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Low-Band-Gap Conjugated Polymers. Improved Model Compounds for the Structural Analysis of Poly(isothianaphthene)

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ABSTRACT: The simulation of the structure of aromatic and quinoid poly(isothianaphthene) (PITN) has been improved by the synthesis of new model compounds. The ^{13}C NMR investigation confirms our previous results that the geometric structure of this low-band-gap conducting polymer shows a strong quinoid character. For the aromatic structure, 1,3-dithienylisothianaphthene and a series of disilylated isothianaphthene oligomers were synthesized. *trans*-3,3′-Bibenzo[*c*]thienylidene was prepared in order to model the quinoid structure. All these new model compounds simulate better neighboring S-atom effects, a structural feature which was not accounted for in the previously reported model compounds.

1. Introduction

In order to design new low-band-gap conjugated polymers in a straightforward way, it is essential to understand the relationship between the structure and the corresponding electronic properties of these materials. Therefore, theoretical techniques to estimate electronic properties based on the structure should be combined with experimental structural data of already known compounds. Since the intrinsic conductivity (without doping) depends on the band gap, the relation[1] between the degree of bond length alternation and the band gap of nondegenerate ground-state conjugated polymers is very useful. The bond length alternation of polythiophene (PT) was reduced by fusing a benzene ring into each unit. The so-obtained poly(isothianaphthene) (PITN, **1**) possesses a 1 ev band gap, as determined by optical absorption, compared to 2 eV for the parent thiophene polymer. This conjugated polymer may be dominated by either a quinoid or an aromatic electronic structure. Investigation of the electronic structure of PITN is not only interesting from a fundamental point of view but also important for the design of PITN derivatives with superior properties. We therefore investigated the structure of PITN[2,3] with a joint experimental and theoretical approach.

The relative stability of the aromatic and quinoid forms of PITN was estimated on the basis of the energy per repeat unit (E_{pru}) using a series of oligomers. The energies of both geometric structures (AM1-optimized) are very close. The planar aromatic form is on the average 2.7 kcal/mol less stable than the quinoid form. Allowing the ITN units to rotate around the inter-ring bonds (to an average optimal dihedral angle of 27°) induces a small stabilization of the aromatic ITN oligomers of the order of 0.5 kcal/mol per repeat unit. The band gap was calculated with a valence effective Hamiltonian (VEH) on the basis of the AM1-optimized geometry of the hexamers. These results showed that the VEH-calculated band gap for quinoid PITN (E_g = 1.19 eV) is in good agreement with the band gap derived from optical spectroscopy (onset of the spectrum of the polymer located at 1.0 eV).[4]

For the experimental structural analysis of PITN, we focused on high-resolution solid-state ^{13}C NMR. The ^{13}C chemical shift of the four inequivalent carbons of PITN (C3, C3a, C4, and C5) could be estimated with the aid of a multipurpose ^{13}C CP/MAS NMR pulse sequence.[5] These values were compared to the data obtained on model molecules, unambiguously possessing either an aromatic or a quinoid structure. Isothianaphthene (**A1**) and 1,3-bis(methylene)benzo[*c*]thiophene (**Q1**), referred to as the "first-order" model compounds, did not represent the structure of PITN well enough because the benzo[*c*]thiophene skeletons are not part of an extended conjugated π-system.

The simulation of the structure of PITN was improved in the so-called "second-order" model compounds 1,3-diphenylisothianaphthene (**A2**) and 1,3-dibenzylideneisothianaphthene (**Q2**). Herein, the central ITN unit is inserted in a conjugated backbone due to the introduction of terminal phenyl rings. For the aromatic model compound **A2**, there is no correspondence whatsoever with PITN. In contrast, the chemical shifts of C3a and C5 in **Q2** are in nice agreement with the values of PITN. The observed significant difference for C3 and C4 was explained by the fact that the shift of these carbons in PITN is also influenced by the S-atom of the neighboring unit. This situation is not accounted for by the second-order model compounds since there are no S atoms in the aromatic side groups.

In this paper, we present the synthesis and the NMR characterization of aromatic (**A3**–**A7**) and quinoid (**Q3** and **Q4**) model compounds with S atoms in the aromatic side groups. Herein, the chemical environment of C3 and C4 is comparable to the situation in the polymer. These "third-order" model compounds allow us to study the influence of the S atom in the neighboring ring and to criticize the usefulness of the previously reported "second-order" model compounds.

2. Experimental Section

2.1. Measurements. ^{1}H and ^{13}C NMR spectra of the model compounds were obtained with a Varian Unity 400 spectrometer. All the spectra were recorded in $CDCl_3$ (the chemical shifts of the carbon and the hydrogen being 77.0 and 7.24 ppm, respectively, from tetramethylsilane (TMS)) at 30 °C except

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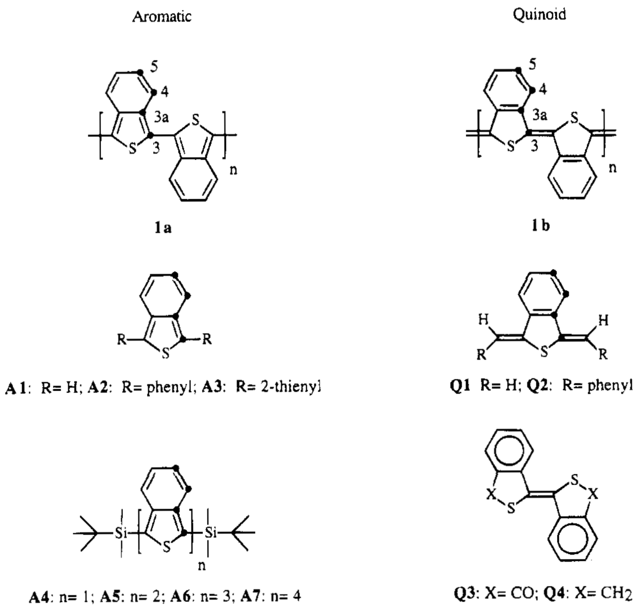


Figure 1. Chemical structures of PITN (**1**) and first-order (**A1** and **Q1**), second-order (**A2** and **Q2**), and third-order (**A3**–**A7** and **Q3**–**Q4**) model compounds.

for *trans*-3,3′-bibenzo[*c*]thienylidene-1,1′-dione, for which we employed $C_2D_2Cl_4$ (δH = 5.98 and δC = 73.7 ppm relative to TMS) at 90 °C because of the lack of solubility. Assignments were based on the coupling patterns, the integration, one-dimensional nuclear Overhauser effect (NOE), attached proton tests (APT), and two-dimensional ^{1}H–^{13}C heteronuclear correlation (HETCOR) experiments optimized for J_{CH} = 140 Hz and J_{CH} = 8 Hz.

The IR spectra were recorded with a Philips Pye Unicam SP-300. The FT-IR and the FT-Raman data were obtained via a IFS 66 FT-IR spectrometer (excitation wavelength: 1064 nm) connected with a Bruker computer (ASPECT 1000) equipped with a Raman FRA 106 module. The mass spectra were obtained via a Finigan 1020 and a TSQ 70 apparatus.

2.2. Aromatic Model Compounds. For the synthesis of the aromatic PITN oligomers (**A4**–**A7**) we followed the method of Okuda et al.[6] The method of Reissert et al.[7] was used for the synthesis of thiophthalic anhydride (**7**). Isothermic crystallization from chloroform/acetonitrile was used for the purification of the oligomers. Solvents were dried and distilled prior to use. The starting materials were purchased from Acros Chimica (previous Janssen Chimica) and used without further purification.

