Macromolecules 1994, *27*, 4327–4334

Coplanarity of Precursor Molecules for Conducting Polymers: 3′-Aryl- and Heteroaryl-Substituted 2,2′:5′,2″-Terthiophenes and Their Dimers

Jouko Kankare,* Jukka Lukkari, Paavo Pasanen, Reijo Sillanpää, Hannu Laine, and Kirsi Harmaa

Department of Chemistry, University of Turku, FIN-20500 Turku, Finland

Csaba Visy

Institute of Physical Chemistry, Attila József University, H-6701 Szeged, Hungary

Received March 4, 1994●

ABSTRACT: The coplanarity of 2,2′:5′,2″-terthiophene and its six 3′-substituted derivatives, namely 3′-phenyl- (13), 3′-(4-methoxyphenyl)- (14), 3′-(4-cyanophenyl)- (15), 3′-(2-thienyl)- (16), 3′-(5-methyl-2-thienyl)- (17), and 3′-(4-pyridyl)-2,2′:5′,2″-terthiophene (18), has been studied by UV spectroscopy and compounds 13 and 17 have also been studied by X-ray diffractometry. For comparison, also an isomer of compound 13, 2′-phenyl-2,3′:5′,2″-terthiophene (20), was synthesized and its structure determined by XRD. Compounds 13–15, 17, 18, and 20 have not been previously reported. The UV spectra reveal that the aromatic and heteroaromatic substituents do not appreciably conjugate with the terthiophene backbone. Single-crystal X-ray diffraction analysis of compounds 13 and 17 shows that in the solid phase these compounds are entirely nonplanar, in contrast with parent terthiophene which is known to be strictly planar. The complete analysis of diffractograms is difficult because of the number of rotational conformers present in the solid phase. The conformational equilibrium of compound 13 is frozen at 183 K, as shown by variable temperature ^{1}H-NMR. Oxidation of terthiophene and compounds 13–16 and 18 with Cu(II) in acetonitrile gives solutions which are shown to contain dimers on the basis of visible–near-infrared (vis–NIR) spectra reported previously. Comparison with the spectra of parent terthiophene shows that in the case of cationic dimers the conjugation of the pendent aromatic side group with the main chain is negligible, but the oligothiophene chain has maintained its coplanarity.

Introduction

The thiophene oligomers produced by combining 2,5-thienylene units have become recently increasingly interesting because of their unique redox properties and their close relationship to conductive polymers. The lower oligomers, thiophene itself and bithiophene, are oxidized to radical cations which are immediately coupled to form conductive polymers. 2,2′:5′,2″-Terthiophene is oxidatively dimerized to sexithiophene which is less easily coupled to higher oligomers.[1] The properties of thiophene oligomers are intimately connected with the coplanarity and conjugation of the heteroaromatic ring system. In the straight-chain, unsubstituted oligothiophenes the only influence on the extent of the conjugation is by the chain length. By adding suitable side groups to the β-position of thiophene units one should be able to control the conjugation by either direct conjugation of the substituent with the thiophene backbone or indirect conjugation by introducing steric restrictions to the coplanarity of the chain rings or to the intermolecular order in the solid phase. This is of considerable value in designing conductive polymers for various purposes. For instance, long alkyl groups introduced in the β-position of thiophene rings are known to increase the solubility of the resulting polymers. One should think that conjugated groups in this position would introduce various favorable properties, such as a lower band-gap and better conductivity. As an example, 3-phenylthiophene is known to polymerize to a polymer having a very good conductivity and capable of undergoing facile doping–undoping processes even in the cathodic region, which is rare among other known polymers.[2] Whether this is due to the conjugation of the phenyl group with the oligothiophene backbone or just the steric enhancement of favorable properties is an interesting question which has raised some controversy. According to Kaeriyama *et al.*[2b] the substituent effects shown by poly(3-(4-methoxyphenyl)thiophene) and poly(3-(4-(trifluoromethyl)phenyl)thiophene) support the conjugation of the pendent aryl group with the main chain. On the other hand, in some recent studies Yoshino *et al.*[3] have deduced from the band-gap of poly(3-phenylthiophene) that the phenyl ring is not coplanar with the thiophene rings and thus is not in conjugation with the main chain. Direct evidence for solving this controversy by single-crystal XRD is not available due to the amorphic and indefinite nature of the polymers. However, oligomers have definite structures and their conformation is more easily evaluated from the spectral properties and XRD. With the proper choice of oligomer, the results can be extrapolated to the polymeric structures. In the present paper we report on the synthesis of a number of 3′-aryl- and heteroaryl-substituted terthiophenes and their properties. In these compounds and their dimers obtained by oxidative coupling the steric environment of the pendent ring substituent corresponds fairly well to the environment of the aryl group in the substituted polythiophene except for the long-distance intramolecular aryl–aryl interaction.

Experimental Section

General Data. NMR spectra were recorded on Bruker AW-80 and JEOL JNM-GX 400 spectrometers. IR spectra were recorded on a Mattson GALAXY 6030 FTIR spectrometer Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 2 spectrometer. The elemental analyses of the new terthiophene derivatives were made on a Perkin-Elmer 2400 elemental analyzer. 2,2′:5′,2″-Terthiophene was synthesized as reported in the literature.[4b] 2-Acetylthiophene, 2-thiophenecarboxaldehyde, 4-pyridinecarboxaldehyde, and Lawesson's reagent

---

* To whom correspondence should be addressed.

● Abstract published in *Advance ACS Abstracts,* June 15, 1994.

0024-9297/94/2227-4327$04.50/0 © 1994 American Chemical Society

were purchased from Aldrich Chemical Co. and used without further purification. 3-Ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bromide was purchased from Fluka AG.

Synthesis of Chalcones. Chalcones were mostly prepared by the standard procedure[5] from 2-acetylthiophene and aromatic or heteroaromatic aldehyde in alkaline solution. An exception was 3-(4-pyridyl)-1-(2-thienyl)-2-propen-1-one (6), the synthesis of which will be described in detail.

3-Phenyl-1-(2-thienyl)-2-propen-1-one (1): from benzaldehyde, yield 72%, mp 82.7–83.4 °C from ethanol (lit.[6] 83.6–84 °C).

3-(4-Methoxyphenyl)-1-(2-thienyl)-2-propen-1-one (2): from anisaldehyde, yield 76%, mp 82 °C from methanol (lit.[7] 83 °C).

3-(4-Cyanophenyl)-1-(2-thienyl)-2-propen-1-one (3): from 4-cyanobenzaldehyde, yield 75%, mp 188 °C from methanol.

1,3-Bis(2-thienyl)-2-propen-1-one (4): from 2-thiophenecarboxaldehyde, yield 46%, mp 97.8–98.7 °C from ethanol (lit.[6] 99.2–99.8 °C).

1-(2-Thienyl)-3-(5-methyl-2-thienyl)-2-propen-1-one (5): from 5-methyl-2-thiophenecarboxaldehyde, yield 78%, mp 95.4–96.0 °C from ethanol (lit.[8] 100 °C).

3-(4-Pyridyl)-1-(2-thienyl)-2-propen-1-one (6). The solution of 21.4 g (0.2 mol) of 4-pyridinecarboxaldehyde, 25.2 g (0.2 mol) of 2-acetylthiophene, 5.0 g (32 mmol) of 2,2′-bipyridine, and 8.0 g (32 mmol) of cobalt(II) acetate tetrahydrate in 200 mL of dimethylformamide was allowed to stand at room temperature for 8 days and kept at 50 °C overnight. The solution was poured with stirring into 2 L of water, was allowed to stand for 4 h, and was filtered. Recrystallization from ethanol gave 20.3 g (47%) of compound **6**, mp 153.1–153.6 °C. IR (cm^{-1}) in KBr: 1651, 1600, 1414, 1223, 991, 818, 764.

