typical site of deprotonation in thiophene and benzo[*b*]thiophene is position 2. When this position is blocked, *e.g.* in dibenzothiophene[20], lithiation takes place in the ortho position to sulfur. The same behavior was observed for lithiation of [1]benzothieno[3,2-*b*][1]benzofuran[18]. Lithiation of heterocycle **1** with butyllithium also resulted in attack of position 1. Although an excess of butyllithium was necessary for a complete metallation, dilithiation was observed only to a small extent. The formed lithium compound was trapped by various electrophilic agents (Scheme 4). The reaction with *N*,*N*-dimethylformamide afforded [1]benzothieno[3,2-*b*][1]benzothiophene-1-carbaldehyde (**27**) (53% yield) along with a small amount of [1]benzothieno[3,2-*b*][1]benzothiophene-1,6-dicarbaldehyde (**28**) (8% yield). Carboxylation of the organometallic intermediate with subsequent esterification of the formed acid with diazomethane led selectively to methyl [1]benzothieno[3,2-*b*][1]benzothiophene-1-carboxylate (**29**) as the sole product. By using iodine, 1-iodo[1]benzothieno[3,2-*b*][1]benzothiophene (**30**) was obtained in a good yield (72%).

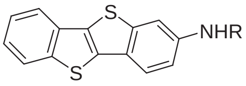


27, E = CHO
29, E = $COOCH_3$
30, E = I

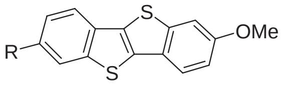
28, E = CHO

SCHEME 4

Nitration of **6** and acylation of **21** are procedures for preparation of unsymmetrical disubstituted derivatives of **1**. Another opportunity to introduce various substituents is based on reduction of nitro groups and transformation of the formed amino groups by standard procedures. Reduction of 2-nitro derivative with iron in a slightly acidic media[17] proceeded smoothly and [1]benzothieno[3,2-*b*][1]benzothiophen-2-amine (**31**) was obtained in high yield. Because it was not quite stable under usual conditions, it was converted to the corresponding amide **32**.



31, R = H
32, R = $COCH_3$



33, R = H
34, R = NO_2
35, R = OMe

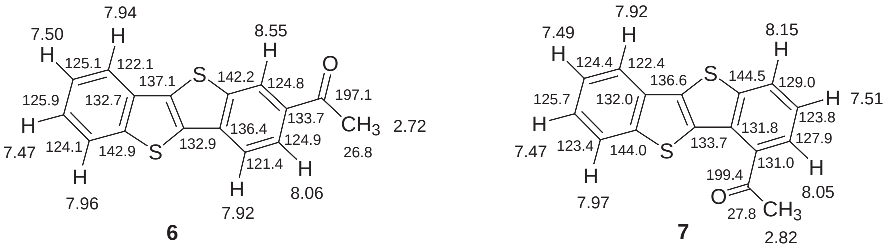
Nitro group belongs to good leaving groups in nucleophilic aromatic substitutions[21]. Thus, 2-nitro derivative **2** reacted smoothly with sodium methoxide in hexamethylphosphoramide to afford 2-methoxy[1]benzothieno[3,2-*b*][1]benzothiophene (**33**) in 58% yield. Stepwise substitution of the nitro groups in 2,7-dinitro derivative **9** was controlled by the substance : sodium methoxide ratio. A triple excess of sodium methoxide led to monosubstitution and 2-methoxy-7-nitro[1]benzothieno[3,2-*b*][1]benzothiophene (**34**) was formed selectively. Increasing the excess of the reagent led to a complete substitution of both nitro groups and 2,7-dimethoxy[1]benzothieno[3,2-*b*][1]benzothiophene (**35**) was obtained in moderate yield (35%).

Structure of all compounds was confirmed by spectroscopic methods. Because of very low solubility of some synthesized compounds, only NMR spectra of both acetyl derivatives **6** and **7** were fully assigned. The positions of substituents in these derivatives were proved by ^{1}H and ^{13}C NMR, ^{1}H-^{1}H COSY and ^{1}H-^{13}C HETCOR experiments (Fig. 1). Structures of other compounds were assigned by analogy of their ^{1}H and ^{13}C NMR spectra and on the basis of our earlier studies of NMR spectra of related substituted heterocycles[18].

The regioselectivity and product distribution in electrophilic substitution reactions of heterocycle **1** were studied. It was proved that the electrophile preferentially enters position 2 and the 4-substituted isomer is the minor product. Electrophilic substitution of the 2-substituted derivatives proceeds selectively to position 7; however, products of 6-, 8- and 9-substitution reactions were usually isolated as by-products. Thus, methods of electrophilic substitution can be used for preparation of 2- and 2,7-substituted derivatives of **1**. Such compounds with substitutents located on the long axis of the molecule are convenient starting materials for the design and synthesis of liquid crystals. Metallation of **1** proceeds in position 1 and various 1-substituted derivatives can be obtained by subsequent reactions with electrophilic agents. Long-chain derivatives of **1** have been found to exhibit mesomorphic behaviour. Synthesis and physical studies of new mesogens will be a subject of further research.

EXPERIMENTAL

Melting points were determined on a Leica VM TG block and are uncorrected. Elemental analyses were carried out on a Perkin–Elmer 2400. IR spectra (wavenumbers in cm^{-1}) were recorded on a Nicolet 740 FT-IR spectrometer in chloroform or KBr. NMR spectra were measured on a Varian Gemini 300 HC (300 MHz for ^{1}H and 75 MHz for ^{13}C), Bruker AMX-3 400 (400 MHz for ^{1}H) and Bruker DRX 500 (500 MHz for ^{1}H and 125 MHz for ^{13}C) spectrome-



6 **7**

FIG. 1
Assignment of ^{1}H and ^{13}C NMR signals in compounds **6** and **7**

ters; chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. Deuteriochloroform or DMSO-d_6 (DMSO) were used as solvents and the signals of solvents served as internal standards. By default APT experiments were used for ^{13}C NMR and thus we were able to assign the multiplicity of these signals. This fact was reflected in the presented spectra to provide most available information. Preparative thin layer chromatography was performed on glass plates (20 × 20 cm) on silica gel (Kieselgel GF_{254}, Merck). For HPLC, an Ecom LCP 4000 pump with reverse phase column Tessek C_{18} 25 × 4.5 0.7 μm and on Escom LCD 2082 UV detector (λ = 256 nm) were used. Methanol or its mixtures with water or dichloromethane were eluents. Mesomorphic properties of liquid crystals were determined on a polarizing microscope (Zeiss) with a heating stage (Linkam) and on a differential scanning calorimeter (Perkin–Elmer 7) for phase transition determination.