(1) 1,3-Bis(*tert*-butyldimethylsilyl)isothianaphthene (A4): mp 78 °C; FT-IR (KBr, ν, cm^{-1}) 3090, 2951, 2928, 2854, 2708, 1470, 1358, 1254, 1138, 1003, 964, 806, 768; FT-Raman (cm^{-1}) 3074 (m), 2957 (s), 2928 (s), 2900 (s), 2858 (s), 1512 (m), 1463 (m), 1448 (s), 1369 (s), 1358 (m), 1300 (m), 1200 (w), 1015 (m), 940 (w), 830 (w), 582 (m), 476 (m), 185 (w); MS (EI, *m*/*e*) 362 (M^+), 305 (M^+ − *tert*-butyl), 249, 233, 173, 159, 145, 131, 73, 57; ^{1}H NMR ($CDCl_3$, 400 MHz, in ppm relative to TMS) 0.54 (s, 12, CH_3–Si), 0.98 (s, 18, CH_3–C), 7.11 (dd, 2, *J* = 2.9/6.7 Hz, H5), 7.83 (dd, 2, *J* = 2.9/6.7 Hz, H4); ^{13}C NMR ($CDCl_3$, 400 MHz, in ppm relative to TMS) −3.9 (Si–**C**H_3), 18.2 (CH_3–**C**), 26.8 (C–**C**H_3), 135.0 (C3), 146.5 (C3a), 122.6 (C5), 124.0 (C4).

(2) Dimer (A5): mp 145–147 °C; FT-IR (KBr, ν, cm^{-1}) 3059, 2951, 2928, 2854, 1466, 1389, 1358, 1250, 1007, 976, 806, 744; FT-Raman (cm^{-1}) 3074 (w), 2957 (w), 2928 (w), 2900 (w), 2858 (w), 1517 (w), 1497 (s), 1449 (s), 1428 (w), 1372 (w), 1320 (m), 1185 (w), 889 (vw), 755 (w), 578 (w), 475 (m), 199 (w); MS (EI, *m*/*e*) 494 (M^+), 437 (M^+ − *tert*-butyl); ^{1}H NMR ($CDCl_3$, 400 MHz, in ppm relative to TMS) 0.56 (s, 12, CH_3–Si), 1.02 (s, 18, CH_3–C), 7.10–7.18 (m, 4, H5 and H6), 7.76 (m, 2, H4), 7.86 (m, 2, H7); ^{13}C NMR ($CDCl_3$, 400 MHz, in ppm relative to TMS) −3.9 (Si–**C**H_3), 18.2 (CH_3–**C**), 26.8 (C–**C**H_3), 129.2 (C3), 145.6 (C3a), 123.9 (C4), 123.7 (C5), 123.6 (C6), 122.0 (C7), 137.5 (C7a), 132.2 (C1).

(3) Trimer (A6): FT-IR (KBr, ν, cm^{-1}) 3063, 2951, 2924, 2854, 1466, 1385, 1358, 1254, 1092, 1003, 980, 806, 768; FT-Raman (cm^{-1}) 3074 (vw), 2957 (vw), 2928 (vw), 2900 (vw), 2858 (vw), 1610 (vw), 1521 (vw), 1489 (m), 1448 (s), 1360 (w), 1331 (m), 1192 (w), 474 (w), 188 (w); MS (EI, *m*/*e*) 626 (M^+), 569 (M^+ − *tert*-butyl); ^{1}H NMR ($CDCl_3$, 400 MHz, in ppm relative to TMS) 0.55 (s, 12, CH_3–Si), 1.02 (s, 18, CH_3–C), 7.14–7.18 (m, 6, H5[A,B] and H6[A]), 7.75 (m, 2, H4[A]), 7.86 (dd, 2, *J* = 3.0/7.0 Hz, H4[B]), 7.94 (m, 2, H7[A]); ^{13}C NMR ($CDCl_3$, 400 MHz, in ppm relative to TMS) −3.9 (Si–**C**H_3), 18.2 (CH_3–**C**), 26.8 (C–**C**H_3), 129.8 (C3[A]), 145.6 (C3a[A]), 124.0 (C4[A]), 123.8 (C5[A]), 123.9 (C6[A]), 121.9 (C7[A]), 137.6 (C7a[A]), 131.6 (C1[A]), 126.7 (C3[B]), 136.5 (C3a[B]), 121.9 (C4[B]), 124.7 (C5[B]).

(4) Tetramer (A7): FT-IR (KBr, ν, cm^{-1}) 3063, 2951, 2924, 2854, 1466, 1408, 1358, 1254, 1007, 976, 802, 768; FT-Raman (cm^{-1}) 1641 (w), 1486 (w), 1444 (s), 1355 (w), 1333 (s), 1196 (w), 1151 (w), 977 (w), 892 (w), 749 (w), 470 (w), 185 (w); MS (EI, *m*/*e*) 758 (M^+), 701 (M^+ − *tert*-butyl); ^{1}H NMR ($CDCl_3$, 400 MHz, in ppm relative to TMS) 0.55 (s, 12, CH_3–Si), 1.02 (s, 18, CH_3–C), 7.12–7.20 (m, 8, H5[A,B] and H6[A,B]), 7.76 (m, 2, H4[A]), 7.89 (m, 2, H4[B]), 7.99 (m, 4, H7[A,B]); ^{13}C NMR ($CDCl_3$, 400 MHz, in ppm relative to TMS) −3.9 (Si–**C**H_3), 18.2 (CH_3–**C**), 26.8 (C–**C**H_3), 130.0 (C3[A]), 145.6 (C3a[A]), 124.0 (C4[A]), 123.8 (C5[A]), 123.9 (C6[A]), 121.9 (C7[A]), 137.7 (C7a[A]), 131.5 (C1[A]), 127.0 (C3[B]), 136.6* (C3a[B]), 122.0 (C4[B]), 124.9 (C5[B]), 125.0 (C6[B]), 121.9 (C7[B]), 136.7* (C7a[B]), 126.1 (C1[B]) (*: may be interchanged).

(5) Bis(*S*-(2-pyridinyl)) benzenedithioate (4; Scheme 1). A solution of 11 mL of triethylamine, 50 mL of THF and 8.9 g (80 mmol) of 2-mercaptopyridine (**3**) is cooled to 0 °C. A solution of 5.8 mL (40 mmol) phthaloyl dichloride (**2**) in 200 mL of THF is added. Immediately, 200 mL of HCl (1%) is added to this reaction mixture. After extraction with chloroform, the combined layers are washed with 500 mL of NaOH (10%), 500 mL of $NaHCO_3$ (1 M), and water. After drying (magnesium sulfate), the product is crystallized from dichloromethane/ether, giving a yield of 70%: mp 109–110 °C; IR (KBr, ν, cm^{-1}) 1680, 1655, 1570, 1450, 1420, 1385, 1315, 1200, 900, 860, 765, 750, 690, 655; MS (EI, *m*/*e*) 242 (M^+ − SAr), 214 (M^+ − COSAr); ^{1}H NMR ($CDCl_3$, 400 MHz, in ppm relative to TMS) 7.26 (t, 2, H5′), 7.61 (dd, 2, H3), 7.71 (td, 2, H4′), 7.75 (dt, 2, H3′), 7.84 (dd, 2, H2), 8.59 (d, 2, H6′); ^{13}C NMR ($CDCl_3$, 400 MHz, in ppm relative to TMS) 123.7 (C5′), 128.5 (C2), 130.4 (C3′), 132.0 (C3), 136.8 (C1), 137.2 (C4′), 150.4 (C6′), 151.3 (C2′), 190.2 (C4).