Synthesis of 1,4-Butanediones. The Stetter reaction[9] of an aldehyde and chalcone catalyzed by 3-ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bromide was used to prepare 1,4-butanediones. The conditions of syntheses were essentially similar, and the synthesis of compound 7 is shown in greater detail.

2-Phenyl-1,4-bis(2-thienyl)-1,4-butanedione (7). Compound 1 (10.65 g, 0.1 mol), 5.6 g (0.1 mol) of 2-thiophenecarboxaldehyde, 0.65 g (2.5 mmol) of 3-ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bromide, and 1.5 g (15 mmol) of triethylamine were refluxed in 25 mL of 1-propanol for 18 h. The solid material which precipitated on cooling was filtered off and recrystallized from 1-propanol to give 11.2 g (69%) of compound 7, mp 148.8–149.5 °C (lit.[10] 145 °C). IR (cm^{-1}) in KBr: 1659, 1416, 1236, 731.

2-(4-Methoxyphenyl)-1,4-bis(2-thienyl)-1,4-butanedione (8): from compound 2 and 2-thiophenecarboxaldehyde in boiling 1-butanol for 12 h, yield 40%, mp 169 °C.

2-(4-Cyanophenyl)-1,4-bis(2-thienyl)-1,4-butanedione (9): from compound 3 and 2-thiophenecarboxaldehyde in boiling 1-butanol for 24 h, yield 60%, mp 189 °C from dichloromethane.

1,2,4-Tris(2-thienyl)-1,4-butanedione (10): from compound 4 and 2-thiophenecarboxaldehyde, in boiling 1-propanol for 17 h, yield 61%, mp 119.4–119.8 °C from ethanol (lit.[10] 117 °C).

1,4-Bis(2-thienyl)-2-(5-methyl-2-thienyl)-1,4-butanedione (11): from compound 5 and 2-thiophenecarboxaldehyde, in boiling 1-propanol for 17 h, yield 39%, mp 127.4–128.7 °C.

1-(4-Pyridyl)-1,4-bis(2-thienyl)-1,4-butanedione (12): from compound 6 and 2-thiophenecarboxaldehyde in boiling 1-propanol for 22 h, yield 26%, mp 161.4–162.2 °C.

1-Phenyl-2,4-bis(2-thienyl)-1,4-butanedione (19): From compound 4 and benzaldehyde in boiling 1-propanol for 18 h, yield 48%, mp 108.0–108.5 °C.

Synthesis of Terthiophenes. 3′-Phenyl-2,2′:5′,2″-terthiophene (13). Compound 7 (3.26 g, 5 mmol) and 2.42 g (3 mmol) of Lawesson's reagent (2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide) were dissolved in 20 mL of toluene, and the solution was refluxed for 45 min. After cooling, the solution was washed with 100 mL of 5% NaOH and three times with 50 mL of water. The toluene layer was dried with $MgSO_4$ and evaporated *in vacuo*. The residue was recrystallized from methanol to give 2.28 g (69%) of 3′-phenyl-2,2′:5′,2″-terthiophene, mp 85.8–86.3 °C IR (cm^{-1}) in KBr: 1489, 827, 765, 698. UV (5 × 10^{-5} M in MeCN, λ_{max} nm (ϵ, M^{-1} cm^{-1})): 258 (1.49 × 10^4), 346 (1.65 × 10^4). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.929 (dd, 1H, J = 5.13, 3.66 Hz), 6.985 (dd, 1H, J = 3.66, 0.97), 7.041 (dd, 1H, J = 5.13, 3.66), 7.146 (s, 1H), 7.178 (dd, 1H, J = 5.13, 0.97), 7.210 (dd, 1H, J = 3.66, 0.97), 7.239 (dd, 1H, J = 5.13, 0.97), 7.35–7.4 (m, 5H, Ph). Anal. Calcd for $C_{18}H_{12}S_3$: C, 66.63; H, 3.73; S, 29.64. Found: C, 66.29; H, 3.69; S, 29.76.

3′-(4-Methoxyphenyl)-2,2′:5′,2″-terthiophene (14). Compound 8 (0.53 g, 1.5 mmol) and 0.35 g (0.9 mmol) of Lawesson's reagent were dissolved in 20 mL of dry toluene, and the solution was refluxed under nitrogen atmosphere for 1 h. After cooling, the reaction mixture was poured into 20 mL of cold 10% solution of NaOH with stirring. The layers were separated, and the toluene layer was extracted once more with the same volume of NaOH solution and washed three times with distilled water. The solution was dried, toluene was evaporated *in vacuo*, and the oily residue was recrystallized from methanol, yield 0.28 g (53%), mp 74 °C. Flash chromatography on silica with chloroform and subsequent recrystallization from methanol gave the product with the melting point of 77 °C. IR (cm^{-1}) in KBr: 1609, 1518, 1497 (vs), 1288, 1246 (vs), 1177, 831, 702. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 3H), 6.90 (m, 2H, Ph), 6.930 (dd, 1H, J = 5.19, 3.66 Hz), 6.999 (dd, 1H, J = 3.66, 1.22), 7.030 (dd, 1H, 5.19, 3.66), 7.113 (s, 1H), 7.169 (dd, 1H, J = 5.19, 1.22), 7.195 (dd, 1H, J = 3.66, 1.22), 7.227 (dd, 1H, J = 5.19, 1.22), 7.30 (m, 2H, Ph). UV (5 × 10^{-5} M in MeCN, λ_{max} nm (ϵ, M^{-1} cm^{-1})): 284 (1.58 × 10^4), 350 (1.63 × 10^4). Anal. Calcd for $C_{19}H_{14}OS_3$: C, 64.37; H, 3.98; S, 27.13. Found: C, 64.05; H, 3.92; S, 27.03.

3′-(4-Cyanophenyl)-2,2′:5′,2″-terthiophene (15). Compound 9 (2.11 g, 6 mmol) and 1.62 g (4 mmol) of Lawesson's reagent were dissolved in dry toluene, and the solution was refluxed for 4 h under a nitrogen atmosphere. The solution was extracted twice with 10% NaOH solution and twice with water. After drying, toluene was evaporated *in vacuo* and the residue was recrystallized from chloroform to give 1.42 g (68%) of compound 15. Flash chromatography on silica with chloroform–dichloromethane (1:1 v/v) gave pure product with the melting point of 140.0 °C. IR (cm^{-1}) in KBr: 2224 (vs), 1605 (vs), 1495, 1416, 1181, 827 (vs), 691 (vs), 565. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.93 (m, 2H), 7.01 (dd, 1H, J = 4.88, 3.66 Hz), 7.100 (s, 1H), 7.177 (dd, 1H, J = 3.66, 1.22), 7.20–7.24 (m, 2H, J = 1.22), 7.45 (m, 2H, Ph), 7.59 (m, 2H, Ph). UV (5 × 10^{-5} M in MeCN, λ_{max} nm (ϵ, M^{-1} cm^{-1})): 283 (1.88 × 10^4), 340 (1.52 × 10^4). Anal. Calcd for $C_{19}H_{11}NS_3$: C, 65.30; H, 3.17; N, 4.01; S, 27.52. Found: C, 64.64; H, 3.15; N, 4.23; S, 27.02.

5′-(2-Thienyl)-2,2′:3′,2″-terthiophene (16). The solution of 8.30 g (0.025 mol) of 1,2,4-tris(2-thienyl)-1,4-butanedione and 6.05 g (0.015 mol) of Lawesson's reagent in 50 mL of toluene was refluxed for 30 min. The solution was washed twice with an 8% solution of NaOH in water and three times with water. After drying and evaporation *in vacuo*, the oily residue was crystallized twice from methanol, once from ethanol, and finally once from methanol, giving 1.88 g (23%) of compound **16**, mp 56.6–57.3 °C (lit.[10] 59–60 °C). IR (cm^{-1}) in KBr: 1501, 1425, 1412, 1229, 1045, 845, 822, 698 (vs). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.017 (dd, 1H, J = 5.13, 3.41 Hz), 7.021 (dd, 1H, J = 5.13, 3.41), 7.042 (dd, 1H, J = 5.13, 3.41), 7.083 (dd, 1H, J = 3.41, 1.22), 7.135 (dd, 1H, J = 3.41, 1.22), 7.213 (dd, 1H, J = 3.41, 1.22), 7.222 (s, 1H), 7.246 (dd, 1H, J = 3.41, 1.22), 7.287 (dd, 1H, J = 3.41, 1.22), 7.304 (dd, 1H, J = 3.41, 1.22). UV (5 × 10^{-5} M in MeCN, λ_{max} nm (ϵ, M^{-1} cm^{-1})): 290 (1.87 × 10^4), 345 (1.44 × 10^4).