[1]Benzothieno[3,2-*b*][1]benzothiophene (**1**)

A mixture of (dichloromethyl)benzene (300 ml, 2.34 mol) and sulfur (80 g, 2.5 mol) was heated in a metal bath (240–270 °C) to reflux for 23 h. The melt was poured onto a layer of silica gel (250 g) and, after cooling, the solid was ground. Chloroform (1 000 ml) and silica gel (250 g) were added, the mixture was refluxed for 30 min and evaporated to dryness. The solid was transferred onto the top of a chromatographic column with silica gel (1 000 g) and eluted with hexane. Fractions containing **1** were collected and evaporated to afford 110.5 g of the product that was purified by crystallization from toluene. Yield 91.6 g (33%) of **1** was obtained; purity 99.5% (HPLC), m.p. 216–218 °C (ref.[22] gives m.p. 211–212 °C).

Nitration of [1]Benzothieno[3,2-*b*][1]benzothiophene (**1**)

To a mechanically stirred solution of compound **1** (20 g, 83.2 mmol) in dry dichloromethane (2 000 ml), a solution of fuming nitric acid in dry dichloromethane (150 ml, 1.206 M solution, 180.9 mmol) was added dropwise at –50 °C within one h. The reaction mixture was stirred for another 30 min and the formed solid was removed by filtration, washed with dichloromethane (3 × 100 ml) and dried to afford 19.7 g (83%) of crude product. After crystallization from toluene, 17.1 g (72%) of pure 2-nitro derivative **2** was obtained. The mother liquor was combined with the dichloromethane filtrate. The organic solution was successively washed with water (500 ml), saturated sodium hydrogencarbonate solution (500 ml), water (500 ml) and brine (500 ml), dried with anhydrous magnesium sulfate and evaporated. Crystallization of the residue from toluene afforded another portion of 2-nitro derivative **2**; the overall yield was 19.1 g (81%). From the mother liquor, 2.1 g (9%) of 4-nitro derivative **3** was isolated by crystallization from propan-2-ol.

2-Nitro[1]benzothieno[3,2-b][1]benzothiophene (**2**). Yellow crystals, m.p. 257–258 °C (ref.[17] gives m.p. 252–253 °C). For $C_{14}H_7NO_2S_2$ (285.3) calculated: 58.93% C, 2.47% H, 4.91% N, 22.47% S; found: 58.72% C, 2.65% H, 4.86% N, 22.34% S. ^{1}H NMR (400 MHz): 8.84 d, 1 H, *J*(1,3) = 1.9 (H-1); 8.32 dd, 1 H, *J*(3,4) = 8.8, *J*(1,3) = 1.9 (H-3); 7.95 m, 3 H (H-4, H-6, H-9); 7.51 m, 2 H (H-7, H-8). ^{13}C NMR (75 MHz): 144.8 s; 143.2 s; 142.0 s; 138.9 s; 132.5 s; 126.5 d; 125.4 d; 124.3 d; 122.4 d; 121.6 d; 120.4 d; 120.4 d. IR ($CHCl_3$): 3 026 w (C–H), 1 519 m (NO_2), 1 347 s (NO_2), 1 334 s (NO_2).

4-Nitro[1]benzothieno[3,2-b][1]benzothiophene (**3**). Orange crystals, m.p. 233–236 °C (ref.[17] gives m.p. 227–229 °C). For $C_{14}H_7NO_2S_2$ (294.3) calculated: 58.93% C, 2.47% H, 4.91% N, 22.47% S; found: 58.88% C, 2.72% H, 4.97% N, 22.52% S. ^{1}H NMR (400 MHz): 8.43 d, 1 H, *J*(2,3) = 8.0 (H-3); 8.24 d, 1 H, *J*(1,2) = 7.8 (H-1); 7.98 m, 2 H (H-6, H-9); 7.53 m, 3 H (H-2, H-7, H-8). ^{13}C NMR (75 MHz): 130.5 d (C-3); 126.5 d; 124.9 d; 123.9 d; 123.6 d; 122.5 d; 121.9 d. IR ($CHCl_3$): 3 013 w (C–H), 1 520 s (NO_2), 1 344 s (NO_2).

Formylation of [1]Benzothieno[3,2-*b*][1]benzothiophene (**1**)

Titanium(IV) chloride (2 ml, 18.23 mmol) was added to a mixture of **1** (1.0 g, 4.16 mmol) in dry dichloromethane (150 ml) at –10 °C under nitrogen atmosphere. After cooling to –60 °C, butyl dichloromethyl ether (2 ml, 14.20 mmol) was added dropwise under stirring and the mixture was kept for another 4 h at this temperature. The reaction was quenched by addition of water (100 ml), the organic layer was subsequently washed with 5% aqueous potassium carbonate (50 ml), water (50 ml), brine (50 ml), and dried with anhydrous magnesium sulfate. Evaporation of the solvent left 1.05 g (94%) of a mixture of **4** and **5** which was separated by crystallization from toluene and column chromatography on silica gel (toluene).

[1]Benzothieno[3,2-b][1]benzothiophene-2-carbaldehyde (**4**). Yield 0.54 g (48%), m.p. 303–306 °C, recrystallization at 196 °C. For $C_{15}H_8OS_2$ (268.4) calculated: 67.14% C, 3.00% H, 23.90% S; found: 66.98% C, 3.28% H, 24.09% S. ^{1}H NMR (400 MHz): 10.08 s, 1 H (CHO); 8.39 s, 1 H (H-1); 7.91 m, 4 H (H-3, H-4, H-6, H-9); 7.47 m, 2 H (H-7, H-8). ^{13}C NMR (75 MHz): 191.2 d (C=O); 142.9 s; 142.3 s; 137.8 s; 137.5 s; 133.1 s; 132.6 s; 130.8 s; 126.8 d; 126.1 d; 125.5 d; 125.2 d; 124.2 d; 122.2 d; 121.9 d. IR: 3 013 w (C–H), 1 692 s (C=O).

[1]Benzothieno[3,2-b][1]benzothiophene-4-carbaldehyde (**5**). Yield 0.28 g (25%), m.p. 193.2–195.6 °C. For $C_{15}H_8OS_2$ (268.4) calculated: 67.14% C, 3.00% H, 23.90% S; found: 67.32% C, 3.21% H, 23.85% S. ^{1}H NMR (400 MHz): 10.30 s, 1 H (CHO); 8.18 d, 1 H, $J(1,2)$ = 7.7 (H-1); 7.95 m, 3 H (H-3, H-6, H-9); 7.58 dd, 1 H, $J(1,2)$ = 7.7, $J(2,3)$ = 7.7 (H-2); 7.48 m, 2 H (H-7, H-8). IR: 3 014 w (C–H), 1 692 s (C=O).

Acetylation of [1]Benzothieno[3,2-*b*][1]benzothiophene (**1**)

A stirred solution of compound **1** (8.0 g, 33.3 mmol) in dichloromethane (600 ml) was cooled to –20 °C and aluminium chloride (16 g, 120 mmol) was added in one portion. After cooling to –70 °C, acetyl chloride (9.5 ml, 134 mmol) was added dropwise within 15 min and the mixture was stirred for 4 h at the given temperature, decomposed with water (300 ml) and diluted with dichloromethane (500 ml) to dissolve all the solid. The organic layer was separated and washed with water (2x100 ml), brine (200 ml), and dried with anhydrous magnesium sulfate. Evaporation of the solvent afforded 9.43 g (100%) of a mixture of **6** and **7**. Separation was achieved by fractional crystallization from toluene and purification by column chromatography on silica gel (toluene).

