Mono-, Di-, and Trisubstituted Acyl and Alkyl Thiophenes
I. Synthesis, Ultraviolet, and Proton Magnetic Resonance Spectra

J. George Pomonis,* Charlotte L. Fatland, and Fredrick R. Taylor[1]
Metabolism and Radiation Research Laboratory, Agricultural Research Service, U.S. Department of Agriculture, Fargo, N.D. 58102

The synthesis of 63 mono-, di-, and trisubstituted acyl and alkyl thiophenes is reported, and the ultraviolet, infrared, and PMR spectra are discussed.

The corroboration of structure by synthesis of mono- and dimethyl branched C_{29}–C_{39} alkanes that had been isolated from certain insect tissue (*16–19*) required the preparation of 63 mono-, di-, and trisubstituted thiophenes as intermediates. In the present paper we report the synthesis, PMR, and absorption spectra of these thiophenes; in a following paper, we shall report the mass spectra.

Results and Discussion

Synthesis. The scheme selected for the synthesis of the branched hydrocarbons via intermediary thiophenes is shown in Figure 1 and was chosen to eliminate ambiguity of the position of the methyl substituent(s) in the synthesis of the hydrocarbons.

Attempts to acylate 3-methylthiophene in the 2-position resulted in intractable mixtures of 2- and 5-acyl-3-methylthiophenes in ratios ranging from 7:3 to 1:1. Because of this difficulty, it was necessary to block the 5-position of **3** with an easily removed group that, at the same time, deactivated the 4-position to electrophillic attack, and the carboxy group was chosen for this purpose.

Ultraviolet spectra. Table I lists the λ_{max} and ϵ_{max} of the UV spectra for the mono-, di-, and trisubstituted thiophenes. The values obtained for the series of 2-acyl- and 2-alkylthiophenes (**2**, **3**) are in agreement with those reported by others for some lower homologs (*3, 10, 12*).

The 2-alkyl-5-carboxythiophenes (**4**) and their methyl esters (**5**) have similar spectra except for inversion of the intensity ratios of the maxima at 274–275 and 254 nm. A comparison of the spectra of the 2,5-disubstituted compounds **4** and **5** with those reported for the mono-2-substituted compounds (*1*) (e.g., 2-carboxy- and 2-carbomethoxythiophene) showed a shift toward the red for the two $\pi \rightarrow \pi^*$ bands in the 2,5-disubstituted compound.

The spectra reported in Table I illustrate the hypsochromic effect of the chloromethyl group as compared with the methyl group (**6** vs. **7**), a slight bathochromic effect of the 2-*n*-alkyl-3-methyl-5-acyl compounds **10** and **12** as compared with **7**, a strong hypsochromic effect, apparently the result of steric inhibition of coplanarity in the case of **10** and **12**, and a bathochromic effect as a result of the introduction of additional alkyl groups into a thiophene of the types **11** and **13**.

PMR spectra. The PMR spectrum for a representative of each type of compound (**2–13**) is reported in the Experimental section. Correlations for the resonances and *J* values of the various protons were similar to those listed for substituted thiophenes (*2, 11*). Generally, the resonance for the aliphatic methyl group had δ values of 0.85–0.89 ppm and appeared as a distorted triplet, which is characteristic of the methyl groups of long-chain aliphatics. The methylene hydrogens (except for the two adjacent to the thiophene ring or the carbonyl group) had δ values of 1.24–1.28 ppm and appeared as a broad singlet. The two protons on the methylene groups adjacent to the thiophene ring or adjacent to the carbonyl group exhibited resonances in the δ 2.78–2.88 ppm range. In addition, the 3-methyl substituent caused an upfield shift in the methylene proton resonance for the methylene hydrogens adjacent to the 2-position in thiophene (i.e., from δ 2.78 to δ 2.60).

The aromatic protons for the various compounds (**2–13**) provided the classic resonances for substituted thiophenes.