5″-Methyl-5′-(2-thienyl)-2,2′:3′,2″-terthiophene (17). The solution of 6.80 g (0.02 mol) of 1,4-bis(2-thienyl)-2-(5-methyl-2-thienyl)-1,4-butanedione and 4.76 g (0.012 mol) of Lawesson's reagent in 40 mL of toluene was refluxed for 30 min. The toluene solution was washed with 100 mL of 10% NaOH and three times with 40 mL of water, dried, and evaporated *in vacuo*. The residue was crystallized from methanol to give 2.86 g (42%) of compound 17, mp 72.6–73.4 °C. Recrystallization from methanol–ethanol (5:3) raised the melting point to 73.1–74.0 °C. IR (cm^{-1}) in KBr: 1634, 1508, 797, 696 (vs). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.468 (d, 3H, J = 0.97 Hz), 6.655 (m, 1H, J = 3.42, 0.97), 6.866 (d, 1H, J = 3.42), 7.015 (dd, 1H, J = 3.66, 1.22), 7.030 (dd, 1H, J = 5.13, 3.66), 7.145 (dd, 1H, J = 3.66, 1.22), 7.185 (s, 1H), 7.189 (dd, 1H, J = 3.66, 1.22), 7.240 (dd, 1H, J = 3.66, 1.22), 7.303 (dd, 1H, J = 5.13, 1.22). UV (5 × 10^{-5} M in MeCN, λ_{max} nm (ϵ, M^{-1} cm^{-1})): 296 (1.93 × 10^4), 345 (1.22 × 10^4). Anal. Calcd for $C_{17}H_{12}S_4$: C, 59.26; H, 3.51; S, 37.23. Found: C, 59.03; H, 3.54; S, 37.20.

3′-(4-Pyridyl)-2,2′:5′,2″-terthiophene (18). The solution of 2.8 g (8.6 mmol) of 1-(4-pyridyl)-1,4-bis(2-thienyl)-1,4-butanedione and 2.08 g (5.1 mmol) of Lawesson's reagent in 20 mL of toluene was refluxed for 30 min. The toluene solution was washed

Table 1. Crystallographic Data for Compounds 13, 20, and 17

compd	13	20	17
empirical formula	$C_{18}H_{12}S_3$	$C_{18}H_{12}S_3$	$C_{17}H_{12}S_4$
fw	324.49	324.49	344.54
cryst syst	monoclinic	monoclinic	monoclinic
lattice params			
a (Å)	29.254(4)	5.807(1)	9.933(2)
b (Å)	5.977(4)	19.111(6)	13.808(2)
c (Å)	18.230(3)	14.292(3)	11.618(2)
α (deg)	90.0	90.0	90.0
β (deg)	103.21(1)	99.68(2)	93.30(2)
γ (deg)	90.0	90.0	90.0
V (Å^3)	3103(3)	1563.6(7)	1590.9(4)
space group (No.)	$C2/c$ (15)	$P2_1/n$ (14)	$P2_1/c$ (14)
Z	8	4	4
D_{calc} (g/cm^3)	1.389	1.378	1.438
μ(Mo Kα) (cm^{-1})	4.48	4.44	5.63
temp (°C)	22	22	22
$2\theta_{max}$ (deg)	50.0	50.0	50.0
no. of observns. ($I > n\sigma(I)$)	1481 (n = 2)	1389 (n = 3)	1641 (n = 2)
no. of variables	226	226	237
residuals: R,R_w	0.073, 0.073	0.049, 0.053	0.046, 0.047
goodness of fit indicator	2.11	1.67	1.46
max shift in final cycle	0.96	0.35	0.38
largest peak in final diffmap (e/Å^3)	0.35	0.28	0.24
abs correction	empirical	empirical	empirical

twice with 20 mL of 10% NaOH and three times with water, dried with $MgSO_4$, and evaporated *in vacuo*. The residue was recrystallized twice from methanol to give 0.934 g (33%) of compound **18**, mp 110.6–110.8 °C. IR (cm^{-1}) in KBr: 1597 (vs), 1408, 818 (vs), 696 (vs). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.968–6.992 (m, 2H), 7.053 (dd, 1H, J = 4.88, 3.42 Hz), 7.169 (s, 1H), 7.221 (dd, 1H, J = 3.66, 1.22), 7.26–7.28 (m, 2H), 7.298–7.314 (m, 2H, Pyr), 8.574–8.590 (m, 2H, Pyr). UV (10^{-4} M in MeCN, λ_{max} nm (ϵ, M^{-1} cm^{-1})): 259 (1.82 × 10^4), 344 (1.54 × 10^4). Anal. Calcd for $C_{17}H_{11}NS_3$: C, 62.74; H, 3.41; N, 4.30; S, 29.55. Found: C, 62.25; H, 3.43; N, 4.48; S, 29.32.

2′-Phenyl-2,3′:5′,2″-terthiophene (20). The solution of 3.26 g (10 mmol) of 1-phenyl-2,4-bis(2-thienyl)-1,4-butanedione and 2.42 g (6 mmol) of Lawesson's reagent in 25 mL of toluene was refluxed for 30 min. The toluene solution was washed twice with 50 mL of 10% NaOH and three times with 30 mL of water, dried, and evaporated *in vacuo*. The residue was recrystallized from methanol to give 2.0 g (62%) of 2′-phenyl-2,3′:5′,2″-terthiophene. Two recrystallizations from methanol gave a pure product, mp 82.9–83.1 °C. IR (cm^{-1}) in KBr: 1493, 1424, 1175, 841, 816, 756, 702. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.926–6.950 (m, 2H), 7.040 (dd, 1H, J = 5.13, 3.66 Hz), 7.193 (dd, 1H, J = 4.40, 1.96), 7.210 (dd, 1H, J = 3.66, 1.22), 7.245 (dd, 1H, J = 3.66, 1.22), 7.276 (s, 1H), 7.33–7.36 (m, 3H, Ph), 7.41–7.44 (m, 2H, Ph). UV (10^{-4} M in MeCN, λ_{max} nm (ϵ, M^{-1} cm^{-1})): 288 (1.88 × 10^4), 331 (1.36 × 10^4). Anal. Calcd for $C_{18}H_{12}S_3$: C, 66.63; H, 3.73; S, 29.64. Found: C, 66.32; H, 3.63; S, 29.41.

Oxidation of Terthiophenes. The oxidation experiments were done with 3 × 10^{-5} M solutions of substituted terthiophenes in acetonitrile. The oxidant was a 2 × 10^{-3} M solution of copper(II) triflate in acetonitrile. The oxidant was dispensed from an "Agla" micrometer syringe in small aliquots, and a couple of minutes after each addition the spectrum was recorded on a spectrophotometer.

Crystallographic Analyses. Diffraction measurements were made on a Rigaku AFC5S four-circle diffractometer using monochromatized Mo Kα radiation (λ = 0.710 96 Å). Crystal data, data collection parameters, and results of the analyses are listed Table 1. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Full-matrix least-squares refinements minimized the function

$$\sum_{hkl} w(|F_o - F_c|)^2$$

where $w = 1/\sigma(F_0)^2$. The structures were solved by direct methods using MITHRIL.