([1]Benzothieno[3,2-b][1]benzothien-2-yl)ethan-1-one (**6**). Yield 8.59 g (91%), m.p. 226–228 °C. For $C_{16}H_{10}OS_2$ (282.4) calculated: 68.06% C, 3.57% H, 22.71% S; found: 68.02% C, 3.80% H, 23.04% S. ^{1}H NMR (500 MHz): 8.55 s, 1 H (H-1); 8.06 d, 1 H, $J(3,4)$ = 8.3 (H-3); 7.96, 1 H (H-6); 7.94, 1 H (H-9); 7.92 d, 1 H, $J(3,4)$ = 8.3 (H-4); 7.50 dd, 1 H (H-8); 7.47 dd, 1 H (H-7); 2.72 s, 3 H (CH_3). ^{13}C NMR (125 MHz): 197.1 s (C=O); 142.8 s (C-5a); 142.2 s (C-10a); 137.1 s (C-9b); 136.4 s (C-4a); 133.7 s (C-2); 132.9 s (C-4b); 132.7 s (C-9a); 125.9 d (C-7); 125.1 d (C-8); 124.9 d (C-3); 124.8 d (C-1); 124.1 d (C-6); 122.1 d (C-9); 121.4 d (C-4); 26.8 q (CH_3). IR ($CHCl_3$): 3 014 m (C–H), 1 679 s (C=O).

([1]Benzothieno[3,2-b][1]benzothien-4-yl)ethan-1-one (**7**). Yield 0.35 g (4%), m.p. 190.5–192.8 °C. For $C_{16}H_{10}OS_2$ (282.4) calculated: 68.06% C, 3.57% H, 22.71% S; found: 67.77% C, 3.88% H, 22.76% S. ^{1}H NMR (500 MHz): 8.15 d, 1 H, $J(1,2)$ = 7.9 (H-1); 8.05 d, 1 H, $J(2,3)$ =

7.5 (H-3); 7.97 m, 1 H (H-6); 7.92 m, 1 H (H-9); 7.51 dd, 1 H, *J*(1,2) = 7.9, *J*(2,3) = 7.5 (H-2); 7.49 m, 1 H (H-8); 7.47 m, 1 H (H-7); 2.82 s, 3 H (CH_3). ^{13}C NMR (75 MHz): 199.4 s (C=O); 144.5 s (C-10a); 144.0 s (C-5a); 136.6 s (C-9b); 133.7 s (C-4b); 132.0 s (C-9a); 131.8 s (C-4a); 131.0 s (C-4); 129.0 d (C-1); 127.9 d (C-3); 125.7 d (C-7); 124.4 d (C-8); 123.8 d (C-2); 123.4 d (C-6); 121.4 d (C-9); 27.8 q (CH_3). IR ($CHCl_3$): 3 013 m (C–H), 1 679 s (C=O).

([1]Benzothieno[3,2-*b*][1]benzothien-2-yl)dodecan-1-one (**8**)

The same procedure as for acetylation of **1** was used starting with dodecanoyl chloride. The crude product **8** was purified by crystallization from toluene. Yield 80%, m.p. 165.6–166.4 °C. For $C_{26}H_{30}OS_2$ (422.7) calculated: 73.89% C, 7.15% H, 15.17% S; found: 73.82% C, 7.20% H, 15.08% S. ^{1}H NMR (300 MHz): 8.53 d, 1 H, *J*(1,3) = 1.6 (H-1); 8.04 dd, 1 H, *J*(1,3) = 1.6, *J*(3,4) = 8.2 (3); 7.92 m, 3 H (H-4, H-6, H-9); 7.46 m, 2 H (H-7, H-8); 3.07 t, 2 H, *J* = 7.3 (CH_2CO); 1.80 m, 2 H; 1.39 m, 4 H; 1.28 m, 12 H; 0.89 t, 3 H, *J* = 6.7 (CH_3). ^{13}C NMR (75 MHz): 199.4 s (C=O); 142.7 s; 142.1 s; 136.8 s; 136.1 s; 133.5 s; 132.8 s; 132.6 s; 125.7 d; 125.0 d; 124.6 d; 124.4 d; 124.0 d; 122.0 d; 121.3 d; 38.9 t; 32.0 t; 29.7 t; 29.6 t; 29.5 t; 29.4 t; 24.6 t; 22.8 t; 14.2 q. IR: 2 915 s (C–H), 2 849 s (C–H), 1 680 m (C=O).

Nitration of 2-Nitro[1]benzothieno[3,2-*b*][1]benzothiophene (**2**)

To a slurry of **2** (100 mg, 0.35 mmol) in dry nitromethane (20 ml), a solution of fuming nitric acid in nitromethane (1.5 ml of 1.2 M solution, 1.8 mmol) was added dropwise at 0 °C. The reaction mixture was stirred for 6 h at 0 °C, concentrated sulfuric acid (0.03 ml) was added and stirring was continued for another 2 h. Then it was diluted with dichloromethane (500 ml) and water (100 ml). The organic layer was washed with water (2 × 100 ml), brine (150 ml), dried with anhydrous magnesium sulfate and the solvents were removed under reduced pressure. An amount of 108 mg (93%) of a mixture of 2,7-dinitro[1]benzothieno[3,2-*b*][1benzothiophene (**9**) and 2,9-dinitro[1]benzothieno[3,2-*b*][1]benzothiophene (**10**) was obtained in a 3 : 1 ratio (by ^{1}H NMR). Crystallization from toluene (300 ml) afforded 20 mg (17%) of pure **9**.

2,7-Dinitro[1]benzothieno[3,2-b][1]benzothiophene (**9**). Orange crystals, m.p. 350 °C dec. (ref.[12] gives m.p. 377–378 °C). For $C_{14}H_6N_2O_4S_2$ (330.3) calculated: 50.90% C, 1.83% H, 8.48% N, 19.41% S; found: 51.12% C, 1.56% H, 8.60% N, 19.56% S. ^{1}H NMR (300 MHz): 8.92 d, 2 H, *J*(1,3) = 2.2 (H-1); 8.41 dd, 2 H, *J*(1,3) = 2.2, *J*(3,4) = 8.8 (H-3); 8.09 d, 2 H, *J*(3,4) = 8.8 (H-4). IR (KBr): 3 096 w (C–H), 1 520 m (NO_2), 1 338 s (NO_2).