(6) 1,2-Dithienoylbenzene (6; Scheme 1). 2-Bromothiophene (4.5 mL, 46 mmol) in 50 mL of THF is added slowly to 1.2 g (46 mmol) of iodine-activated magnesium in 50 mL of THF. After stirring for 3.5 h, this solution is slowly added to 7.95 g (23 mmol) of bis(*S*-(2-pyridinyl)) benzenedithioate (**4**) in 150 mL of THF at 0 °C. After stirring for another 30 min, the reaction is completed by adding 200 mL of a dilute hydrochloric acid solution (10%). The resulting mixture is extracted with diethyl ether. The diethyl ether solution is washed with 500 mL of NaOH (10%), 500 mL of $NaHCO_3$ (1 M), and water and finally dried with magnesium sulfate. After evaporation of the solvent a light brown product is obtained in a yield of 95%. This product is used as such in further reactions. Crystallization from chloroform/*n*-hexane results in white crystals: mp 148–149 °C; IR (KBr, ν, cm^{-1}) 1620, 1585, 1570, 1510, 1410, 1350, 1340, 1280, 1260, 1220, 1150, 1045, 910, 880, 840, 820, 780, 725, 700, 650; MS (EI, *m*/*e*) 298 (M^+), 215 (M^+ − COAr), 187 (M^+ − COAr), 111 (COAr), 104, 76; ^{1}H NMR ($CDCl_3$, 400 MHz, in ppm relative to TMS) 7.03 (dd, 2, *J* = 5.0/3.8 Hz, H4′), 7.44 (d, 2, *J* = 3.8 Hz, H3′), 7.60 (dd, 2, *J* = 5.4/3.4 Hz, H3), 7.63 (d, 2, *J* = 5.0 Hz, H5′), 7.70 (dd, 2, *J* = 5.4/3.4 Hz, H2); ^{13}C NMR ($CDCl_3$, 400 MHz, in ppm relative to TMS) 128.0 (C4′), 129.2 (C2), 130.6 (C3), 134.9 (C5′), 135.1 (C3′), 139.3 (C1), 144.0 (C2′), 188.2 (C4).

(7) 1,3-Dithienylisothianaphthene (A3; Scheme 1). To a solution of 0.58 g (2 mmol) of 1,2-dithienoylbenzene (**6**) in 40 mL of dried acetonitrile is added 1.7 g (6.1 mmol) of P_4S_{10} and 2.0 g (24 mmol) of sodium hydrogen carbonate. After stirring for 4 h at a temperature of 30 °C, 50 mL of water is added. The precipitate formed is filtered off and dissolved in diethyl ether. After extraction of the remaining water solution with diethyl ether, the combined fractions are dried (magnesium sulfate). Further purification is performed by column chromatography (silica, *n*-hexane/chloroform) and crystallization from *n*-hexane/chloroform, resulting in orange crystals (52%): mp 96–97 °C; IR (KBr, ν, cm^{-1}) 1520, 1215, 1180, 1100, 1065, 1030, 995, 845, 830, 820, 720, 690, 550, 510, 485, 415; FT-Raman (cm^{-1}) 1612, 1532 (s), 1510, 1452 (vs), 1398, 1349, 1317, 1075, 1048, 833, 488, 471, 184; MS (EI, *m/e*) 298 (M$^+$), 132 (M$^+$ − 2Ar); ^{1}H NMR (CDCl$_3$, 400 MHz, in ppm relative to TMS) 7.13 (dd, 2, J = 6.9/3.0 Hz, H5 and H6), 7.14 (dd, 2, J = 5.2/3.6 Hz, H4′), 7.34 (d, 2, J = 3.6 Hz, H3′), 7.36 (d, 2, J = 5.2 Hz, H5′), 7.94 (dd, 2, J = 6.9/3.0 Hz, H4 and H7); ^{13}C NMR (CDCl$_3$, 400 MHz, in ppm relative to TMS): 121.5 (C4), 124.8 (C5), 125.5 (C5′), 125.6 (C3′), 126.5 (C3), 127.9 (C4′), 135.4 (C3a), 135.7 (C2′).

2.3. Quinoid Model Compounds. (1) *trans*-3,3′-Bibenzo[*c*]thienylidene-1,1′-dione (Q3; Scheme 2). *trans*-3,3′-Bibenzo[*c*]thienylidene-1,1′-dione (**Q3**) is prepared according to the procedure described by Bird and Wong[8] (yield 35–45%): subl pt 350 °C; IR (KBr, ν, cm^{-1}) 1690, 1590, 1570, 1470, 1280, 1230, 1200, 915, 830, 765, 695; MS (*m/e*) 296, 280, 268, 252, 240, 232, 224, 204, 195, 176, 163, 152, 134, 120; ^{1}H NMR (400 MHz, C$_2$D$_2$Cl$_4$, 90 °C, in ppm relative to TMS) 8.34 (d, 2, J = 7.5 Hz, H4), 8.00 (d, 2, J = 7.5 Hz, H7), 7.83 (t, 2, J = 7.5 Hz, H5), 7.61 (t, 2, J = 7.5 Hz, H6); ^{13}C NMR (100 MHz, C$_2$D$_2$Cl$_4$, 90 °C, in ppm relative to TMS) 190.1 (C1), 142.3 (C3a), 134.3 (C7a), 133.8 (C5), 129.4 (C6), 128.3 (C3), 126.9 (C4), 124.4 (C7).

(2) *trans*-3,3′-Bibenzo[*c*]thienylidene (Q4; Scheme 2). To a solution of 0.54 g (14.3 mmol) of NaBH$_4$ in 7.5 mL of diglyme (dried by refluxing with CaH$_2$), stirred at room temperature in an atmosphere of N$_2$, is added portionwise 1.18 g (4 mmol) of *trans*-3,3′-bibenzo[*c*]thienylidene-1,1′-dione (**Q3**). To this mixture is added dropwise during ~30 min a solution of boron trifluoride etherate in 3 mL of diglyme. The ratio of NaBH$_4$:BF$_4$ is 3:4, as required stoichiometrically for the formation of B$_2$H$_6$. Stirring at room temperature is continued for 2 h. The reaction mixture is worked up by addition of ice water, followed by filtration, washing, and drying under vacuum. Column chromatography of the crude product on silica gel using chloroform as eluant yields **Q4** (45%) as a red crystalline product: mp 138–140 °C; IR (KBr, ν, cm^{-1}) 2920, 2040, 1590, 1470, 1440, 815, 755, 705; MS (*m/e*) 268, 235, 221, 202, 189, 134; ^{1}H NMR (400 MHz, CDCl$_3$, 30 °C, in ppm relative to TMS) 8.24 (d, 2, J = 7.6 Hz, H4), 7.39 (t, 2, J = 7.6 Hz, H6 or H5), 7.35 (d, 2, J = 7.6 Hz, H7), 7.25 (t, 2, J = 7.6 Hz, H5 or H6), 4.51 (s, 4, H1); ^{13}C NMR (100 MHz, CDCl$_3$, 30 °C, in ppm relative to TMS) 141.0 (C7a), 140.4 (C3a), 127.4 (C3), 126.9 (C5 and C6), 125.2 (C4), 125.0 (C7), 38.0 (C1).

3. Results: Full ^{1}H and ^{13}C Chemical Shift Assignment

3.1. General Approach. The model compounds we are interested in for the ^{13}C NMR characterization of PITN often contain exclusively aromatic carbons. The resonances, representing these carbons in the ^{13}C spectra, are thus located in a small chemical shift region. For the structural analysis of our model compounds we need to perform a full proton and carbon chemical shift assignment. Therefore we developed a routine which permits discrimination between carbon or proton atoms even if their NMR signals are very close together in the spectra. In addition this routine can be applied to most organic compounds.