Compound 13. After considerable time was used for crystallizing compound **13** from various solvents in order to obtain a crystal of necessary dimensions, a slightly yellow crystal plate with dimensions 0.05 × 0.14 × 0.20 mm recrystallized from methanol was finally chosen. The unit cell parameters were determined by least-squares refinements of 23 carefully centered reflections (21° < 2θ < 28°). The data obtained were corrected for Lorentz and polarization effects and for dispersion. A total of 3090 reflections were collected by the ω-2θ scan mode ($2\theta_{max}$ = 50°), giving 3021 unique reflections (R_{int} = 0.023). Using the criterion $I > 2\sigma(I)$ 1481 reflections were considered to be significant data. The three check reflections monitored after every 150 reflections showed only statistical fluctuations during the course of the data collection.

The disordered structure of the molecules in the cell caused considerable difficulties in the data refinement. The thiophene rings have rotational conformers which during the refinement procedure seemed to demand the presence of two geometrical isomers. In the early stage of refinement the two positions of disordered S and C atoms were replaced by virtual Ti atoms which have the same electron density as the sum of S and C. In the final calculations the fixed population parameters obtained from the population values of the Ti atoms were given to the S and C atoms. Refinement of all non-hydrogen atoms, except the disordered S and C, with anisotropic and hydrogen atoms with fixed isotropic temperature parameters (1.2 times the B_{eq} of the carrying atom) reduced the R value to 0.073. Neutral atomic scattering factors were those included in the program.

Compound 20. Due to the ambiguous diffractometric results of compound **13**, its geometric isomer, compound **20**, was synthesized and its structure determined by X-ray diffractometry. Again, considerable difficulties were met in growing crystals with suitable dimensions, but finally, a colorless needlelike crystal with dimensions 0.10 × 0.15 × 0.25 mm was obtained from methanol. The unit cell parameters were obtained from 16 carefully centered reflections (20° < 2θ < 26°). A total of 3145 reflections were collected, giving 2903 unique reflections (R_{int} = 0.036) of which 1389 were selected according to the criterion $I > 3\sigma(I)$. The refinement was done in the same way as with compound **13**. In this case the rotational conformers of the terminal rings had to be taken into account by using the similar replacement of the disordered S and C atoms by virtual Ti atoms.

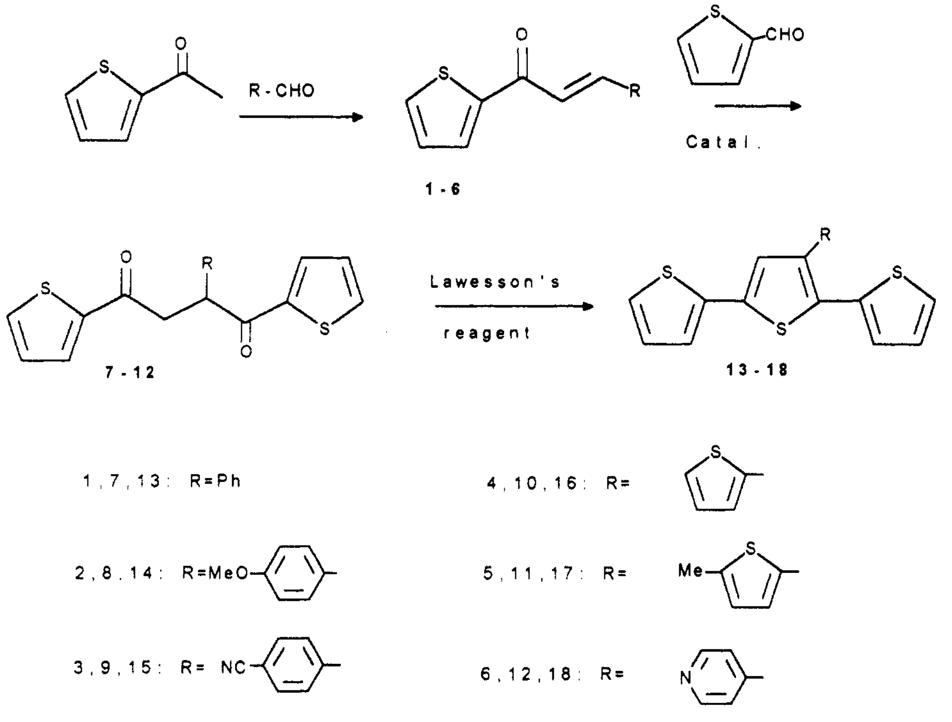
Compound 17. A colorless prismatic crystal with dimensions 0.12 × 0.15 × 0.25 mm was obtained by recrystallization from methanol. The unit cell parameters were obtained from 25 carefully centered reflections (24° < 2θ < 34°). A total of 3116 reflections were collected, giving 2939 unique reflections, of which 1641 were selected according to the criterion $I > 2\sigma(I)$. A correction for secondary extinction was also applied. The refinement was done analogously to the previous case.

Results and Discussion

Synthesis. A number of terthiophene derivatives have been synthesized previously, mainly by Wynberg and his group.[4] The terthiophene derivatives having aryl groups in the middle ring have been practically unknown. The only compound described previously in the literature[10] and synthesized also in this work is 5′-(2-thienyl)-2,2′:3′,2″-terthiophene (**16**). We describe in this work the synthesis and properties of six new 3′-aryl- or heteroaryl-substituted terthiophenes. The three-step synthesis of these compounds is shown in Scheme 1.

The first step, the synthesis of chalcone by Claisen condensation of an aromatic aldehyde and methyl ketone, is generally a rather straightforward and high-yield method.[5] One known exception to this is pyridinecarboxaldehydes. In this case the initially formed chalcone undergoes a very fast Michael addition reaction with the excess of methyl ketone. This is such a predominant reaction that, e.g., in the reaction between acetophenone and 4-pyridinecarboxaldehyde only 22% yield of chalcone was obtained although a 100% excess of aldehyde was

Scheme 1



used.[11] In our hands the synthesis under the conditions described in ref 11 but with 2-acetylthiophene instead of acetophenone yielded only intractable tar. An alternative method for the Claisen condensation has been described by Irie and Watanabe.[12] In this method the alkali metal hydroxide used as a catalyst is replaced by the complex of cobalt(II) with 2,2′-bipyridine. High yields were obtained for the reactions between pyridinecarboxaldehydes and acetophenone with a lower tendency for side reactions. In our case this catalyst gave a 47% yield of 3-(4-pyridyl)-1-(2-thienyl)-2-propen-1-one (**6**) but only after a 1-week reaction time.

The second step, the reaction between 2-thiophenecarboxaldehyde and the chalcone produced in the Claisen condensation, is known as the Stetter reaction.[9] In our hands this reaction did not proceed between 2-thiophenecarboxaldehyde and 3-phenyl-1-(2-thienyl)-2-propen-1-one (**1**) as reported by Stetter and Rajh[13] when catalyzed by sodium cyanide. No reaction occurred, as monitored by HPLC, although the reagents and solvent (DMF) were dried and a nitrogen atmosphere was used. However, when 3-ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bromide was used as the catalyst in boiling 1-propanol or 1-butanol, the reaction proceeded well and gave reasonable yields in most cases. The last step, the ring closure of the middle thiophene ring of terthiophene, was done by using Lawesson's reagent.[4b] This reaction was successful in every occasion attempted. An improved method for purification of the product was found. The organophosphates formed as side products in the reaction could be removed by pouring the reaction mixture into dilute sodium hydroxide solution and extracting the terthiophene derivative from the mixture. The final purification was done by crystallizing from methanol.