2,9-Dinitro[1]benzothieno[3,2-b][1]benzothiophene (**10**). ^{1}H NMR (300 MHz): 8.92 s, 1 H (H-1); 8.47 dd, 1 H, *J*(6,8) = 1.1, *J*(7,8) = 8.0 (H-8); 8.37 d, 1 H, *J*(3,4) = 8.8 (H-3); 8.30 dd, 1 H, *J*(6,8) = 1.1, *J*(6,7) = 8.0 (H-6); 8.07 d, 1 H, *J*(3,4) = 8.8 (H-4); 7.66 dd, 1 H, *J*(6,7) = *J*(7,8) = 8.8 (H-7).

Acetylation of ([1]Benzothieno[3,2-*b*][1]benzothien-2-yl)ethan-1-one (**6**)

To a solution of **6** (500 mg, 1.77 mmol) and aluminum chloride (1.0 g, 7.50 mmol) in dry dichloromethane (50 ml), acetyl chloride (0.6 ml, 8.45 mmol) was slowly added at –30 °C under stirring. The reaction temperature was allowed to raise to room temperature. After 75 h, water (50 ml) was added, the precipitate was filtered off and washed successively with ethanol (2 × 20 ml) and dichloromethane (20 ml). The solid was crystallized from toluene to afford 260 mg (45%) of **11**. The mother liquor was combined with the original filtrate, washed successively with water (50 ml), brine (50 ml), and dried with anhydrous magnesium sulfate. Solvents were evaporated and the residue was separated by column chromatography on silica gel (toluene). Product **14** was separated by preparative TLC (chloroform) of a mixed fraction from the chromatography.

([1]Benzothieno[3,2-b][1]benzothiophene-2,7-diyl)bis(ethan-1-one) (**11**). Orange crystals, m.p. 310 °C dec. For $C_{18}H_{12}O_2S_2$ (324.4) calculated: 66.64% C, 3.73% H, 19.77% S; found: 66.34% C, 3.95% H, 19.80% S. ^{1}H NMR (300 MHz): 8.59 d, 2 H, $J(1,3) = 2.2$ (H-1); 8.10 dd, 2 H, $J(3,4) = 8.8$; 8.00 d, 2 H (H-4); 2.74 s, 6 H (CH_3). ^{13}C NMR (75 MHz): 142.8 s; 136.4 s; 136.0 s; 134.4 s; 125.1 d; 124.9 d; 121.9 d; 26.8 q (CH_3). IR (KBr): 1 679 s (C=O).

([1]Benzothieno[3,2-b][1]benzothiophene-2,8-diyl)bis(ethan-1-one) (**12**). Yield 45 mg (8%), m.p. 240–242 °C. ^{1}H NMR (300 MHz): 8.57 d, 1 H, $J(1,3) = 1.5$ (H-1); 8.51 d, 1 H, $J(7,9) = 1.5$ (H-9); 8.08 dd, 1 H, $J(3,4) = 8.4$, $J(1,3) = 1.5$ (H-3); 8.05 dd, 1 H, $J(6,7) = 8.5$, $J(7,9) = 1.5$ (H-7); 7.99 d, 1 H, $J(6,7) = 8.5$ (H-6); 7.95 d, 1 H, $J(3,4) = 8.4$ (H-4); 2.75 s, 3 H (CH_3-8); 2.73 s, 3 H (CH_3-2). IR: 1 680 s (C=O).

([1]Benzothieno[3,2-b][1]benzothiophene-1,7-diyl)bis(ethan-1-one) (**13**). Yield 15 mg (3%), m.p. 268–270 °C. ^{1}H NMR (300 MHz): 8.56 d, 1 H, $J(6,8) = 1.2$ (H-6); 8.17 d, 1 H, $J(3,4) = 8.0$ (H-4); 8.13 d, 1 H, $J(2,3) = 7.4$ (H-2); 8.08 dd, 1 H, $J(8,9) = 8.2$, $J(6,8) = 1.2$ (H-8); 8.04 d, 1 H, $J(8,9) = 8.2$ (H-9); 7.64 dd, 1 H, $J(3,4) = 8.0$, $J(2,3) = 7.4$ (H-3); 2.83 s, 3 H (CH_3-1); 2.73 s, 3 H (CH_3-7). ^{13}C NMR (75 MHz): 197.3 s (C=O); 197.1 s (C=O); 142.7 s; 141.9 s; 138.1 s; 136.6 s; 136.1 s; 134.3 s; 134.0 s; 131.5 s; 128.1 d; 126.9 d; 125.1 d; 124.8 d; 124.7 d; 121.8 d; 26.8 q (CH_3); 26.3 q (CH_3). IR (KBr): 1 663 s (C=O).

([1]Benzothieno[3,2-b][1]benzothiophene-2,9-diyl)bis(ethan-1-one) (**14**). Yield 7 mg (1%), m.p. 227–230 °C. ^{1}H NMR (300 MHz): 8.56 s, 1 H (H-1); 8.17 d, 1 H, $J(6,7) = 8.0$ (H-6); 8.09–8.05 m, 2 H (H-3, H-8); 7.95 d, 1 H, $J(3,4) = 8.0$ (H-4); 7.54 dd, 1 H, $J(6,7) = 8.0$, $J(7,8) = 7.7$ (H-7); 2.84 s, 3 H (CH_3); 2.74 s, 3 H (CH_3).

Acetylation of ([1]Benzothieno[3,2-*b*][1]benzothien-4-yl)ethan-1-one (**7**)

In an analogous manner, the reaction of **7** (50 mg, 0.177 mmol) with acetyl chloride (0.1 ml, 1.40 mmol), catalyzed with aluminium chloride (10 mg, 0.075 mmol) in dry dichloromethane (10 ml), afforded after 96 h of stirring and the same workup as above 50 mg of a mixture of products. They were separated by a double preparative TLC (chloroform).

([1]Benzothieno[3,2-b][1]benzothiophene-2,9-diyl)bis(ethan-1-one) (**14**). Yield 25 mg (45%).

([1]Benzothieno[3,2-b][1]benzothiophene-4,9-diyl)bis(ethan-1-one) (**15**). Yield 5 mg (9%), greenish crystals, m.p. 290 °C dec. ^{1}H NMR (300 MHz): 8.18 dd, 2 H, $J(1,2) = 8.0$, $J(1,3) = 1.1$ (H-1); 8.05 dd, 2 H, $J(2,3) = 7.7$, $J(1,3) = 1.1$ (H-3); 7.53 dd, 2 H, $J(1,2) = 8.0$, $J(2,3) = 7.7$ (H-2); 2.83 s, 6 H (CH_3).

([1]Benzothieno[3,2-b][1]benzothiophene-3,9-diyl)bis(ethan-1-one) (**16**). Yield 11 mg (20%), greenish crystals, m.p. 227–231 °C. ^{1}H NMR (300 MHz): 8.49 s, 1 H (H-4); 8.21 d, 1 H, $J(1,2) = 8.8$ (H-1); 8.16 dd, 1 H, $J(6,7) = 8.0$, $J(6,8) = 1.1$ (H-6); 8.06 dd, 1 H, $J(7,8) = 7.7$, $J(6,8) = 1.1$ (H-8); 7.96 m, 1 H (H-2); 7.52 dd, 1 H, $J(6,7) = 8.0$, $J(7,8) = 7.7$ (H-7); 2.82 s, 3 H (CH_3); 2.75 s, 3 H (CH_3).