In this procedure, we have to start with the analysis of the molecular structure in order to assign unambiguously at least one carbon or hydrogen atom. For this purpose one can make use of *chemical shift* (e.g. the shift difference between a carbonyl carbon atom and an aromatic carbon atom is large enough to be distinguished), *first-order splitting or coupling pattern,*[9] *coupling values,*[10] and *peak areas*. If necessary, *specific 1D-NMR techniques* (NOE and APT, e.g.) can be applied to obtain an additional objective criterion for an unambiguous assignment. In some cases even the *heteronuclear coupling behavior* of a particular carbon atom in 2D-NMR experiments may be used (see also the assignment of 1,3-dithienylisothianaphthene). The shifts of these atoms are then used as starting points to elaborate a pathway for further assignment using 2D-NMR techniques. In most cases a full proton and carbon shift assignment can be achieved using direct ^{1}H−^{13}C heteronuclear correlations (optimized for J_{CH} = 140 Hz) and long range ^{1}H−^{13}C heteronuclear correlations (optimized for J_{CH} = 8 Hz). In situations where the molecular structure does not allow a full chemical shift assignment based on two-dimensional ^{1}H−^{13}C heteronuclear correlation (HETCOR) alone, additional 2D-NMR experiments (COSY, ...) can be performed in order to obtain an unambiguous assignment.

3.2. Aromatic Model Compounds. (1) Disilylated Isothianaphthene Monomer (A4). The integration allows us to attribute the singlets at 0.54 and 0.98 ppm in the aliphatic part of the ^{1}H NMR spectrum to the methyl groups attached to silicon and to the methyl groups of the *tert*-butyl group, respectively. The three carbons of the silicon end group were assigned in the ^{13}C NMR spectrum on the basis of an attached proton test (APT) and the integration. In the APT, the signals of CH and CH$_3$ carbons remain positive while those of C and CH$_2$ carbons become negative when proper parameters are used. Thereby the signals at −3.9, +18.2, and +26.8 ppm correspond with the methyl carbon attached to the silicon atom, the quaternary carbon atom, and the methyl carbon of the *tert*-butyl group, respectively. The methyl carbon attached to the silicon atom can be used as a starting point for further analysis of the HETCOR spectra.

For reasons of symmetry the protons H4[A] and H7[A] have identical chemical shifts, as have H5[A] and H6[A]. The same remark can be made for the ^{13}C chemical shifts. A distinction between the protons H4[A] and H5[A] was made on the basis of a NOE effect (due to the spatial proximity, Figure 4) between H4[A] and the methyl groups attached to silicon. In this double resonance experiment, the singlet at 0.54 ppm was selectively irradiated. This permits us to assign the signals at 7.83 and 7.11 ppm to H4[A] and H5[A], respectively. As for all the oligomers two groups of signals are observed in the ^{1}H NMR spectra. The group at 7.11 ppm can be assigned to H5/H6 and the group at 7.7–8.0 ppm to H4/H7 of both isothianaphthene ring systems.

The assignment of H4[A] and H5[A] allows the assignment of the two protonated carbon atoms C4[A] and C5[A] to the signals at 124.0 and 122.6 ppm, respectively, with the aid of the direct HETCOR spectrum optimized for J_{CH} = 140 Hz (Figure 2).

For the assignment of the quaternary carbons the HETCOR spectrum optimized for J_{CH} = 8 Hz is used (Figure 3). Herein, correlations appear due to geminal and vicinal couplings. The starting point is the methyl groups attached to silicon (0.54 ppm). The signal at 135.0 ppm shows a correlation with the protons of these methyl groups. Since these aliphatic protons are too far removed from C3a[A] (four bonds), the correlation arises from the coupling with C3[A]. The remaining

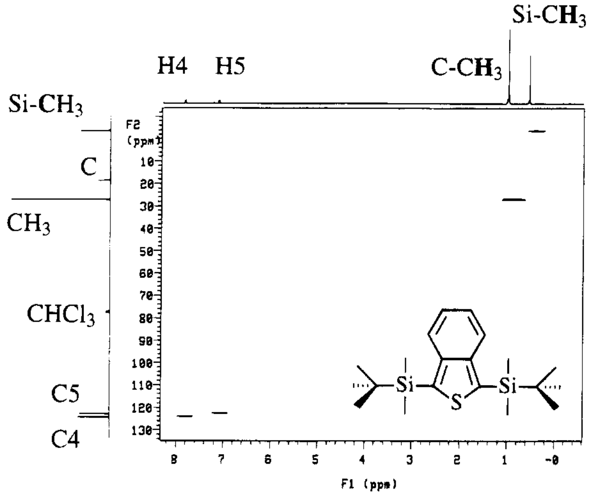


Figure 2. 2D heteronuclear ^{1}H$-^{13}$C correlation spectrum of **A4** optimized for J_{CH} = 140 Hz (CDCl$_3$, 30 °C).

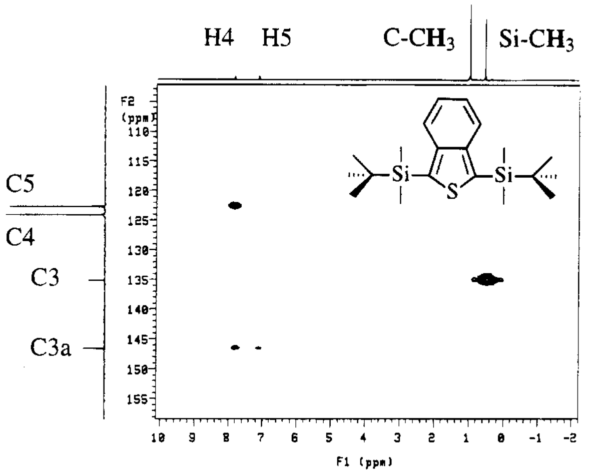


Figure 3. 2D heteronuclear ^{1}H$-^{13}$C correlation spectrum of **A4** optimized for J_{CH} = 8 Hz (CDCl$_3$, 30 °C).

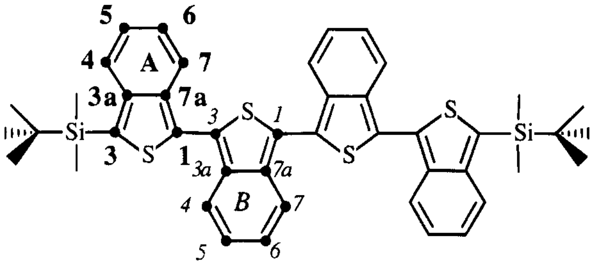


Figure 4. Numbering of the disilylated oligomers **A4**$-$**A7**.

quaternary signal at 146.5 ppm is therefore assigned to C3a[A] which is confirmed by the correlation with H7[A] and H5[A].

Assignments of the aliphatic nuclei of the silicon end groups in the other oligomers (di-, tri-, and tetramer) are performed by following the same strategy as for the monomer mentioned above.

(2) Disilylated Isothianaphthene Dimer (A5). In comparison to the monomer, two new signals in the ^{1}H NMR (H6[A] and H7[A]) appear. The hydrogens H5[A] and H6[A] collapse in the region 7.10$-$7.18 ppm because of the small difference in chemical environment. The hydrogens H4[A] and H7[A] are represented in the spectrum by two double doublets at 7.76 and 7.86 ppm, respectively. Differentiation between both hydrogen atoms could be made using NOE as in the monomer. This allows us to assign H4[A] to the signal at 7.76 ppm.

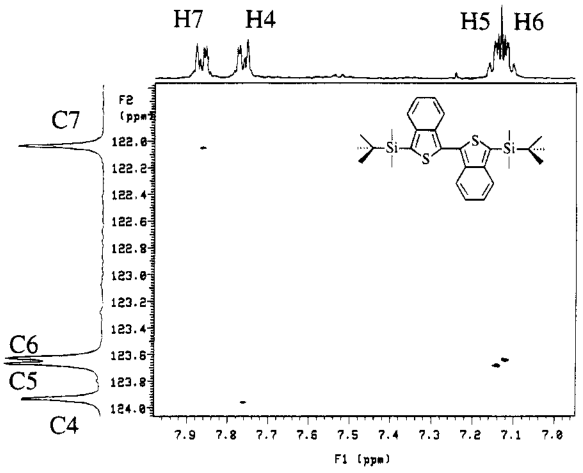


Figure 5. 2D heteronuclear ^{1}H$-^{13}$C correlation spectrum of **A5** optimized for J_{CH} = 140 Hz (CDCl$_3$, 30 °C).