Structure. The terthiophene derivatives were characterized by ultraviolet spectroscopy. Figure 1 shows the UV spectra recorded in acetonitrile. What is most noteworthy in these spectra is that (a) the position of the long-wavelength band for every derivative is nearly the same, 350 nm, and (b) the molar absorptivity at 350 nm of the parent compound, terthiophene, is 30–50% higher than with the 3′-aryl derivatives. The fact that the position of the absorption maximum does not appreciably depend on the substituent shows that the ring substituent does not conjugate with the rest of the π-system, implying nonplanarity of the compounds. The decrease of the molar absorptivity can be explained by the conformational equilibrium of the coupled thiophene rings. The parent terthiophene molecule is mainly coplanar because the steric interaction between the ring hydrogens does not exist and apparently the interaction between the ring hydrogen and the sulfur atom of the adjacent ring is very small or even attractive. This is confirmed by the X-ray diffraction of the terthiophene crystal,[14] which shows nearly complete coplanarity. A more recent study by Barbarella *et al.* shows that even tetrathiophene having methyl substituents in every ring maintains coplanarity in the solid phase.[15] Although measured in the solid phase, this coplanarity indicates an energy minimum at the coplanar conformation, and even in solution terthiophene may to a large extent preserve its coplanarity. This equilibrium is disturbed by adding substituents to the middle ring. The steric interaction between the substituent and the adjacent ring may introduce the second minimum to the torsional energy profile, and the compound may exist in solution as two conformers in comparable concentrations. The effective concentration of the coplanar conformer is then lower, and correspondingly, the absorbance at 350 nm is decreased.

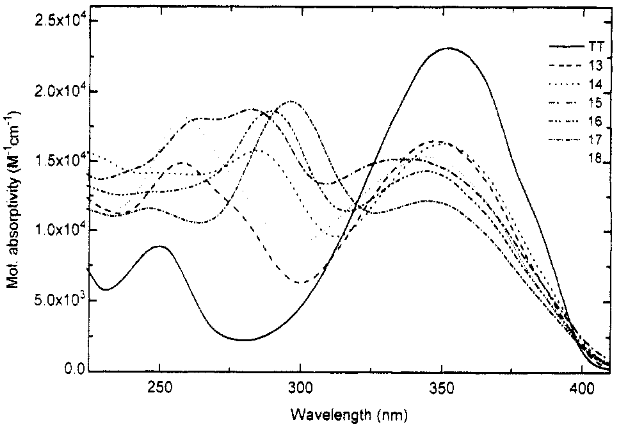


Figure 1. Electronic absorption spectra of terthiophene (TT) and its 3′-substituted derivatives.

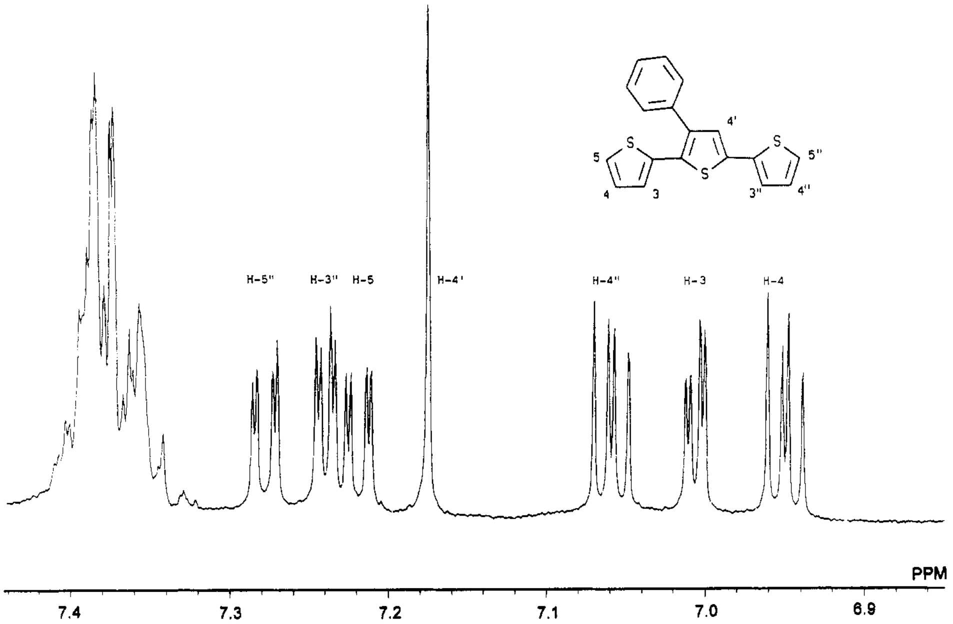


Figure 2. 400-MHz ^{1}H-NMR spectrum of 3′-phenyl-2,2′:5′,2″-terthiophene (**13**) in dichloromethane-d_2 at room temperature.

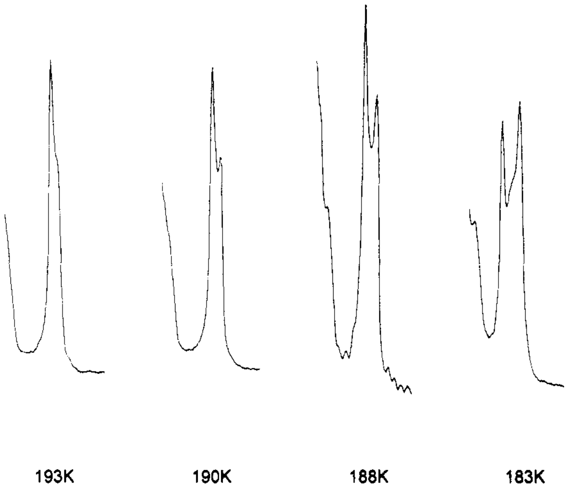


Figure 3. Splitting of the $H_{4'}$ singlet in the 400-MHz ^{1}H-NMR spectrum of 3′-phenyl-2,2′:5′,2″-terthiophene (**13**) at low temperatures in dichloromethane-d_2.

In principle the existence of a conformational equilibrium can be confirmed by NMR spectroscopic measurements. For this purpose the 400-MHz proton NMR spectra of 3′-phenylterthiophene in CD_2Cl_2 were recorded at variable temperatures. The spectrum taken at room temperature (Figure 2) exhibits two well-resolved AMX spin systems, the analyses of which were confirmed by a modified LAOCOON 3 iterative program.[16] The chemical shifts of the protons H_{3-5} consistently indicate a marked shielding effect in comparison with the counterparts $H_{3''-5''}$. The phenomenon must be of conformational origin, because such long-range shift effects by even polar but sterically small substituents are negligible in related systems.[17] Accordingly, the former protons seem to be located out of plane while the latter ones fall around the periphery of the anisotropic phenyl ring, on an average. This interpretation implies a rather irregular steric arrangement, where the phenyl ring tends to escape total coplanarity and conjugation with the thiophene rings.

The multiconformational equilibrium could be partially frozen out at about 183 K, where the signal of the proton $H_{4'}$ splits with a chemical shift separation of 5 Hz (Figure 3). From this fact one can estimate the rotational barrier height (Gibbs free energy of activation) to be ca. 40.3 ± 0.5 kJ/mol.[18] The result is well in line with the reported values for the rotation of bonds connecting sp^2 centers[19] and allows for a ready equilibration between the minima at room termperature in solution. The value probably represents the rotation around the $C_{3'}$–Ph bond, as it is the sterically most constrained among the molecular movements in this structure.