([1]Benzothieno[3,2-b][1]benzothiophene-1,9-diyl)bis(ethan-1-one) (**17**). Yield 5 mg (9%), greenish crystals, m.p. 258–261 °C. ^{1}H NMR (300 MHz): 8.14–8.08 m, 3 H (H-2, H-6, H-8); 8.02 dd, 1 H, $J(3,4) = 7.7$, $J(2,4) = 1.1$ (H-4); 7.58 dd, 1 H, $J(2,3) = 7.7$, $J(3,4) = 7.7$ (H-3); 7.49 dd, 1 H, $J(6,7) = 7.7$, $J(7,8) = 7.7$ (H-7); 2.83 s, 3 H (CH_3); 2.81 s, 3 H (CH_3).

([1]Benzothieno[3,2-*b*][1]benzothiophene-2,7-diyl)bis(dodecan-1-one) (**18**)

To a stirred solution of **1** (500 mg, 2.08 mmol) in dry dichloromethane (50 ml), aluminium chloride (1.5 g, 11.25 mmol) was added at –10 °C. The solution was cooled to –70 °C and dodecanoyl chloride (2.5 ml, 10.48 mmol) was added dropwise. After 1 h, the temperature was allowed to rise to room temperature and stirring was continued for another 48 h. The reaction mixture was then diluted with water (10 ml), the precipitated solid was filtered off and washed with methanol (2 × 10 ml). Crystallization from toluene afforded 580 mg (46%) of **18**. Transition temperatures: Cr-134-SmX-187-SmA-227-Iso. For $C_{38}H_{52}O_2S_2$ (605.0) calculated: 75.45% C, 8.66% H, 10.60% S; found: 75.40% C, 8.55% H, 10.53% S. ^{1}H NMR (300 MHz): 8.58 d, 2 H, *J*(1,3) = 1.1 (H-1); 8.09 dd, 2 H, *J*(1,3) = 1.1, *J*(3,4) = 8.2 (H-3); 7.99 d, 2 H, *J*(3,4) = 8.2 (H-4); 3.08 t, 4 H, *J* = 7.1 (CH_2); 1.80 m, 4 H (CH_2); 1.19–1.45 m, 32 H; 0.89 t, 6 H (CH_3). IR: 2 959 m (C–H), 2 915 s (C–H), 2 848 s (C–H), 1 682 s (C=O).

Nitration of ([1]Benzothieno[3,2-*b*][1]benzothien-2-yl)ethan-1-one (**6**)

Fuming nitric acid in nitromethane (3 × 0.5 ml of 1.206 M solution, 1.8 mmol) was added dropwise in 3 portions to a solution of **6** (100 mg, 0.354 mmol) in nitromethane (20 ml) at 0 °C within 3 h. Sulfuric acid (0.01 ml) was then added, the reaction mixture was stirred for another 2 h, poured into water (100 ml) and extracted with dichloromethane (2 × 100 ml). The combined organic solutions were washed with water (100 ml), brine (100 ml), and dried with anhydrous magnesium sulfate. The solvent was removed at reduced pressure and the crude mixture of product **19** and **20** (2 : 1 ratio, overall yield 95%) was crystallized from toluene to afford 28 mg (24%) of pure **19**. Because the minor isomer **20** could not be obtained in analytical purity, its structure was deduced from ^{1}H NMR spectra.

(7-Nitro[1]benzothieno[3,2-b][1]benzothien-2-yl)ethan-1-one (**19**). Orange crystals, m.p. 315–320 °C dec. For $C_{16}H_9NO_3S_2$ (327.4) calculated: 58.70% C, 2.77% H, 4.28% N, 19.59% S; found: 58.94% C, 2.99% H, 4.35% N, 19.30% S. ^{1}H NMR (300 MHz): 8.90 s, 1 H (H-6); 8.60 s, 1 H (H-1); 8.38 d, 1 H, *J*(8,9) = 8.2 (H-8); 8.12 d, 1 H, *J*(3,4) = 8.8 (H-3); 8.04 m, 2 H (H-4, H-9); 2.75 s, 3 H (CH_3). IR (KBr): 1 678 s (C=O), 1 517 m (NO_2), 1 330 s (NO_2).

(9-Nitro[1]benzothieno[3,2-b][1]benzothien-2-yl)ethan-1-one (**20**). ^{1}H NMR (300 MHz): 8.61 s, 1 H (H-1); 8.48 d, 1 H, *J*(7,8) = 8.2 (H-8); 8.29 d, 1 H, *J*(6,7) = 7.7 (H-6); 8.05 d, 1 H (H-3); 8.02 d, 1 H (H-4); 7.61 dd, 1 H, *J*(6,7) = 7.7, *J*(7,8) = 8.2 (H-7); 2.72 s, 3H (CH_3).

2-Ethyl[1]benzothieno[3,2-*b*][1]benzothiophene (**21**)

A mixture of **6** (3.0 g, 10.62 mmol), potassium hydroxide (1.5 g, 26.73 mmol) and hydrazine hydrate (4.0 ml, 80% aqueous solution, 65.8 mmol) in diethylene glycol (100 ml) was heated to 100–110 °C for 45 min and to 210–220 °C for another 5 h. After cooling to room temperature, the formed precipitate was filtered off and washed with methanol (2 × 15 ml). Column chromatography on silica gel (hexane) and crystallization from methanol–toluene (2 : 1) afforded 2.58 g (90%) of **21**, m.p. 129.6–130.0 °C. For $C_{16}H_{12}S_2$ (268.4) calculated: 71.60% C, 4.51% H, 23.89% S; found: 71.70% C, 4.55% H, 23.94% S. ^{1}H NMR (300 MHz): 7.91 d, 1 H, *J*(6,7) = 7.7 (H-6); 7.84 d, 1 H, *J*(8,9) = 7.7 (H-9); 7.80 d, 1 H, *J*(3,4) = 7.7 (H-4); 7.75 s, 1 H (H-1); 7.48–7.36 m, 2 H (H-7, H-8); 7.31 d, 1 H, *J*(3,4) = 7.7 (H-3); 2.82 q, 2 H, *J* = 7.7 (CH_2); 1.34 t, 3 H, *J* = 7.7 (CH_3). IR ($CHCl_3$): 2 959 w, 2 926 w, 1 448 m, 1 429 m, 1 334 m, 1 296 m, 1 254 m, 1 059 w, 951 w.