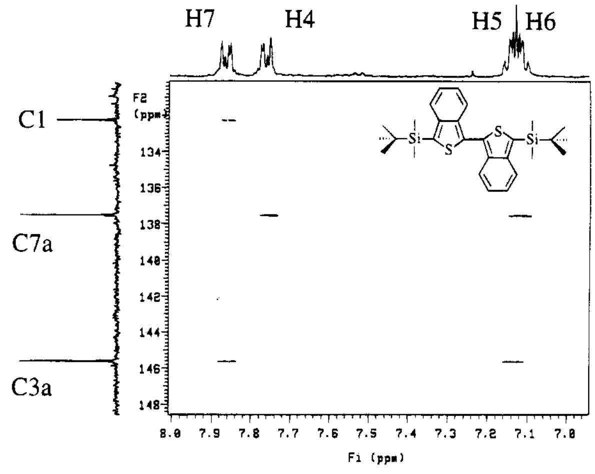


Figure 6. 2D heteronuclear ^{1}H$-^{13}$C correlation spectrum of **A5** optimized for J_{CH} = 8 Hz (CDCl$_3$, 30 °C).

The remaining proton signal at 7.86 ppm can therefore be assigned to H7[A].

In the aromatic part of the ^{13}C NMR spectrum we see four new signals compared to the monomer. The protonated carbons C4[A] and C7[A] are assigned with a 2D-HETCOR spectrum optimized for J_{CH} = 140 Hz (Figure 5) to the signals at 123.9 and 122.0 ppm, respectively. Using 2D-COSY distinction could be made between C5[A] and C6[A] which can therefore be assigned to the signals at 123.7 and 123.6 ppm, respectively.

For the assignment of the quaternary carbon atoms again the starting point common to all oligomers can be used. In the 2D-HETCOR spectrum optimized for J_{CH} = 8 Hz, C3[A] correlates with the proton of the methyl group attached to the silicon atom and is thus assigned to the signal at 129.2 ppm. This assignment is further confirmed by the vicinal coupling with H4[A], assigned previously by means of NOE. Thoroughly exploring the 2D-HETCOR spectrum optimized for J_{CH} = 8 Hz, we find two groups of ^{13}C signals. The signals at 137.5 and 145.6 ppm show a correlation with the H5[A]/H6[A] multiplet as well as with H4[A] or H7[A] (Figure 6). On the other hand the signals at 129.2 and 132.2 ppm just show a correlation with H4[A] or H7[A]. As only C3a[A] can show long range couplings with H7[A] and H5[A] and only C7a[A] can show long range couplings with H4[A] and H6[A], we can assign the signals at 137.5 and 145.6 ppm to C7a[A] and C3a[A], respectively. In the remaining group the signal at 129.2 ppm has been assigned to C3[A] previously by its correlation with the proton of the methyl group attached to the silicon atom. The remaining quaternary signal at 132.2 ppm can therefore be assigned to C1[A], which is confirmed by its long range coupling with H7[A].

From this assignment it appears that in qualitative ^{13}C NMR spectra the signals of C1[A] and C3[A] show a lower intensity compared to C3a[A] and C7a[A]. Also within the monomer this intensity difference between C3[A] and C3a[A] can be observed. The lower intensity of C1[A] and C3[A] originates from an inadequate relaxation through dipole–dipole interactions with neighboring protons. C3a[A] and C7a[A] on the other hand are subject to a more efficient relaxation due to the relative closer proximity of the aromatic protons, resulting in a higher intensity of the ^{13}C NMR signals. Therefore the C1[A] and C3[A] groups show longer spin–lattice relaxation times and smaller NOE effects, which is reflected by smaller intensities in qualitative ^{13}C NMR spectra. This feature can be used in the further analysis of the trimer and tetramer.

(3) Disilylated Isothianaphthene Trimer (A6). For reasons of symmetry the protons H4[B] and H7[B] have identical chemical shifts, as have H5[B] and H6[B]. The same remark can be made for the ^{13}C chemical shifts. Due to very similar chemical environments, in the ^{1}H NMR spectrum of the trimer the new proton H5 of the B isothianaphthene ring collapses with H5 and H6 of the A ring (7.10–7.18 ppm). We can assign the multiplet at 7.10–7.18 ppm to H5[A], H6[A], and H5[B].

To find the signal of H4[A], we have to use the NOE effect (due to the spatial proximity) between H4[A] and the methyl groups attached to silicon. This allows us to assign the signal at 7.75 ppm to H4[A]. H4[B] is represented in the spectrum by a double doublet (7.86 ppm), which is less distorted than the patterns of H4[A] and H7[A] because of molecular symmetry. The remaining multiplet at 7.94 ppm can then be assigned to H7[A].

As the ^{1}H NMR spectrum has been assigned completely, the protonated carbons C4[A], C7[A], and C4[B] are assigned with a 2D-HETCOR spectrum optimized for J_{CH} = 140 Hz. C4[A] is assigned to the signal at 124.0. C7[A] and C4[B] have to be assigned to the same signal at 121.9 ppm. However, at the 140 Hz optimization level no distinction could be made between C5[A], C6[A], and C5[B] because of the overlap in the ^{1}H dimension.

Considering the quaternary carbons, in analogy to the monomer and dimer they can be divided into two groups. The carbons C3[A], C1[A], and C3[B] are removed from the aromatic protons further than the carbons C3a[A], C7a[A], and C3a[B], resulting in smaller intensities.

In the first group C3[A] can be assigned through the very specific long range coupling with the silicon end group to 129.8 ppm. Through comparison of this result with the shift of C3[A] in the dimer (Figure 7), there is only a difference in chemical shift of about 0.6 ppm. It seems reasonable to expect the shift of C1[A] not to undergo substantial changes; therefore in comparison with the dimer we can assign the shift at 131.6 ppm to C1[A]. The shift difference is in this case even lower: 0.4 ppm. The remaining signal at 126.7 ppm within this subgroup of quaternary carbon atoms should then be considered as new and can be assigned to C3[B].

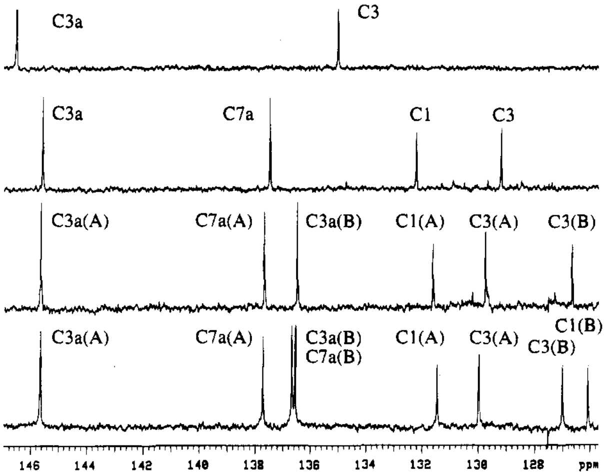


Figure 7. Proton-decoupled ^{13}C NMR spectra of **A4–A7** showing the signals from the quaternary carbon atoms.

The second group of quaternary carbon atoms can be assigned using 2D-HETCOR optimized for J_{CH} = 8 Hz due to the long range coupling of C3a[A], C7a[A], and C3a[B] with H7[A], H4[A], and H7[B], respectively, to 145.6, 137.6, and 136.5 ppm. The fact that the signal of C3a[A] is isolated (145.6 ppm) from the others can be explained by the influence of the bulky end groups. This is further confirmed by the chemical shift of C7a[B] in the tetramer (136.6 or 136.7 ppm, Figure 7).