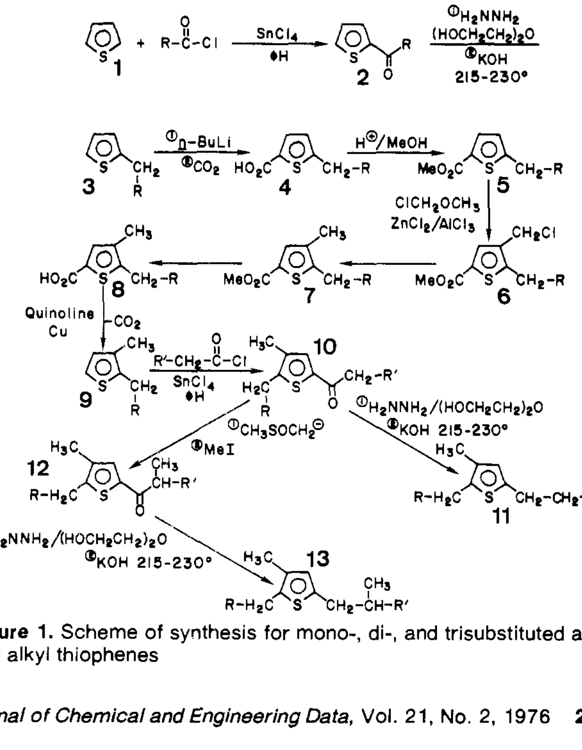

Figure 1. Scheme of synthesis for mono-, di-, and trisubstituted acyl and alkyl thiophenes

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[1] Present address, School of Medicine, University of New Mexico, Albuquerque, N.M. 87106.

Compounds **2** and **3** had typical ABM and ABC splitting patterns, respectively. Both the free acid **4** and the methylester **5** had spectra that showed the typical AB pattern (i.e., a pair of doublets with *J* values in agreement with reported coupling constants for the protons of the 3 and 4 positions) (*5*). In contrast, the AB pattern for compound **9** had a coupling constant of 5.0 cps for the pair of doublets. The $\Delta\delta$ values of the 4 and 5 protons of **9** were of smaller magnitude than the $\Delta\delta$ values of compounds **4** and **5** or than those reported in the literature for similar compounds (*10*).

Table I. Summary of Melting Points and/or Ultraviolet Data[a] for Some Selected Substituted Thiophenes

Cmpd	R	Bp (mm Hg) or mp	λ_{max}, nm	Log ϵ_{max}
2a	$-C_8H_{17}$	bp 85–96° (0.025)	275, 258	3.86, 3.97
b	$-C_{12}H_{25}$	bp 130–135° (0.04)	274, 258	3.89, 4.04
c	$-C_{14}H_{29}$	mp 31–33°	275, 258	3.88, 3.98
d	$-C_{16}H_{33}$	bp 170–178° (0.025) mp 44–45°	275, 258	3.87, 3.98
e	$-C_{18}H_{37}$	bp 195–200° (0.025)	275, 258	3.87, 3.98
f	$-C_{19}H_{39}$	mp 58–58.5°	275, 258	3.87, 3.97
3a	$-C_8H_{17}$	Liq[b]	234	3.92
b	$-C_{12}H_{25}$	Liq[b]	234	3.91
c	$-C_{14}H_{29}$	Liq[b]	234	3.87
d	$-C_{16}H_{33}$	Liq[b]	235	3.87
e	$-C_{18}H_{37}$	mp 25–27°	235	3.90
f	$-C_{19}H_{39}$	mp 30–31°	234	3.87
4a	$-C_8H_{17}$	mp 75–76°		
b	$-C_{12}H_{25}$	mp 91–92°	274, 254	4.03, 4.24
c	$-C_{16}H_{33}$	mp 95–96°	275, 254	4.00, 4.27
d	$-C_{18}H_{37}$	mp 98.5–100°	274, 254	4.00, 4.31
5a[c]	$-C_8H_{19}$	Liq[b]	275, 254	4.03, 3.91
b	$-C_{12}H_{25}$	mp 36–37°	275, 254	4.06, 3.98
c	$-C_{14}H_{29}$	mp 46–47°	275, 254	4.05, 3.97
d	$-C_{16}H_{33}$	mp 49.5–50°	275, 254	4.06, 3.95
e	$-C_{18}H_{37}$		275, 254	4.04, 3.97
6a	$-C_8H_{17}$	mp 44–45°	277, 255	3.97, 3.93
b	$-C_{12}H_{25}$	mp 54–55°	278, 255	3.97, 3.92
c	$-C_{14}H_{29}$	mp 60–61°	278, 256	3.98, 3.93
d	$-C_{16}H_{33}$	mp 62–64°	277, 255	4.00, 3.92
e	$-C_{18}H_{37}$	mp 67.5–68°	278, 256	3.98, 3.93
7a	$-C_8H_{17}$		284, 254	3.96, 3.94
b	$-C_{12}H_{25}$	mp 42–43.5°	284, 254	3.96, 3.93
c	$-C_{14}H_{29}$	mp 45–46°	283, 254	3.96, 3.94
d	$-C_{16}H_{33}$	mp 50–51°	284, 254	3.99, 3.93
e	$-C_{18}H_{37}$	mp 57–58°	285, 254	4.00, 3.91
8a[c]	$-C_{12}H_{25}$	mp 97–98°	283, 253	3.98, 3.94
b	$-C_{14}H_{29}$		284, 252	3.99, 3.92
c	$-C_{16}H_{33}$		284, 253	3.96, 3.92
d	$-C_{18}H_{37}$	mp 104–105°	285, 253	3.99, 3.94
9a	$-C_{12}H_{25}$	Liq[b]	236	3.81
b	$-C_{14}H_{29}$	Liq[b]	236	3.80
c	$-C_{16}H_{33}$	Liq[b]	236	3.79
d	$-C_{18}H_{37}$	Liq[b]	236	3.81