2-Dodecyl[1]benzothieno[3,2-*b*][1]benzothiophene (**22**)

The same procedure as for preparation of **21** was used with **8**. Yield 94%, m.p. 107.6–108.5 °C. For $C_{26}H_{32}S_2$ (408.2) calculated: 76.41% C, 7.89% H, 15.69% S; found: 76.26% C, 9.03% H, 12.13% S. ^{1}H NMR (300 MHz): 7.91 d, 1 H, *J*(6,7) = 7.7 (H-6); 7.84 dd, 1 H, *J*(7,9) = 1.7, *J*(8,9) = 7.7 (H-9); 7.79 d, 1 H, *J*(3,4) = 8.2 (H-4); 7.72 s, 1 H (H-1); 7.46 ddd, 1 H, *J*(7,9) = 1.7, *J*(6,7) = 7.7, *J*(7,8) = 8.2 (H-7); 7.39 ddd, 1 H, *J*(6,8) = 1.7, *J*(8,9) = 7.7, *J*(7,8) = 8.2 (H-8); 7.29 dd, 1 H, *J*(1,3) = 1.7, *J*(3,4) = 8.2 (H-3); 2.76 t, 2 H, *J* = 7.7 (CH_2); 1.67 m, 2 H (CH_2); 1.34 m, 2 H (CH_2); 1.26 m, 16 H; 0.88 t, 3 H, *J* = 6.6 (CH_3). IR: 2 928 s (C–H), 2 855 m (C–H), 1467 w, 1 459 w, 1 431 w, 1 339 w, 1 254 w, 1 057 w, 852 w.

Acylation of 2-Dodecyl[1]benzothieno[3,2-*b*][1]benzothiophene (**22**)

To a stirred solution of **22** (100 mg, 0.245 mmol) in dry dichloromethane (10 ml), aluminium chloride (100 mg, 0.75 mmol) was added at –10 °C, the solution was cooled to –78 °C and dodecanoyl chloride (0.35 ml, 1.47 mmol) was added dropwise. The mixture was stirred for 4 h and the reaction was then quenched by addition of water (10 ml). Organic layer was separated, washed with water (15 ml) and brine (15 ml), and dried with anhydrous magnesium sulfate. The residue after evaporation was purified by column chromatography (silica gel, toluene–hexane 1 : 2). Crystallization from hexane afforded 100 mg (69%) of **23**. Chromatography of the mother liquor gave another portion of **23** (16 mg, 11%) and 7 mg of an inseparable mixture of **24** and **25** in a 3 : 2 ratio. The structures of both compounds and their ratio were determined from ^{1}H NMR.

(7-Dodecyl[1]benzothieno[3,2-b][1]benzothien-2-yl)dodecan-1-one (**23**). Transition temperatures: Cr-130-SmC-150-SmA-174-Iso. For $C_{38}H_{39}OS_2$ (590.4) calculated: 77.23% C, 9.21% H, 10.85% S; found: 77.18% C, 9.09% H, 10.56% S. ^{1}H NMR (300 MHz): 8.53 s, 1 H (H-1); 8.05 d, 1 H, *J*(3,4) = 8.3 (H-4); 7.89 d, 1 H, *J*(8,9) = 8.5 (H-9); 7.82 d, 1 H, *J*(3,4) = 8.3 (H-3); 7.73 s, 1 H (H-6); 7.31 d, 1 H, *J*(8,9) = 8.5 (H-8); 3.07 t, 2 H, *J* = 7.5 ($COCH_2$); 2.78 t, 2 H, *J* = 7.5 (CH_2); 1.83–1.67 m, 4 H (CH_2); 1.27 m, 34 H; 0.89 t, 6 H, *J* = 6.4 (CH_3). ^{13}C NMR (75 MHz): 199.4 s (CO); 143.0 s; 141.9 s; 141.3 s; 136.9 s; 136.3 s; 133.3 s; 132.0 s; 130.6 s; 126.1 d; 124.6 d; 124.4 d; 123.4 d; 121.6 d; 121.1 d; 38.9 t; 36.2 t; 32.0 t; 29.7 t; 29.6 t; 29.4 t; 29.3 t; 24.6 t; 22.8 t; 14.2 q. IR: 2 918 s (C–H), 2 859 s (C–H), 1 679 m (C=O).

(7-Dodecyl[1]benzothieno[3,2-b][1]benzothien-4-yl)dodecan-1-one (**24**). ^{1}H NMR (300 MHz): 8.09 d, 1 H, *J*(2,3) = 7.7 (H-3); 8.00 d, 1 H, *J*(1,2) = 7.7 (H-2); 7.79 d, 1 H (H-9); 7.70 s, 1 H (H-6); 7.44 m, 1 H (H-2); 7.28 d, 1 H (H-8); 3.14 t, 2 H, *J* = 7.4 ($COCH_2$); 2.78 t, 2 H, *J* = 7.5 (CH_2); 1.83–1.67 m, 4 H (CH_2); 1.27 m, 34 H; 0.89 t, 6 H, *J* = 6.4 (CH_3).

(2-Dodecyl[1]benzothieno[3,2-b][1]benzothien-4-yl)dodecan-1-one (**25**). ^{1}H NMR (300 MHz): 7.85–7.92 m, 2 H (H-6, H-9); 7.91 s, 1 H (H-6); 7.80 s, 1 H (H-1); 7.40–7.47 m, 2 H (H-7, H-8); 3.14 t, 2 H, *J* = 7.4 ($COCH_2$); 2.83 t, 2 H, *J* = 7.5 (CH_2); 1.67–1.83 m, 4 H (CH_2); 1.27 m, 34 H; 0.89 t, 6 H, *J* = 6.4 (CH_3).

2,7-Didodecyl[1]benzothieno[3,2-*b*][1]benzothiophene (**26**)

To a stirred slurry of **18** (200 mg, 0.33 mmol) in diethylene glycol (15 ml), potassium hydroxide (100 mg, 1.78 mmol) and hydrazine (0.5 ml, 80% aqueous solution, 8.23 mmol) were added successively. The reaction mixture was then heated to 120 °C for 1 h and to 220–230 °C for another 5 h, cooled to room temperature. The resulting precipitate was filtered off and washed with methanol (2 × 15 ml). After purification by column chromatography (silica gel, hexane) and crystallization from ethanol, 169 mg (90%) of **26** was isolated. Transition temperatures: Cr-105-SmA-117-Iso. For $C_{38}H_{56}S_2$ (577.0) calculated: 79.10% C, 9.78% H, 11.11% S; found: 79.03% C, 9.88% H, 11.13% S. ^{1}H NMR (300 MHz): 7.75 d, 2 H, *J*(3,4) = 8.3 (H-4); 7.69 d, 2 H, *J*(1,3) = 1.4 (H-1); 7.26 dd, 2 H, *J*(3,4) = 8.3, *J*(1,3) = 1.4 (H-3); 2.76 t, 4 H, *J* = 7.7 (CH_2); 1.70 m, 4 H (CH_2); 1.35 m, 8 H (CH_2); 1.27 m, 28 H (CH_2); 0.89 t, 6 H, *J* = 6.8 (CH_3). ^{13}C NMR (MHz): 142.2 s; 139.9 s; 132.4 s; 131.1 s; 125.8 d; 123.2 d; 121.0 d; 36.2 t; 32.0 t; 31.8 t; 29.7 t; 29.7 t; 29.6 t; 29.4 t; 29.4 t; 22.8 t; 14.2 q. IR: 2 917 s (C–H), 2 849 s (C–H).