As the shifts of C5[A], C6[A], and C5[B] could not be assigned using 2D-HETCOR optimized for J_{CH} = 140 Hz, we have to revert to the 2D-HETCOR spectrum optimized for J_{CH} = 8 Hz. C5[A], C6[A], and C5[B] show a vicinal long range coupling with H7[A], H4[A], and H7[B] and can therefore be assigned to 123.8, 123.9, and 124.7 ppm. This is also confirmed by comparison of the shifts of C5[A] and C6[A] in the dimer. The difference in chemical shift is only 0.2 ppm, and the signal at 124.7 ppm appears to be the new signal compared to the dimer.

(4) Disilylated Isothianaphthene Tetramer (A7). Due to very similar chemical environments, in the ^{1}H NMR spectrum of the tetramer the new proton H6 of the B isothianaphthene ring merges with H5 and H6 of the A ring and H5 of the B ring. We can therefore assign the multiplet at 7.10–7.18 ppm to H5[A], H6[A] and H5[B], H6[B].

The assignment of H4[A] is again based on the NOE effect between H4[A] and the methyl groups attached to silicon. This allows us to assign the signal at 7.76 ppm to H4[A]. If we take into account that the H7 protons of both rings have almost identical chemical environments, we may assume that the shifts of H7[A] and H7[B] will merge, as is the case with the H5 and H6 protons. On the basis of integration and comparison with the trimer we thus assign the multiplet at 7.99 ppm to these protons. The remaining multiplet at 7.89 ppm can then be assigned to H4[B].

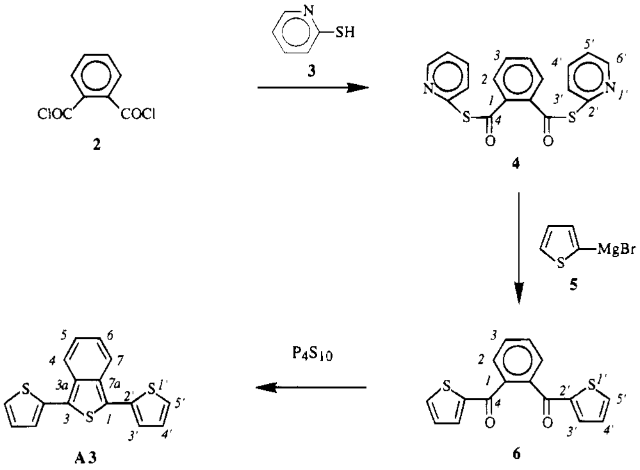
On the basis of direct heteronuclear coupling we can now try to assign the protonated carbon atoms. H4[A] shows a coupling with the carbon shift at 124.0 ppm, which can thus be assigned to C4[A]. In the case of the H4[B] multiplet we note a coupling with the signal at 122.0 ppm, assigning thereby C4[B]. The multiplet belonging to the H7 protons shows a correlation with the signal at 121.9 ppm. Therefore this signal can be assigned to C7[A] and C7[B]. At the 140 Hz optimization level the coalescence of the proton shifts of H5 and H6 again prevent the assignment of the corresponding carbon atoms. However further assignment can be performed through the 2D-HETCOR optimized for $J_{CH} = 8$ Hz. H4[A] can show a long range coupling with C5[A] (geminal) and C6[A] (vicinal). On the other hand H4[B] can show a long range coupling with C5[B] (geminal) and C6[B] (vicinal). This makes it possible to break down this group of protonated carbon atoms into two groups. The signals at 123.8 and 123.9 ppm should belong to ring A and the signals at 124.9 and 125.0 ppm to ring B. This is confirmed by comparison with the other oligomers since chemical shifts are not subject to drastic changes when the carbon atoms are situated in an identical chemical environment, going from one oligomer to another. As we note only one long range coupling signal and since the 2D-HETCOR is optimized for $J_{CH} = 8$ Hz, we may assume the signals to originate from a vicinal coupling. On the basis of this vicinal coupling of H4[A] and H4[B] we therefore can assign C6[A] and C6[B] to 123.9 and 125.0 ppm. As a consequence the remaining signals C5[A] and C5[B], coupling with the H7 multiplet, are assigned to 123.8 and 124.9 ppm.

Due to the differences in intensities we can again divide the quaternary carbon signals into two groups, the C1/C3 carbon atoms with a lower signal intensity and the C3a/C7a carbon atoms with a higher signal intensity. In the first group we can assign C3[A] based on its long range coupling with the protons of the methyl groups attached to silicon. In this way the signal at 130.0 ppm corresponds with C3[A]. From comparison (Figure 7) with dimer and trimer there is a remarkable similarity in the shifts of this carbon atom. Further assignment of the quaternary carbon atoms is however not possible through the 2D-HETCOR optimized for $J_{CH} = 8$ Hz. Therefore we have to base our assignment on the comparison of tetramer with dimer and trimer (Figure 7). Former assignments prove this to be a reliable alternative. This way we are able to assign C1[A] and C3[B] to 131.5 and 127.0 ppm, respectively. The signal at 126.1 ppm appears to be the new signal and can therefore be assigned to C1[B]. In the second group of quaternary carbon atoms again no assignment can be performed with regard to the 2D-HETCOR optimized for $J_{CH} = 8$ Hz. Therefore the assignment of C3a[A], C7a[A], C3a[B], and C7a[B] to 145.6, 137.7, 136.6*, and 136.7* ppm, respectively is also based on comparison with the smaller oligomers (*: may be interchanged) (Figure 7).

(5) 1,3-Dithienylisothianaphthene (A3). 1,3-Dithienylisothianaphthene was synthesized by a cyclization[11] of *o*-dithienoylbenzene with diphosphorus pentasulfide. The reaction of 2-thienylmagnesium bromide (**5**) with phthaloyl dichloride (**2**) results in a rather low yield of the *o*-aryl diketone due to several competitive reactions. The main problem in this context is the intramolecular attack of the oxygen atom of one of the carbonyl groups, giving rise to disubstituted phthalides. Therefore, **2** was first converted into bis(*S*-(2-pyridinyl)) benzenedithioate (**4**) before performing the Grignard reaction[12] (Scheme 1).

For the assignment of the starting points we first need to analyze the ^{1}H NMR spectrum. On the basis of the coupling constants and the coupling patterns we can distinguish between the protons of the thiophene ring ($\delta = 7.14$, 7.34, and 7.36 ppm) and the protons of the isothianaphthene ring ($\delta = 7.13$ and 7.94 ppm). Furthermore, the specific coupling pattern of H4′, one of our starting points, allows us to assign H4′ to the multiplet at 7.14 ppm. This multiplet overlaps with one of the signals belonging to an isothianaphthene proton.

Scheme 1. Synthesis of 1,3-Dithienylisothianaphthene

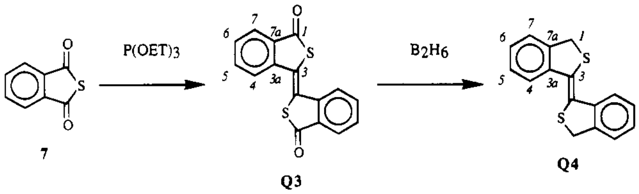


The long range 2D-HETCOR, showing mainly vicinal couplings, also shows geminal and direct correlations. Since C3/C1 is the only quaternary carbon atom to show a long range coupling with a proton from the isothianaphthene ring and a proton from the thiophene ring and since quaternary carbon atoms can easily be distinguished from protonated carbon atoms using the attached proton test (APT) 1D-NMR experiment or the direct 2D-HETCOR experiment, the starting point C3/C1 can be assigned to 126.5 ppm. As C3/C1 can only couple with H4/H7 and H3′ since the other protons are too far removed from C3 (more than three bonds), we can assign them to 7.94 and 7.34 ppm, respectively. By this we can completely assign the ^{1}H NMR spectrum since the two remaining signals belong each to another ring system. H5/H6 of the isothianaphthene ring corresponds with the double doublet at 7.13 ppm, and H5′, with the double doublet at 7.36 ppm. The carbons C3a/C7a can be assigned to 135.4 ppm since it is the only signal to show a long range coupling with H7/H4 as well as H5/H6 and C3a/C7a is the only quaternary carbon that fulfills these requirements.