Cmpd	R	R′	Bp (mm Hg) or mp	λ_{max}, nm	Log ϵ_{max}
10a	$-C_{12}H_{25}$	$-C_4H_9$	Liq[b]		
b	$-C_{12}H_{25}$	$-C_6H_{13}$	mp 31.5–32°	298, 264	4.01, 3.91
c	$-C_{12}H_{25}$	$-C_8H_{17}$	mp 33.5–35°		
d	$-C_{12}H_{25}$	$-C_{10}H_{21}$	mp 44.5°	298, 264	4.02, 3.91
e	$-C_{12}H_{25}$	$-C_{12}H_{25}$	mp 42–43°		
f	$-C_{12}H_{25}$	$-C_{14}H_{29}$	mp 40–40.5°	297, 263	4.02, 3.92
g	$-C_{12}H_{25}$	$-C_{16}H_{33}$	mp 39–40°	298, 265	4.02, 3.92
h	$-C_{12}H_{25}$	$-C_{17}H_{35}$	mp 39.5–40°		
i	$-C_{14}H_{29}$	$-C_{14}H_{29}$	mp 45°	298, 264	3.96, 3.90
j	$-C_{14}H_{29}$	$-C_{16}H_{33}$	mp 47.5–48°	297, 263	4.00, 3.89
k	$-C_{16}H_{33}$	$-C_{14}H_{29}$	mp 44–49.5°	296, 264	4.01, 3.90
l	$-C_{18}H_{37}$	$-C_{12}H_{25}$	mp 49–50°	298, 264	4.00, 3.91
11a	$-C_{12}H_{25}$	$-C_{16}H_{33}$	mp 37–38°	241	3.90
b	$-C_{12}H_{25}$	$-C_{18}H_{35}$	mp 39.5–41°	241	3.89
c	$-C_{14}H_{29}$	$-C_{14}H_{29}$	mp 41.5–42.5°	241	3.90
d	$-C_{14}H_{29}$	$-C_{16}H_{33}$	mp 42.5–43°	241	3.89
e	$-C_{16}H_{33}$	$-C_{14}H_{29}$	mp 43.5–44.5°	241	3.89
12a	$-C_{12}H_{25}$	$-C_{12}H_{17}$	Liq[b]	298, 257	4.01, 3.89
b	$-C_{12}H_{25}$	$-C_{16}H_{33}$	Liq[b]	297, 257	4.00, 3.91
c	$-C_{12}H_{25}$	$-C_{18}H_{37}$	mp 39–40°	298, 251	4.01, 3.90
d	$-C_{18}H_{37}$	$-C_{12}H_{25}$	mp 54–55°	298, 257	3.99, 3.91
13a	$-C_{12}H_{17}$	$-C_8H_{17}$	Liq[b]	241	3.90
b	$-C_{12}H_{25}$	$-C_{16}H_{33}$	Glass[b]	242	3.90
c	$-C_{18}H_{37}$	$-C_{12}H_{25}$	Glass[b]	241	3.89

[a] Solvent: heptane unless otherwise indicated. [b] Many liquids resisted vacuum distillation and were purified by column chromatography on alumina. [c] Determined in EtOH.

The chemical shift of aromatic hydrogen in the trisubstituted thiophenes (**6–8** and **10–13**) varied in accordance with the electronic nature of the substituents.