[1]Benzothieno[3,2-*b*][1]benzothiophene-1-carbaldehyde (**27**)

Butyllithium (0.8 ml of 2 M solution in hexanes, 1.6 mmol) was added dropwise to a solution of **1** (100 mg, 0.416 mmol) in dry THF (10 ml) at –78 °C under nitrogen atmosphere. The cooling bath was removed and the mixture was stirred at room temperature for 40 min and recooled to –78 °C. *N*,*N*-Dimethylformamide (2 ml, 26 mmol) was added, temperature was raised to room temperature and the mixture was stirred for 90 min. The reaction was quenched by addition of water (2 ml) and the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (20 ml), washed with water (2 × 20 ml) and brine, and dried with anhydrous magnesium sulfate. The solid after evaporation was separated by column chromatography on silica gel (hexane–toluene 1 : 1) and crystallized from ethyl acetate to afford compounds **27** and **28**.

[1]Benzothieno[3,2-b][1]benzothiophene-1-carbaldehyde (**27**). Yield 59 mg (53%), m.p. 201–203 °C. For $C_{15}H_8OS_2$ (268.3) calculated: 67.14% C, 3.00% H, 23.90% S; found: 67.02% C, 3.26% H, 24.07% S. ^{1}H NMR (300 MHz): 10.30 s, 1 H (CHO); 8.19 d, 1 H, *J*(3,4) = 7.7 (H-4); 7.96 m, 3 H (H-2, H-6, H-9); 7.69 dd, 1 H, *J*(3,4) = 7.7, *J*(2,3) = 7.2 (H-3); 7.48 m, 2 H (H-7, H-8). ^{13}C NMR (75 MHz): 191.2 d (CHO); 142.7 s; 140.1 s; 137.9 s; 134.5 s; 133.0 s; 132.5 s; 131.3 d; 127.2 d; 125.5 d; 125.1 d; 124.8 d; 124.0 d; 122.0 d. IR: 3 012 w (C–H), 1 683 s (C=O).

[1]Benzothieno[3,2-b][1]benzothiophene-1,6-dicarbaldehyde (**28**). Yield 9 mg (8%), m.p. 305–310 °C dec. ^{1}H NMR (300 MHz): 10.32 s, 2 H (CHO); 8.29 d, 2 H, *J*(3,4) = 7.7 (H-4); 8.01 d, 2 H, *J*(2,3) = 7.2 (H-2); 7.74 dd, 2 H, *J*(3,4) = 7.7, *J*(2,3) = 7.2 (H-3). IR: 3 021 m (C–H), 1 674 m (C=O).

Methyl [1]Benzothieno[3,2-*b*][1]benzothiophene-1-carboxylate (**29**)

Compound **1** (100 mg, 0.416 mmol) in THF (10 ml) was lithiated with butyllithium in hexanes (1 ml, 2.0 mmol) as above. The cooled reaction mixture was poured onto ground dry ice (about 10 g). After evaporation of excess of carbon dioxide, ethyl acetate (200 ml) was added, the resulting solution was washed successively with 5% solution of hydrochloric acid (100 ml), water (2 × 100 ml) and brine (100 ml), and dried with anhydrous magnesium sulfate. The solvent was removed under reduced pressure, the formed solid was dissolved in dry THF (20 ml) and a solution of diazomethane in ether was added until permanent yellow color persisted. After 20 min, the solvent was evaporated and the crude product was crystallized from ethyl acetate. Yield 60 mg (48%) of **28** was obtained; m.p. 193.3–195.8 °C. For $C_{16}H_{10}O_2S_2$ (298.4) calculated: 64.41% C, 3.38% H, 21.49% S; found: 64.52% C, 3.61% H, 21.56% S. ^{1}H NMR (300 MHz): 8.18 d, 1 H, *J*(3,4) = 7.7 (H-4); 8.10 d, 1 H, *J*(2,3) = 7.7 (H-2); 7.96 m, 2 H (H-6, H-9); 7.55 dd, 1 H, *J*(2,3) = 7.7, *J*(3,4) = 7.7 (H-3); 7.46 m, 2 H (H-7, H-8);

3.94 s, 3 H (OCH_3). ^{13}C NMR (75 MHz): 166.4 s (CO); 142.5 s; 134.3 s; 133.0 s; 127.1 d; 125.9 d; 125.3 d; 125.1 s; 125.0 d; 124.5 d; 124.0 d; 121.9 d; 52.5 q. IR: 3 011 w (C–H), 1 708 m (C=O), 1 284 s (C–O).

1-Iodo[1]benzothieno[3,2-*b*][1]benzothiophene (**30**)

Lithiation of **1** (5 g, 20.8 mmol) in dry THF (250 ml) with 2.5 M solution of butyllithium in hexanes (20 ml, 50 mmol) was performed as with **27**. The solution of iodine (10 g, 39.4 mmol) in dry THF (50 ml) was added at –75 °C, the cooling bath was removed and the mixture was finally stirred at room temperature for 20 min. Excess of iodine was destroyed by addition of aqueous solution of sodium thiosulfate (100 ml of 10% aqueous solution), the organic layer was separated and evaporated to dryness. The crude product was dissolved in dichloromethane (200 ml) and the solution was washed successively with water (100 ml) and brine (100 ml), and dried with anhydrous magnesium sulfate. The residue after evaporation was purified by crystallization from toluene, affording 5.5 g (72%) of **30**, m.p. 160–162 °C. For $C_{14}H_7IS_2$ (366.2) calculated: 45.91% C, 1.93% H, 34.65% I, 17.51% S; found: 46.02% C, 1.98% H, 34.32% I, 17.55% S. ^1H NMR (300 MHz): 7.88 m, 3 H (H-4, H-6, H-9); 7.72 d, 1 H, $J(2,3) = 7.7$ (H-2); 7.44 m, 2 H (H-7, H-8); 7.18 dd, 1 H, $J(2,3) = 7.7$, $J(3,4) = 8.7$ (H-3). IR: 1 537 w, 1 451 w, 1 418 w, 1 384 w, 1 335 w, 1 096 w, 806 w.