In the direct 2D-HETCOR optimized for $J_{CH} = 140$ Hz the five expected direct correlation signals are found. As the assignment of the ^{1}H-NMR spectrum is completed, all the protonated carbon atoms can be assigned: C4/C7 to 121.5 ppm, C5′ to 125.5 ppm, C3′ to 125.6 ppm, C4′ to 127.9 ppm, and C5/C6 to 124.8 ppm. Finally, from H4′ we can assign C2′ through a vicinal long range coupling to 135.7, which is confirmed by the fact that C2′ is the only remaining quaternary carbon atom not being assigned previously.

3.3. Quinoid Model Compounds. (1) *trans*-3,3′-Bibenzo[*c*]thienylidene-1,1′-dione (Q3). *trans*-3,3′-Bibenzo[c]thienylidene-1,1′-dione has already been synthesized by the reaction of 2-thiophthalic anhydride with 2 equiv of triethyl phosphite in xylene[13] and with an excess of triethyl phosphite.[8] For this compound, a melting point of ±350 °C was reported. However thermogravimetric analysis (TGA) of this product shows weight loss at 350 °C. The physical transition observed at 350 °C using differential scanning calorimetry (DSC) disappeared when cooling down. These observations indicate that we are dealing with a sublimation point instead of a melting point. Infrared,[13] mass spectrometry[14] and X-ray diffraction[15] analyses are already

Scheme 2. Synthesis of the Quinoid Model Compounds Q3 and Q4



described elsewhere, but no NMR data are available from these reports.

We first focus on the ^1H NMR spectrum of **Q3**. At this stage we can only subdivide the four multiplets on the basis of their coupling pattern. H5 and H6 will show a triplet (7.83 or 7.61 ppm). H4 and H7 on the other hand will show a doublet (8.34 or 8.00 ppm). For further assignment we have to make an appeal to the HETCOR optimized for $J_{CH} = 8$ Hz. Carbonyl carbon atoms have shifts situated in the region between 160 and 200 ppm. This allows us to assign C1 unambiguously to 190.1 ppm. As C1 can only have a vicinal coupling with H7, the shift at 8.00 ppm arises from H7. Therefore H4 can be assigned to 8.34 ppm. C3 is the only carbon atom to show a vicinal coupling with H4 and not at all with H5 or H6 (triplet), as a result of which we can assign C3 to the shift at 128.3 ppm. The remaining carbon atoms C3a and C7a can be assigned through their vicinal coupling with H7 and H4 to 142.3 and 134.3 ppm, respectively. Since C3a and C7a can only show long range coupling with H5 and H6, respectively, the shifts of these protons can be assigned to 7.83 and 7.61 ppm, respectively. The assignment of H5 and H6 was further confirmed by a 2D-COSY experiment. With all the ^1H NMR chemical shifts known, the protonated carbons can be unambiguously assigned with a 2D heteronuclear correlation experiment optimized for $J_{CH} = 140$ Hz.

At this stage, it should be noticed that the ^{13}C chemical shift for C3a and C5 of this compound **Q3** previously reported by us[16] is not correct since H5 and H6 were interchanged at that time.

(2) *trans*-3,3′-Bibenzo[*c*]thienylidene Q4 was synthesized by the reduction of the corresponding dione **Q3**. We chose diborane (B_2H_6) as the reducing agent since it was previously used for the reduction of 1,8-naphthalide to 2,1,3-*peri*-naphthopyran.[17] Sodium boron hydride ($NaBH_4$) and boron trifluoride etherate ($BF_3{\cdot}Et_2O$) were employed for the in situ generation of B_2H_6.

The signal at 4.51 ppm in the ^1H NMR spectrum corresponds with the aliphatic protons H1. The two triplets in the aromatic part of the ^1H NMR spectrum of **Q4** arise from the protons H5 and H6, whereas the doublets arise from H4 and H7. The aliphatic carbon atom C1 resonates at 38.0 ppm, which is confirmed by its direct coupling with H1 in the 2D-HETCOR experiment optimized for $J_{CH} = 140$ Hz. For further assignment we first have to analyze the 2D-HETCOR experiment optimized for $J_{CH} = 8$ Hz. H7 can be assigned to 7.35 ppm on the basis of its long range vicinal coupling with C1, since other protons are more than three bonds removed from C1. Therefore H4 can be assigned to the remaining doublet at 8.24 ppm. In the same way C3 can be assigned to 127.4 ppm through its long range vicinal coupling with H4. This is confirmed by the very low intensity of the C3 signal originating from an inadequate relaxation through dipole−dipole interactions with neighboring protons. The assignment of the ^{13}C NMR spectrum can be completed using the 2D-HETCOR experiment optimized for $J_{CH} = 140$ Hz. C4 and C7 can thus be assigned to 125.2 and 125.0 ppm. The carbon signals of C5 and C6 collapse at 126.9 ppm in the carbon spectrum. For this reason we did not perform a selective irradiation experiment for the unambiguous assignment of H5 and H6. Finally, a distinction between the two remaining quaternary carbons was made on the basis of a shorter spin−lattice relaxation time (T1) for C7a relative to C3a, which results in a smaller intensity for C3a compared to C7a. This makes it possible to assign 141.0 and 140.4 ppm to C7a and C3a, respectively. This is further confirmed in the 2D-HETCOR experiment optimized for $J_{CH} = 8$ Hz where C3a and C7a show a vicinal long range coupling with H7 and H4, respectively.

Table 1. ^{13}C Chemical Shifts ($CDCl_3$) of the Disilylated Monomer (A4), Dimer (A5), Trimer (A6), and Tetramer (A7) of Isothianaphthene

			A6		A7	
	A4	**A5**	ring A	ring B	ring A	ring B
C3	135.0	129.2	129.8	126.7	130.0	127.0
C3a	146.5	145.6	145.6	136.5	145.6	136.6[a]
C4	124.0	123.9	124.0	121.9	124.0	122.0
C5	122.6	123.7	123.8	124.7	123.8	124.9
C6		123.6	123.9		123.9	125.0
C7		122.0	121.9		121.9	121.9
C7a		137.5	137.6		137.7	136.7[a]
C1		132.2	131.6		131.5	126.1

[a] May be interchanged.

4. Discussion

The ^{13}C chemical shifts of the carbons C3, C3a, C4, and C5 of the central part of the third-order aromatic and quinoid model compounds will now be used to be compared with the corresponding second-order model compounds and to the values of PITN. The comparison to the second-order model compounds allows us to determine the influence of the S atom in the aromatic side groups and to criticize the usefulness of the previously reported second-order model compounds. The third-order aromatic and quinoid model compounds have to be mutually compared in order to check whether the ^{13}C shift of these carbons is a selective criterion of the geometric structure of PITN. Finally, these shifts are compared to the polymer data. The latter were determined with the aid of a multipurpose solid-state ^{13}C CP/MAS NMR pulse sequence. For the quaternary carbons, C3 and C3a, chemical shifts of 126 and 139 ppm (±0.5 ppm), respectively were obtained while the protonated carbons are located at 125 and 128.5 ppm (±1 ppm). We assumed that $\delta C5 > \delta C4$, a feature which was observed in the aromatic as well as the quinoid model compounds (second- and third-order).

4.1. Aromatic Model Compounds. (1) 1,3-Dithienylisothianaphthene: A3. In comparison to 1,3-diphenylisothianaphthene (**A2**), it appears that the chemical shifts of C3a, C4, and C5 of **A3** remain largely unaffected (Table 2). This means that the S atom of the neighboring thiophene ring has no significant influence on the chemical shift of C4 (nor a very weak electronic interaction through space with H4), which can only be explained by a rotation around the inter-ring (C3−C2′) bond. In contrast, the introduction of a S atom in the neighboring ring(s) has induced a change in the chemical shift of C3 of about 8 ppm (electronic interaction through the bonds). The shift of this carbon in the second-order model compound was therefore useless in the comparison to PITN.