Analysis of portions of the spectra of compounds **12** and **13** was difficult. The single methine proton appeared as a diffuse multiplet at $\approx$3.05 δ in compound **12**. The chemical shift for the methine proton in compound **13** was displaced upfield from that of **12** so that it was masked under the four methylene protons at 2.55 δ. Repetitive integration of this area and comparison of the ratios of the area of the single aromatic proton to the one at 2.55 δ consistently gave values of 5:1 for the eight compounds in that series.

The broad diffuse multiplet at 2.55 δ for **13**, like the methine proton mentioned previously, has been assigned to the methylene protons adjacent to the thiophene ring at positions 2 and 5. The peak, which was originally a triplet, deteriorated to a nondescript multiplet. Additional ambiguity of the PMR spectra for compounds **12** and **13** was observed in the methyl region of the spectrum at $\sim$0.88 δ. The methyl group that was attached to the methine group should ideally appear as a doublet. Unfortunately, the doublet overlapped the triplets of the terminal methyl groups of the alkyl chains so that the peaks appeared as a multiplet integrating for nine protons.

Experimental

Because several homologous compounds were synthesized for each of the types shown in Figure 1 (**2** → → → **13**), only the synthesis of one example of each type is described. Each compound was characterized by IR, PMR, and mass spectrometry (MS). Ultraviolet spectra were recorded for a representative number of compounds of each type. Melting points for all solids were recorded, and boiling points were recorded whenever feasible.

Compounds were purified by distillation, recrystallization, or column chromatography. Compounds for MS analysis were trapped as single peaks from the GLPC effluent stream. Gas chromatography was performed by means of a Beckman Model GC-4 or a Hewlett-Packard Model 5700A by using 12 ft × $\frac{1}{8}$-in. stainless-steel columns packed with 3% OV-101 on Gas Chrom Q, 100–120 mesh. The instruments were programmed at 4°/min from either 150–300° or 200–300° and were equipped with a flash-heated injector (250°) and a flame ionization detector at a setting of 350°. Helium flow rate was 15 ml/min; H_2 and air flow rates were 20 and 240 ml/min, respectively.

Ultraviolet spectra were determined with a Carey Model 14 spectrometer by using a 1-cm quartz cell. Infrared spectra were recorded with a Perkin-Elmer Model 337 or 710 spectrometer. Proton magnetic resonance spectra were determined in CCl_4 or $CDCl_3$ by using a Varian Model A-60A spectrometer with Me_4Si as internal standard. Samples for mass spectral analysis were trapped in glass capillaries from the GLPC and were subsequently mounted in the solids probe of the MS. The MS analyses were determined with a Varian Model M-66 cycloidal spectrometer or a Varian MAT CH5-DF spectrometer at an ionizing potential of 70 eV.

2-Acylthiophenes. All 2-acylthiophenes were synthesized according to classical procedures (*9, 20, 21*). The synthesis of 2-tridecanoylthiophene (**2**; R = $C_{12}H_{25}$) served as an example for all 2-acylthiophenes; $SnCl_4$ (0.18 mol; 47.8 g) was added dropwise with good stirring to a cooled (−5 to 0°) solution of 83.0 g (0.36 mol) tridecanolychloride and 30.0 g (0.36 mol) thiophene in 300 ml of alumina chromatographed C_6H_6. The addition was at a rate so as to keep the temperature between 0 and 5°. After addition was completed, the reaction mixture was stirred for 1 h. Slow addition of 1 N H_2SO_4 at 10° hydrolyzed the mixture, which was then extracted with $CHCl_3$. The organic layer was washed with $NaHCO_3$ and water and then dried (Na_2SO_4). The solvents were removed in vacuo, and the residual liquid was chromatographed on neutral alumina. Alternatively, the compound was distilled: bp 130–135°/0.04 mm Hg; yield 89.9 g (90%). M^+ = 280; IR (neat): 3100 cm^{-1} (arom C—H); 1665 cm^{-1} (C═O); 1420, 1355, 1240, 855 cm^{-1} (2-substituted thiophene) (*15*); 720 cm^{-1} ($(CH_2)_{11}$—). PMR (CCl_4); 0.84 δ (*t*, 3 *p*, *J* = 5.0 Hz); 1.25 δ (*s*, 20 *p*); 2.84 δ (*t*, 2 *p*, *J* = 7.3); 7.05, 7.58 δ (*m*, 1 *p*, 2 *p*).