[1]Benzothieno[3,2-*b*][1]benzothiophen-2-amine (**31**)

Ammonium chloride (3 ml of 5% aqueous solution, 2.8 mmol) was added to a mixture of **2** (1.0 g, 3.5 mmol), iron powder (3.4 g, 60.9 mmol) and toluene (140 ml) under vigorous stirring at 80 °C. The mixture was kept at this temperature for 5 h, cooled to room temperature and the solid phase was removed by filtration and washed with toluene (2 × 20 ml). The filtrate was dried with anhydrous magnesium sulfate, the solvent was removed under reduced pressure and 880 mg (98%) of amine **31** was obtained as a pink solid, m.p. 206–208 °C (ref.[16] gives m.p. 205–206 °C). ^1H NMR (400 MHz): 7.86 d, 1 H, $J(6,7) = 8.0$ (H-6); 7.77 d, 1 H, $J(8,9) = 7.9$ (H-9); 7.64 d, 1 H, $J(3,4) = 8.4$ (H-4); 7.41 dd, 1 H, $J(8,9) = 7.9$, $J(7,8) = 7.2$ (H-8); 7.32 dd, 1 H, $J(6,7) = 8.0$, $J(7,8) = 7.2$ (H-7); 7.15 d, 1 H, $J(1,3) = 2.0$ (H-1); 6.80 dd, 1 H, $J(3,4) = 8.4$, $J(1,3) = 2.0$ (H-3); 3.83 s, 2 H (NH_2). ^{13}C NMR (75 MHz): 144.5 s; 144.3 s; 141.5 s; 133.6 s; 133.5 s; 129.9 s; 125.5 s; 124.7 d; 124.0 d; 123.9 d; 122.3 d; 120.9 d; 114.3 d; 108.6 d. IR (KBr): 3 486 w (NH), 3 400 w (NH), 3 010 m (C–H).

N-([1]Benzothieno[3,2-*b*][1]benzothien-2-yl)acetamide (**32**)

To a stirred solution of amine **31** (1.0 g, 3.9 mmol) in toluene (100 ml), acetic anhydride (0.5 ml, 5.3 mmol) was added and the reaction mixture was then stirred for 40 min. The precipitated product was filtered off, washed with toluene (2 × 30 ml) and dried. Crystallization from ethanol afforded 0.81 g (70%) of **32**, m.p. 259–261 °C. For $C_{16}H_{11}NOS_2$ (297.4) calculated: 64.62% C, 3.73% H, 4.71% N, 21.56% S; found: 64.25% C, 4.20% H, 4.36% N, 21.81% S. ^1H NMR (300 MHz, DMSO): 10.26 s, 1 H (NH); 8.52 s, 1 H (H-1); 8.12 d, 1 H, $J(3,4) = 7.7$ (H-3); 7.97 m, 2 H (H-6, H-9); 7.56 d, 1 H, $J(8,9) = 8.65$ (H-8); 7.48 m, 2 H (H-4, H-7); 2.11 s, 3 H (CH_3). ^{13}C NMR (75 MHz, DMSO): 168.6 s (C=O); 142.4 s; 141.2 s; 137.2 s; 132.7 s; 132.5 s; 131.5 s; 127.8 s; 125.4 d; 125.1 d; 124.4 d; 121.8 d; 121.3 d; 117.6 d; 113.6 d; 24.1 q (CH_3). IR (KBr): 1 666 m (C=O).

2-Methoxy[1]benzothieno[3,2-*b*][1]benzothiophene (**33**)

A stirred solution of **2** (235 mg, 0.824 mmol) in dry HMPA (10 ml) was treated at 70 °C with sodium methoxide (200 mg, 3.70 mmol) for 20 min. Another portion of sodium methoxide (50 mg, 0.93 mmol) was added, the reaction mixture was stirred for another 45 min and poured into saturated ammonium chloride solution. The resulting mixture was washed with toluene (3 × 30 ml), the combined organic layers were washed with water (2 × 50 ml) and brine (50 ml), dried with anhydrous magnesium sulfate and evaporated to dryness. Column chromatography (silica gel, hexane–toluene 5 : 1) of the crude product afforded 130 mg (58%) of pure **33**, m.p. 178–180 °C. For $C_{15}H_{10}OS_2$ (270.4) calculated: 66.64% C, 3.73% H, 23.72% S; found: 66.60% C, 3.79% H, 23.63% S. ^{1}H NMR (300 MHz): 7.90 d, 1 H, *J*(6,7) = 7.7 (H-6); 7.83 d, 1 H, *J*(8,9) = 7.2 (H-9); 7.77 d, 1 H, *J*(3,4) = 8.8 (H-4); 7.39 m, 3 H (H-1, H-7, H-8); 7.07 dd, 1 H, *J*(1,3) = 1.8, *J*(3,4) = 8.8 (H-3); 3.92 s, 3 H (OCH_3). ^{13}C NMR (75 MHz): 157.7 s; 143.8 s; 141.6 s; 133.2 s; 133.1 s; 131.1 s; 126.9 s; 124.7 d; 124.3 d; 123.9 d; 122.1 d; 121.0 d; 114.3 d; 106.9 d; 55.7 q. IR: 1 602 m, 1 260 s (C–O), 1 227 s (C–O).

2-Methoxy-7-nitro[1]benzothieno[3,2-*b*]benzothiophene (**34**)

To a solution of **9** (100 mg, 0.303 mmol) in HMPA (20 ml) under nitrogen atmosphere, sodium methoxide (54 mg, 1.00 mmol) was rapidly added at 70 °C. The reaction mixture was stirred for 40 min and worked up as with **33**. The crude product was subjected to column chromatography (silica gel, hexane–toluene 1 : 2) which afforded 37 mg (39%) of **34**, m.p. 262–265 °C (toluene) (ref.[12] gives m.p. 275–277 °C). For $C_{15}H_9NO_3S_2$ (315.4) calculated: 57.13% C, 2.88% H, 4.44% N, 20.33% S; found: 57.22% C, 2.91% H, 4.33% N, 20.26% S. ^{1}H NMR (300 MHz): 8.82 d, 1 H, *J*(6,8) = 2.2 (H-6); 8.28 dd, 1 H, *J*(6,8) = 2.2, *J*(8,9) = 8.8 (H-8); 7.88 d, 1 H, *J*(8,9) = 8.8 (H-9); 7.83 d, 1 H, *J*(3,4) = 8.8 (H-4); 7.41 d, 1 H, *J*(1,3) = 2.2 (H-1); 7.12 dd, 1 H, *J*(1,3) = 2.2, *J*(3,4) = 8.8 (H-3); 3.94 s, 3 H (OCH_3). IR: 1 512 m (NO_2), 1 350 s (NO_2), 1 265 s (C–O), 1 225 s (C–O).

2,7-Dimethoxy[1]benzothieno[3,2-*b*]benzothiophene (**35**)

Under analogous conditions as with **33**, 32 mg (35%) of **35** was obtained from **9** (100 mg, 0.303 mmol), sodium methoxide (100 mg, 1.85 mmol) in HMPA (20 ml), m.p. 237 °C (toluene). For $C_{16}H_{12}O_2S_2$ (300.4) calculated: 63.97% C, 4.03% H, 21.35% S; found: 64.06% C, 4.05% H, 21.28% S. ^{1}H NMR (300 MHz): 7.70 d, 2 H, *J*(3,4) = 8.5 (H-4); 7.38 d, 2 H, *J*(1,3) = 2.2 (H-1); 7.05 dd, 2 H, *J*(1,3) = 2.2, *J*(3,4) = 8.5 (H-3); 3.91 s, 6 H (CH_3). IR: 1 600 m, 1 264 s (C–O), 1 220 s (C–O).

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