The ultimate answer to the conformation in the solid state is given by the structure determination by X-ray diffraction. Although admittedly the crystal forces have some influence, with a certain reservation some conclusions can be drawn about the possible conformation in solution on the basis of the solid state conformation. Two of the compounds, the 3′-phenyl (**13**) and 3′-(5-methyl-2-thienyl) (**17**), derivatives could be obtained as crystals of suitable dimensions for the X-ray diffraction. Considerable difficulties were met in refining the diffraction results. These compounds seem to crystallize as mixtures of conformers. Especially hard was the interpretation of data for compound **13**. At first the only explanation seemed to be the presence of two positional isomers, which is highly improbable on the synthetic basis. In order to cancel this possibility, the isomer of compound **13**, 2′-phenyl-2,3′:5′,2″-terthiophene (**20**), was synthesized. Compounds **13** and **20** are remarkably similar, e.g. their melting points differ only by approximately 1 deg. However, as expected, their UV spectra are different due to the different conjugational backbones. Also, their IR spectra differ sufficiently to confirm that if the compound whose structure we attempted to solve by X-ray diffraction is a mixed crystal, the amount of isomer **20** is negligible. Substituted thiophenes undergo a photochemically induced valence bond isomerization whereby the interchange of carbon atoms 2 and 3 together with their substituents occurs.[20] This rearrangement would explain the results of the X-ray diffraction if the isomerization occurs also by the influence of X-ray irradiation, but because the three checking reflections recorded after every 150 reflections stayed constant within statistical fluctuations, this is rather improbable. It should be noted that the conformational disorder in the crystals of thiophene derivatives has been observed previously. Similar difficulties in the exact structure determination have been met by Hieber *et al.* with precursors for some low-gap polymers.[21] For this reason accurate bond lengths could not be obtained, but the general structure shown in Figure 4 is considered to be reliable. It can be seen that the molecule is entirely puckered, with no ring being coplanar with any other ring.

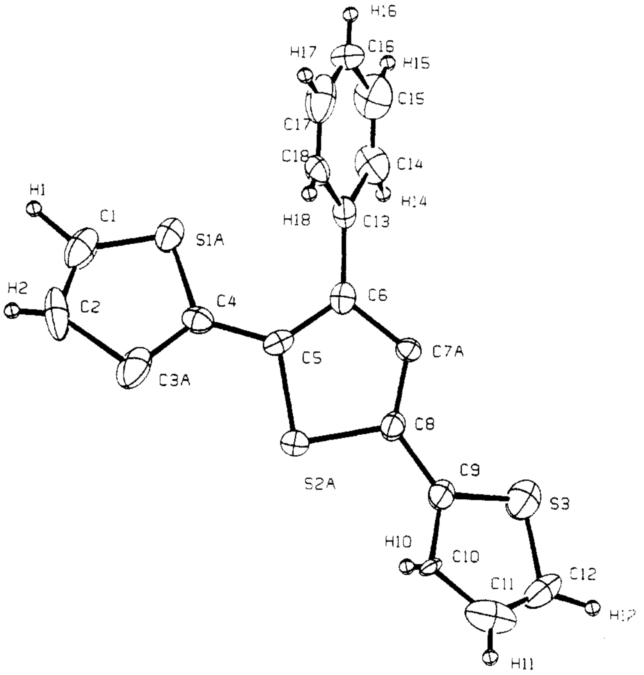


Figure 4. Perspective view of the 3′-phenyl-2,2′:5′,2″-terthiophene (**13**) with 30% thermal contours for all non-hydrogen atoms.

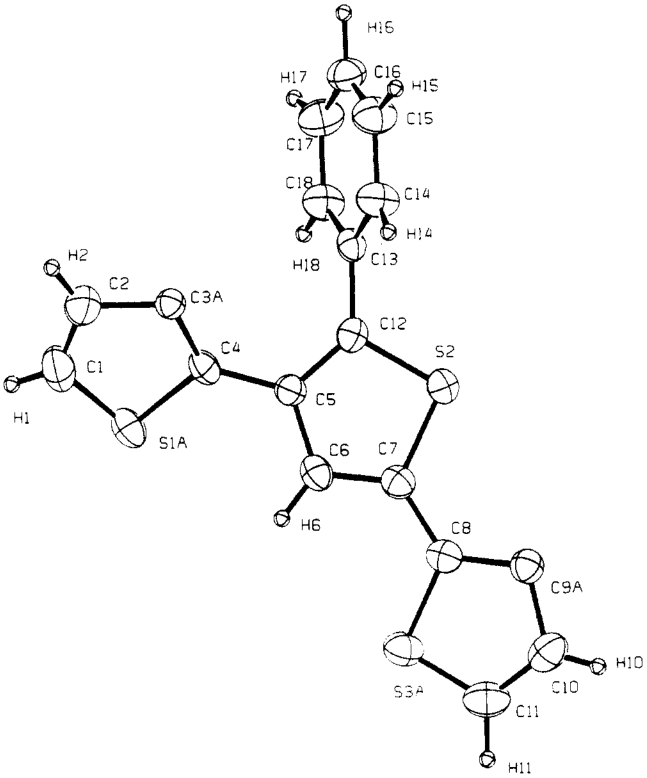


Figure 5. Perspective view of 2′-phenyl-2,3′:5′,2″-terthiophene (**20**) with 30% thermal contours for all non-hydrogen atoms.

For the sake of comparison, the structure of isomer **20** was solved by X-ray diffraction. Also in this case the presence of different rotamers in the solid phase prevented the accurate structure determination, but the general shape and nonplanarity of the molecule can be solved (Figure 5).

Being a five-membered ring, the thienyl group is sterically less demanding than the phenyl group, and to study this effect two branched quaterthiophenes were synthesized. Of the two 3′-(2-thienyl) derivatives, the crystal of 3′-(5-methyl-2-thienyl)terthiophene (**17**) (or in the IUPAC nomenclature 5″-methyl-5′-(2-thienyl)-2,2′:3′,2″-terthiophene) was large enough to give 3116 reflections, of which 1641 were considered to be statistically significant, and the structure could be refined reasonably well. The structure of compound **17** is shown in Figure 6. However, it seems that even in this case the molecule assumes two conformations in the solid state. What is interesting in this compound is that although the conventional conjugative pathway *via* 2,2′-coupling of the thiophene rings is prevented by the near-perpendicular orientation of the rings, the ring bonded to the 3′-position is much closer to coplanarity, the torsion angle being less than 20°. The torsion angles of the connecting bonds between the rings in these three compounds are shown in Table 2.

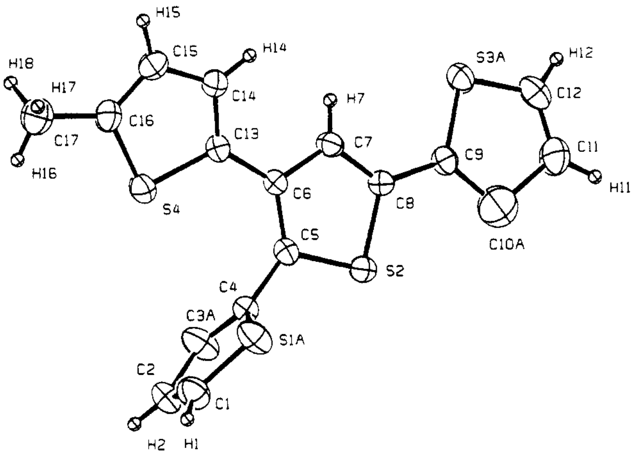


Figure 6. Perspective view of 5″-methyl-5′-(2-thienyl)-2,2′:3′,2″-terthiophene (**17**) with 30% thermal contours for all non-hydrogen atoms.

Table 2. Selected Torsion Angles of Compounds 13, 17, and 20

compd	bond[a]	angle (deg)
13	C(3A)–C(4)–C(5)–C(6)	−156(1)
	C(4)–C(5)–C(6)–C(13)	8(1)
	C(5)–C(6)–C(13)–C(14)	−116.1(7)
	C(5)–C(6)–C(13)–C(18)	63.8(9)
	C(7A)–C(8)–C(9)–C(10)	138.4(8)
17	C(3A)–C(4)–C(5)–C(6)	95(2)
	C(4)–C(5)–C(6)–C(13)	−2.0(7)
	C(5)–C(6)–C(13)–C(14)	160.9(5)
	C(7)–C(6)–C(13)–C(14)	−17.5(7)
	C(7)–C(8)–C(9)–C(10A)	177(2)
20	C(3A)–C(4)–C(5)–C(6)	135.6(8)
	C(4)–C(5)–C(12)–C(13)	−3.9(9)
	C(5)–C(12)–C(13)–C(14)	109.6(7)
	C(5)–C(12)–C(13)–C(18)	−69.8(8)
	C(6)–C(7)–C(8)–C(9A)	−160.3(8)

[a] Numbering of carbon atoms refers to Figures 4–6.