2-Alkylthiophenes. The synthesis of 2-*n*-tridecylthiophene (**3**; R = $C_{12}H_{25}$) will serve as an example of the Wolff-Kishner reduction. A solution of 33.8 g (0.1188 mol) 2-tridecanoylthiophene and 59.5 g (1.188 mol) hydrazine hydrate in 225 ml diethylene glycol (DEG) was heated to 225–230° with good stirring. During the 2-h heating period, 65 ml of distillate was removed from the reaction. After cooling, 56 g KOH was added, and the open flask was heated with stirring to 230°. After cooling, the mixture was acidified with dilute HCl and extracted with $CHCl_3$. The $CHCl_3$ extract was dried (Na_2SO_4) and the solvent removed in vacuo. The residual yellow oil was chromatographed twice on neutral alumina (grade I) by elution with hexane. Yield 27.3 g (85%) M^+ = 226; IR (neat): 3065 cm^{-1} (arom C—H); 1440, 1370, 1240, 820 cm^{-1} (2-substituted thiophene) (*15*); 725 cm^{-1} (—$CCH_2)_{12}$—). PMR (CCl_4): 0.85 δ (*t*, 3 *p*, *J* = 5); 1.24 δ (2, 22 *p*); 2.75 δ (*t*, 2 *p*, *J* = 8); 6.78 δ (*m*, 3 *p*).

2-Carboxy-5-n-alkylthiophenes. All 2-carboxy-5-alkylthiophenes were prepared by carbonation of the lithio derivative (*9, 22*) according to the procedure of Gronowitz et al. (*11*). The 2-carboxy-5-*n*-tridecylthiophene (**4**; R = $C_{12}H_{35}$) was obtained in 84.7% yield after recrystallization from Me_2CO—C_6H_{14}; mp 91–92°; M^+ = 310; IR (KBr): broad band centered at 3000 cm^{-1} (—OH stretch); 1675 cm^{-1} (—C═O); 1295 cm^{-1} (C—O); 945 cm^{-1} (—OH deformation); 728 cm^{-1} (—$(CH_2)_{12}$—). PMR ($CDCl_3$); 0.88 δ (*t*, 3 *p*, *J* = 5); 1.28 δ (*s*, 26 *p*); 2.86 δ (5, 2 *p*, *J* = 6.7); 7.22 δ (*d*, 2 *p*, *J* = 3.5); 12.44 δ (2, 1 *p*).

2-Carbomethoxy-5-n-alkylthiophenes. (**5**; R = $C_{12}H_{25}$): Esterification of 2-carboxy-5-*n*-tridecylthiophenic acids. A solution of 60 g (0.2 mol) (**4**; R = $C_{12}H_{25}$) in 1000 ml abs. MeOH and 350 ml MeOH saturated with gaseous HCl was heated under reflux for 24 h. The solution was then reduced to half volume and cooled. The white crystals were collected after recrystallization from MeOH on a Buchner funnel; 97.1% yield, mp 36–37°; M^+ = 324; IR (KBr); 3100 cm^{-1} (arom C—H); 1700 cm^{-1} (C═O); 1280 cm^{-1} (C—O); 725 cm^{-1} (—$(CH_2)_{12}$—). PMR (CCl_4) = 0.89 δ (*t*, 3 *p*, *J* = 5); 1.25 δ (*s*, 22 *p*); 280 δ (*t*, 2 *p*, *J* = 7.5); 3.80 δ (*s*, 3 *p*); 7.10 δ (*d*, 2 *p*, *J* = 4).

2-Carbomethoxy-4-chloromethyl-5-n-alkylthiophene. The synthesis of 2-carbomethoxy-4-chloromethyl-5-*n*-tridecylthiophene (**6**; R = $C_{12}H_{25}$) exemplifies the chloromethylation reaction (*8, 14*). To a well-stirred solution of 26.6 g (0.086 mol) of **5** (R = $C_{12}H_{25}$) and 12.5 g (0.173 mol) $MeOCH_2Cl$ in 125 ml CS_2 was added 11.05 g (0.086 mol) freshly fused $ZnCl_2$/1% $AlCl_3$ (*6*), and the mixture was stirred for 35 h. The solution was poured on crushed ice, and the whole was extracted with Et_2O. After drying (Na_2SO_4), the solvent was removed in vacuo, and the solid was recystallized from MeOH, 87% yield; mp 54–55°; M^+ = 372 ($^{35}Cl/^{37}Cl$ = 1.0/0.331); IR; 3080 cm^{-1} (arom C—H); 1730 cm^{-1} (C═O); 1260 cm^{-1} (C—O); 715 cm^{-1} (—$C(CH_2)_{13}$—); 640 cm^{-1}. PMR (CCl_4): 0.88 δ (*t*, 3 *p*, *J* = 5); 1.24 δ (*s*, 22 *p*); 2.83 δ (*t*, 2 *p*, *J* = 7.0); 3.80 δ (*s*, 3 *p*); 4.44 δ (*s*, 2 *p*); 7.58 δ (*s*, 1 *p*).