The general nonplanarity of these compounds is indeed the most important result of the structure determination by XRD. Even though the extrapolation to solution should be done with considerable caution, the result shows clearly that the minima in the torsional energy profile around the connecting bonds are very shallow and even rather weak interactions suffice to cause changes in the coplanarity. This explains the well-known phenomena of thermochromism, solvatochromism, and piezochromism in which energetically rather weak external effects cause rotation around the ring-connecting bonds with concomitant dramatic changes in the absorption spectra of poly(3-alkylthiophenes).

Oxidative Dimerization. Oxidation of terthiophene by ferric chloride in dichloromethane is known to yield sexithiophene[1] which is further oxidized to mono- and dications, the simple models of "polarons" and "bipolarons" of doped conductive polymers. Further oxidative coupling of sexithiophene to higher oligomers either with itself or

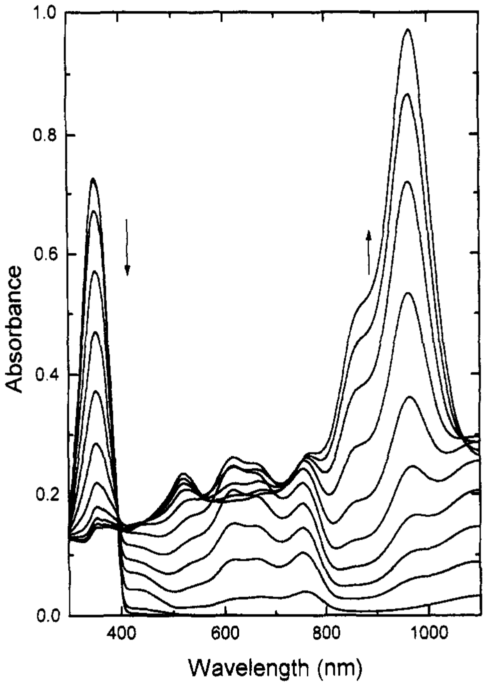


Figure 7. Electronic absorption spectra of 2,2':5',2''-terthiophene recorded during repeated additions of oxidant. The solution of terthiophene is 3 × 10^{-5} M in acetonitrile, and the oxidant is 2 × 10^{-3} M solution of copper(II) triflate in acetonitrile. Each aliquot corresponds to the removal of 0.15 e/molecule.

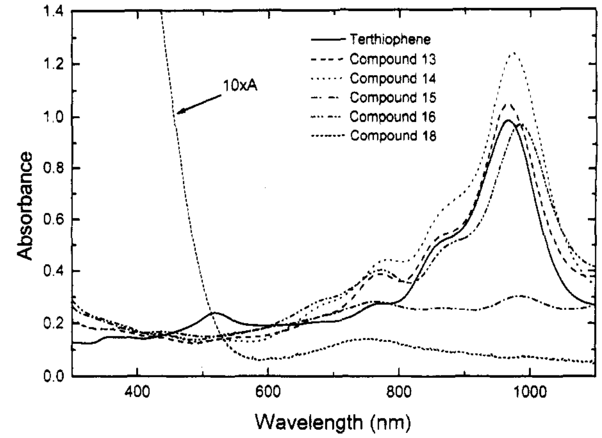


Figure 8. Electronic absorption spectra of oxidized terthiophene derivatives in acetonitrile. The concentration of terthiophenes in each solution is 3 × 10^{-5} M, and oxidation is done by addition of excess of copper(II) triflate.

Table 3. UV–Vis–NIR Absorption Maxima (nm) of Terthiophene Derivatives in Neutral and Oxidized Forms

compd	neutral form	oxidized form
13	257, 345, 425 (d)	680 (sh), 765, 865 (sh), 965, >1100
14	284, 350, 425 (d, w)	523 (w), 685 (sh), 773, 867 (sh), 971
15	264, 283, 335, 433 (d)	675 (sh), 756, 883, 991, >1100
16	290, 344, 435 (d)	540 (sh), 690 (sh), 768, 880 (sh), 985, >1100
18	259, 344	750 (vw), 870 (sh, vw), 1005 (vw)
terthiophene	351, 425 (d)	617, 655, 755, 870 (sh), 968, >1100

[a] Abbreviations: d = dimer, sh = shoulder, w = weak, vw = very weak.

with terthiophene seems to be a slow process, mainly because of the unusual stability of the dication. No systematic study on the influence of substituents on the oxidation and coupling of terthiophene derivatives has been reported. Oxidation of terthiophene can be accomplished either electrochemically or chemically. Electrochemical oxidation is complicated by the deposition of oligomeric material on the electrode, and hence in this work it was decided to use homogeneous chemical oxidation. Although ferric chloride in dichloromethane has been used previously,[1] acetonitrile was chosen as the solvent in order to allow easy comparison with the electrochemical studies, where acetonitrile is far more common as a solvent. However, ferric chloride is not a good oxidant in acetonitrile and some other oxidant had to be chosen. It has been reported that copper(II) is a good oxidant in the polymerization of bithiophene.[22] The oxidation potential of the Cu(II)–Cu(I) couple is enhanced by the preferential solvation of Cu(I) by acetonitrile. Another advantage of copper(II) compared with iron(III) is the lower absorbance in the visible region. Copper(II) triflate (trifluoromethanesulfonate) was chosen for the oxidant because the triflate anion is noncomplexing and the salt is easily dried and soluble in acetonitrile.

Figure 7 shows the absorption spectra of terthiophene in acetonitrile with repeated additions of copper(II) triflate solution. The oxidation reaction after each addition was rapid. It can be seen that at the first additions the peak at ca. 760 nm starts to increase with the simultaneous decrease in the intensity of the 350-nm peak of terthiophene. With the further additions the peak at ca. 970 nm starts to increase, becoming finally dominant. Similar experiments were done with each terthiophene derivative, and the vis-NIR spectra of oxidized compounds after the last addition of oxidant are shown in Figure 8. The location of absorption maxima have been collected in Table 3, where we can see that substitution at the β-position of the middle thiophene ring does not markedly affect the π → π* transition of the studied neutral terthiophene derivatives and their oxidation products. The spectra of the oxidized species exhibit typical poorly resolved doublets in accordance with the spectra previously reported.[1,23,24] Terthiophene not blocked at the terminal α-position has been shown to undergo rapid dimerization to the corresponding hexamer,[1] and taking into account the shift caused by solvents of different polarities, our results are in reasonable accordance with the reported λ_{max} values for oxidized sexithiophene. With all terthiophenes studied, the evolution of the spectral features after addition of oxidant reveals that the peaks between 600 and 800 nm and above 1100 nm move together and constitute the final transitions at low oxidation levels (below 1 e/monomer). On the other hand, the doublet in the range 850–1000 nm is formed only at higher oxidation levels, although it is often present as an intermediate after the addition of oxidant. Therefore, we conclude that the former transitions belong to the radical cations of the hexamers and the latter transitions to the corresponding dications. The peaks around 430 nm most probably correspond to the neutral hexamers (the absorbance maximum of neutral sexithiophene is 432 nm in dichloromethane[1]).