2-Carbomethoxy-4-methyl-5-n-alkylthiophenes (*7*). Zn dust/HOAc reduction of **6** (R = $C_{12}H_{25}$) to **7** (R = $C_{12}H_{25}$) according to the procedure of Janda (*14*) was used to synthesize all the trisubstituted thiophenes. Zn dust (15.3 g; 0.23 mol) was added in small amounts to a well-stirred solution of 29 g (0.08 mol) **6** (R = $C_{12}H_{25}$) in 280 ml glacial acetic acid, and the solution was heated under reflux for 18 h. The hot solution was poured through glass wool into 4.5 l. ice H_2O. The precipitated compound was collected by filtration and recrystallized from MeOH at −18°; yield 25.8 g (99%); mp 43–44°, M^+ = 336; IR: 3080 cm^{-1} (arom C—H); 1710 cm^{-1} (C=O), 1260; 1295 cm^{-1} (C—O); 725 cm^{-1} (—(CH$_2$)$_{12}$—). PMR (CCl$_4$): 0.88 δ (*t*, 3 *p*, *J* = 5); 1.26 δ (*s*, 22 *p*); 2.13 δ (*s*, 3 *p*); 2.69 δ (*t*, 2 *p*, *J* = 7.0); 3.80 δ (*s*, 3 *p*); 7.39 δ (*s*, 1 *p*).

2-n-Alkyl-3-methylthiophenes. The synthesis of 3-methyl-2-*n*-tridecylthiophene (**9;** R = $C_{12}H_{25}$) as described is typical for this group. A solution of 29 g (0.086 mol) 2-carbomethoxy-3-methyl-2-*n*-tridecylthiophene and 6.25 g (0.09 mol) 85% KOH in 1500 ml MeOH and 250 ml H_2O was refluxed for 18 h. After cooling, the solution was acidified with 7 ml glacial HOAc, reduced to ¼ volume by distillation in vacuo, and cooled. The solid was collected in a Buchner funnel to yield 98% product; mp 96–98°; M^+ = 324; ir: broad band centered @ 3000 cm^{-1} (—acid—OH); 1660 cm^{-1} (C=O).

The acid (**8;** R = $C_{12}H_{25}$) was dissolved in 130 ml redistilled quinoline, and 10.4 g copper dust was then added (*7*). After refluxing for 4 h with good stirring, the solution containing the decarboxylated product **9** (R = $C_{12}H_{25}$) was poured on ice and H_2SO_4 (30 ml) mixture. The Et_2O extract was dried (Na_2SO_4), and the solvent was removed in vacuo. The crude oil was percolated through a column of Woelm acid alumina (grade I, 200 g) with hexane. The clear liquid had M^+ = 280; IR; 3070 cm^{-1} (arom C—H); 725 cm^{-1} (C—(CH$_2$)$_{12}$—); 700 cm^{-1} (2,3-disubstituted thiophene) (*13, 15*). PMR (CCl$_4$); 0.89 δ (*t*, 3 *p*, *J* = 5); 1.26 δ (*s*, 22 *p*); 2.08 δ (*s*, 3 *p*); 2.60 δ (*t*, 2 *p*, *J* = 7); 6.71 δ (*d*, 2 *p*, *J* = 5.0).