The exact assignment of the transitions of the oxidized species is difficult and several interpretations can be found in the literature. The doublets separated by ca. 0.2 eV have been explained by transitions between the modified molecular orbitals of the monomers[1,24] or by vibronic coupling.[24,25] An interesting possibility has been suggested by Miller *et al.* who reported three transitions in the range 400–800 nm for terminally blocked terthiophenes.[25,26] One of these was assigned to the radical cation and the other two to its associative dimer (π-dimer). However, their spectra were recorded at low temperatures (below +5 °C) and they differ from the other reported spectra, which show only two closely spaced peaks for monocationic species.[1,23,24] Our hexamer monocations also exhibit only two closely spaced transitions in the range 600–800 nm, together with transition(s) above 1100 nm, with the exception of unsubstituted terthiophene. Although we cannot identify the three transitions in the case of terthiophene, we can conclude that in the conditions employed, the substituted hexamers show no evidence of π-dimer formation. The peak observed at 523 nm for **14** in acetonitrile is of intermediary character and has been assigned to the corresponding monomer radical cations. The position of the absorption maximum goes along well with the reported value (522 nm) for an isolated terthiophene radical cation enclosed in zeolite channels[23] and the transition shows a similar doublet character typical for the reported spectra.[23,24]

It is seen that three of the compounds, the oxidation products of parent terthiophene and its 3′-phenyl and 3′-(4-methoxyphenyl) derivatives, have very similar spectra with only an insignificant shift in the 970-nm peak. This shows that the benzene ring of the substituent does not significantly conjugate with the sexithiophene ring system. This is in accordance with the UV, NMR, and X-ray results of the corresponding nonoxidized terthiophenes. One would have expected the cationic nature of the molecule to stabilize the planar conformation of the molecule and even to facilitate the extension of conjugation into the benzene ring. This phenomenon can be clearly seen, e.g., in the planar shape of the biphenyl cation.[27] An interesting result is obtained for 3′-(4-cyanophenyl)-2,2′:5′,2″-terthiophene (**15**). The position of the mono- and dication peaks is nearly the same as with the other oxidized terthiophenes, but the height of the dication peak is considerably lower at the expense of the monocation peak. One would not expect the *p*-cyanophenyl group to possess lower steric requirements than the unsubstituted phenyl group, and hence the only explanation is the substituent effect of the cyano group. The negative resonance effect of the cyano group imparts a positive partial charge on the carbon atom attached to the thiophene ring. This has an inductive effect, decreasing the stability of the dication more than the monocation even though the direct conjugative interaction is prevented by the perpendicular orientation of the phenyl ring. 3′-(4-Pyridyl)-2,2′:5′,2″-terthiophene (**18**) could be only slightly oxidized under these conditions, giving very weak absorption maxima in the near-infrared region.

Conclusions

The most important goal of this study has been to get some information on the influence of substituents on the oligothiophene backbone and consequently develop useful rules for the estimation of the properties of conductive polymers based on the polythiophene chain. It is well-known that alkyl groups exert favorable effects on polythiophenes, sometimes increasing conductivity and in the case of large alkyl groups even increasing solubility. A phenyl group directly attached to the thiophene rings is said to increase conductivity[2] compared to the parent polythiophene. This work shows unambiguously that the phenyl group attached to thiophene cannot be on the same plane with the oligothiophene ring system for steric reasons. Hence the reported improved properties of poly(3-phenylthiophene) must originate from the solid phase properties, i.e. the better orientation and self-organization of the polymer chains.[2,3]

Oxidation of terthiophenes generates dimers in a very fast reaction. The NIR spectra of the dimeric cations, which are the primary products of the oxidation reaction, show that the ring substituents have only a small effect on the conjugative system. In general, a ring substituent directly attached to the oligothiophene backbone seems to be sterically too hindered to attain a coplanar configuration, even in the case of a five-membered ring. Although for this reason the conjugative effects are small, the variation of the steric requirements by different ring systems is still producing interesting interchain effects by changing the packing properties of the chains in the solid phase. The results on the electropolymerization of 3′-substituted terthiophenes are a subject of another publication.[28]

Acknowledgment. This investigation was supported by a grant awarded by the Academy of Finland. We thank Ms. Marjatta Kuisma for some of the syntheses and Ms. Tiina Palomaa for the elemental analyses and FT-IR spectra.

Supplementary Material Available: Tables of atomic positional parameters, bond distances, bond angles, and isotropic displacement parameters for compounds **13**, **17**, and **20** (6 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Fichou, D.; Horowitz, G.; Xu, B.; Garnier, F. *Synth. Met.* **1990**, *39*, 243.

(2) (a) Sato, M.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc., Chem. Commun.* **1987**, 1725. (b) Idem. *Makromol. Chem.* **1989**, *190*, 1233.

(3) (a) Onoda, M.; Nakayama, H.; Morita, S.; Yoshino, K. *Synth. Met.* **1993**, *55*, 275. (b) Idem. *J. Appl. Phys.* **1993**, *73*, 2859.

(4) (a) Kooreman, H. J.; Wynberg, H. *Recl. Trav. Chim.* **1967**, *86*, 37. (b) Wynberg H.; Metselaar, J. *Synth. Commun.* **1984**, *14*, 1.

(5) Kohler, E. P.; Chadwell, H. M. *Organic Syntheses*; Wiley: New York, 1941; Collect. Vol. I, pp 78–80.

(6) Marvel, C. S.; Quinn, J. M.; Showell, J. S. *J. Org. Chem.* **1953**, *18*, 1730.

(7) Hanson, G. A. *Bull. Soc. Chim. Belg.* **1958**, *67*, 1646.

(8) Buu-Hoi, N. P.; Xuong, Ng D.; Sy, M. *Bull. Soc. Chim. Fr.* **1956**, 1646.

(9) (a) Stetter, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 639. (b) Stetter, H.; Kuhlmann, H. *Org. React.* **1991**, *40*, 407.

(10) Perrine, D. M.; Bush, D. M.; Kornak, E. P.; Zhang, M.; Cho, Y. H.; Kagan, J. *J. Org. Chem.* **1991**, *56*, 5095.

(11) Marvel, C. S.; Coleman, L. E.; Scott, G. P. *J. Org. Chem.* **1955**, *20*, 1785.

(12) Irie, K.; Watanabe, K.-I. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1366.

(13) Stetter, H.; Rajh, B. *Chem. Ber.* **1976**, *109*, 534.

(14) Van Bolhuis, F.; Wynberg, H.; Havinga E. E.; Meijer, E. W.; Staring E. G. J. *Synth. Met.* **1989**, *30*, 381.

(15) Barbarella, G.; Zambianchi, M.; Bongini, A.; Antolini, L. *Adv. Mater.* **1992**, *4*, 282.

(16) Laatikainen, R. *J. Magn. Reson.* **1977**, *27*, 169.

(17) Rossi, R.; Carpita, A.; Ciofalo, M. *Gazz. Chim. Ital.* **1990**, *120*, 793.

(18) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982; p 96.

(19) Jackman, L.; Cotton, F., Eds.; *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Academic Press: New York, 1975.

(20) Wynberg, H. *Acc. Chem. Res.* **1971**, *4*, 65.

(21) Hieber, G.; Hanack, M.; Wurst, K.; Strähle, J. *Chem. Ber.* **1991**, *124*, 1997.

(22) Inoue, M. B.; Velazquez, E. F.; Inoue, M. *Synth. Met.* **1988**, *24*, 223.

(23) Caspar, J. V.; Ramamurthy, V.; Corbin, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 600.

(24) Guay, J.; Kasai, P.; Diaz, A.; Wu, R.; Tour, J. M.; Dao, L. H. *Chem. Mater.* **1992**, *4*, 1097.

(25) Zinger, B.; Mann, K. R.; Hill, M. G.; Miller, L. L. *Chem. Mater.* **1992**, *4*, 1113.

(26) (a) Hill, M. G.; Mann, K. R.; Miller, L. L.; Penneau, J.-F. *J. Am. Chem. Soc.* **1992**, *114*, 2728. (b) Hill, M. G.; Penneau, J.-F.; Zinger, B.; Mann, K. R.; Miller, L. L. *Chem. Mater.* **1992**, *4*, 1106.

(27) Buntinx, G.; Poizat, O. *J. Chem. Phys.* **1989**, *91*, 2153.

(28) Visy, Cs.; Lukkari, J.; Kankare, J. *Macromolecules* **1994**, *27*, 3322.