2-n-Acyl-4-methyl-5-tridecylthiophenes. This compound was synthesized as described below for conversion of **9** to **10** (R = $C_{12}H_{25}$; R′ = $C_{16}H_{33}$). $SnCl_4$ (40.05 g; 0.016 mol) was added dropwise to a well-stirred solution of 8.7 g (0.034 mol) **9** (R = $C_{12}H_{25}$) and 9.45 g (0.034 mol) of octadecyl chloride in 100 ml $CHCl_2CHCl_2$ which had been cooled to −10°. After stirring for 2.5 h, the reaction mixture was hydrolyzed with careful addition of 3 N HCl and then extracted with $CHCl_3$. The dried (Na_2SO_4) solvent was removed in vacuo, and the residue was then placed on 400 g of dry neutral alumina (grade I), and the desired fraction was eluted with $CHCl_3$:MeEtCO(4:1). Recrystallization of the compound from Me_2CO yielded 13.05 g (77%), mp 51.5–52.5°; M^+ = 546; IR: 3060 cm^{-1} (arom C—H); 1675 cm^{-1} (C=O); 1242 cm^{-1} (C—O); 725 cm^{-1} (—(CH$_2$)—$_4$). PMR (CCl$_4$): 0.88 δ (*t*, 6 *p*, *J* = 5); 1.26 δ (*s*, 52 *p*); 2.13 δ (*s*, 3 *p*); 2.69 δ (*t*, 4 *p*, *J* = 6.5); 7.27 δ (*s*, 1 *p*).

3-Methyl-5-octadecyl-2-tridecylthiophene. Compound **11;** (R = $C_{12}H_{25}$; R′ = $C_{16}H_{33}$) will serve as an example for the other tri-*n*-alkylthiophenes synthesized by Wolff-Kishner reduction. The same procedure for the reduction of **2** → **3** was used. Thus, 3.0 g (0.006 mol) **10** was reduced to yield 1.5 g (51%) of **11** after chromatography on alumina; mp 37–38°; M^+ = 532; IR: 3050 cm^{-1} (arom C—H), 835 cm^{-1} (thiophene), 725 cm^{-1} (—(CH$_2$)—$_4$). PMR (CCl$_4$): 0.88 (*t*, 6 *p*, *J* = 5); 1.26 δ (*s*, 54 *p*); 2.03 δ (*s*, 3 *p*); 2.60 δ (*m*, 4 *p*); 6.26 δ (*s*, 1 *p*).

5-(2-Methyl-octodecanoyl)-3-methyl-2-tridecylthiophene. (Compound **12;** (R = $C_{12}H_{25}$; R′ = $C_{16}H_{33}$). Sodium methylsulfinylmethide reagent (*4*) was prepared from 2.0 g 58% NaH suspension in mineral oil and 25 ml DMSO by heating with a 60° oil bath until H_2 gas evolution ceased (ca. 1 h). To the solution was added 2.0 g (0.004 mol) **10,** and the mixture was heated at 60° with good stirring for 2 h and at 80° for 1 h. To the cooled solution was then added 5 ml of MeI, and stirring was continued for 18 h. The reaction mixture was poured on ice, acidified, and extracted with Et_2O. The solvents were removed in vacuo, and the residue was chromatographed on alumina and eluted with hexane:benzene (10:1). The product was obtained as a waxy solid (1.7 g, 83% yield), mp 30–32°; M^+ = 560; IR: 3040 cm^{-1} (arom C—H); 1640 cm^{-1} (C=0); 720 cm^{-1} (—(CH$_2$)—$_4$). PMR (CCl$_4$); 0.88 δ (*m*, 9 *p*); 1.25 δ (broad *s*, 50 *p*); 2.13 δ (*s*, 3 *p*); 2.69 δ (*t*, 4 *p*); 3.05 δ (diffuse *m*, 1 *p*); 7.28 (*s*, 1 *p*).

5-(2-Methyloctadecyl)-3-methyl-2-tridecylthiophene. Compound **13;** (R = $C_{12}H_{25}$; R′ = $C_{16}H_{33}$ was synthesized by Wolff-Kishner reduction of **12** (R = $C_{12}H_{25}$; R′ = $C_{16}H_{33}$) as described for **3** and **11.** Thus, 300 mg (0.0005 mol) **12** yielded 150 mg of a colorless oil (50%) after chromatography through acid alumina with hexane as eluting solvent; M^+ = 546; IR: 3060 cm^{-1} (arom C—H); 825 cm^{-1} (thiophene); 720 cm^{-1} (—(CH$_2$)—$_4$). PMR (CCl$_4$): 0.89 δ (*m*, 9 *p*); 1.25 δ (broad *s*, 52 *p*); 2.02 δ (*s*, 3 *p*); 2.55 δ (diffuse *m*, 5 *p*); 6.28 δ (*s*, 1 *p*).

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