Table 2. Comparison of the ^{13}C Chemical Shift Data of PITN and the Aromatic (A2, A3, and A7) and the Quinoid (Q2, Q3, and Q4) Model Compounds

	δ (ppm)			
	C3	C3a	C4	C5
A2	134.2	135.3	121.2	124.2
A3	126.5	135.4	121.5	124.8
A7	126.1	136.7	121.9	125.0
PITN	**126.0**	**139.0**	**125.0**	**128.5**
Q4	127.4	140.4	125.2	126.9
Q3	128.3	142.3	126.9	133.8
Q2	136.8	139.1	120.8	128.5

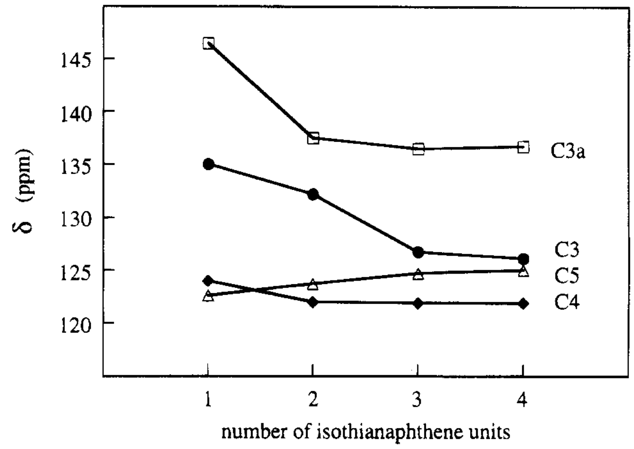


Figure 8. Evolution of the ^{13}C chemical shifts of the "central" carbon atoms C3, C3a, C4, and C5 of the isothianaphthene oligomers of **A4**–**A7** as a function of the chain length.

(2) Disilylated Isothianaphthene Oligomers (A4–A7). The ^{13}C chemical shift data of the oligomers are summarized in Table 1. In general, comparable carbons seem to have comparable chemical shifts in the different oligomers except for C3[A] in the monomer and the dimer (135.0 cf. 129.2 ppm). For these oligomers to be useful as model compounds for the corresponding polymer, they should contain one or more isothianaphthene rings which are no longer influenced by the end groups. This is indicated by a convergence of the chemical shift as a function of chain length. Therefore, we plotted the ^{13}C chemical shifts of the "central" carbons as a function of chain length (Figure 8). It should be noticed that the central aromatic carbons are uniformly referred to as C3, C3a, C4, and C5 although they correspond to C1, C7a, C7, and C6 in ring A of the dimer and in ring B of the tetramer, respectively. From Figure 8, it can be seen that C4 and C5 are almost independent of the end groups. Therefore the chain length is not important as far as the shifts of these carbons are concerned. For C3a, only the shift in the monomer is not suitable. The shift of the central C3 in the dimer (C1[A]) is still affected by the end groups, and a convergence is only reached starting from the trimer. For these oligomers, at least three isothianaphthene units are necessary in order to use the central part as a model for the structure of the corresponding polymer (for ^{13}C NMR purposes). The data in Figure 8 also illustrate that the usefulness of a certain molecule as a model compound can only be determined with the aid of a better model compound (e.g. if the data of the tetramer were not available, the convergence of C3 could not be observed). Therefore, the trimer and the tetramer can now be used to criticize the previous model compounds. The chemical shifts of the carbons of the central unit of the tetramer are very close to those observed for **A3** (Table 2). The introduction of some critical structural requirements (an aromatic isothianaphthene ring with aromatic side groups possessing a S atom) in a molecule seems to be enough to function as a useful model compound.

4.2. Quinoid Model Compounds. (1) *trans*-3,3′-Bibenzo[*c*]thienylidene-1,1′-dione (Q3). *trans*-3,3′-Bibenzo[*c*]thienylidene-1,1′-dione was the first molecule which gave us an idea about the influence of a S atom in the neighboring (quinoid) ring. As can be seen from Table 2, the shifts of C3, C4, and C5 have changed drastically in comparison to the second-order model compound **Q2**. The changes for C3 and C4 may be mainly caused by the neighboring S atom although it is hard to differentiate it from the contribution of the carbonyl end groups.

(2) *trans*-3,3′-Bibenzo[*c*]thienylidene (Q4). The influence of the carbonyl end groups, as mentioned above, has been removed in **Q4**. From the comparison with **Q2**, it appears that the neighboring S atom has a very strong effect on the shift of C3. This feature has previously been observed in the aromatic model compounds. But in contrast to the aromatic case, the shift of C4 has also significantly changed. As a consequence, the interaction between H4 and the neighboring S atom, mainly weakened in aromatic isothianaphthene systems by inter-ring rotation, is more intense in planar quinoid systems. If one takes into account the shift differences as a result of the electron-withdrawing effect of a carbonyl end group, it is clear that the data from **Q3** follow the same trend and are consistent with the data from **Q4**.

4.3. Comparison to PITN. The ^{13}C chemical shift data of the disilylated tetramer (**A7**) and *trans*-3,3′-bibenzo[*c*]thienylidene (**Q4**) will now be used for the comparison to the polymer data. We should however first check whether the shifts of C3, C3a, C4, and C5 are significantly different in an aromatic and in a quinoid environment. As we can see from Table 2, the shift of C3 is comparable in both structures and cannot be considered to be a selective criterion for the geometric structure. The other carbons C3a, C4, and C5 however show differences of about 2–4 ppm between the aromatic and the quinoid model compounds. The shifts of these carbons in PITN and the quinoid model compound **Q4** correspond well while there is no correspondence whatsoever between PITN and the aromatic tetramer (**A7**). These data confirm our previous results that the geometric structure of PITN shows a strong quinoid character.

5. Synopsis

In order to analyze the geometric structure of insoluble PITN, we estimated the ^{13}C chemical shift of the four inequivalent carbons (C3, C3a, C4, and C5) on the basis of a multipurpose solid-state ^{13}C CP/MAS NMR pulse sequence. These data were used to compare to those of model molecules unambiguously possessing either an aromatic or a quinoid structure. The "first-order" model compounds **A1** and **Q1** appeared to be useless for the comparison to the polymer data since the benzo[*c*]thiophene skeletons were no part of a conjugated π-system. The simulation of the structure of PITN was improved in the "second-order" model compounds **A2** and **Q2**. For the aromatic model compound, there is no correspondence whatsoever with PITN while the chemical shifts of C3a and C5 in the quinoid model compound are in nice agreement with the values of PITN. The observed significant difference for C3 and C4 was explained by the fact that the shift of these carbons in PITN is also influenced by the S atom of the neighboring unit. This situation is not accounted for in the second-order model compounds since they possess no S atoms in the aromatic side groups. This phenomenon obliged us to synthesize new "third-order" model compounds in which the chemical environment of C3 and C4 is also comparable to that in the polymer. The synthesis and the NMR characterization of these molecules are discussed in detail in the Experimental Section and Results of this paper.

For the aromatic third-order model compound **A3**, it appeared that the ^{13}C chemical shifts of C3a, C4, and C5 remain largely unaffected in comparison to the second-order model compound **A2**. This means that the S atom in the neighboring thiophene ring has no significant influence on the chemical shift of C4. In contrast, the S atom in the neighboring ring(s) has induced a change in the shift of C3 of about 8 ppm. This third-order model compound seemed to be a very good model for aromatic PITN since the ^{13}C data are very close to those of the central isothianaphthene ring in a disilylated aromatic tetramer (**A7**).

For the third-order quinoid model compound **Q4**, the neighboring S atom has a strong influence on the shift of C3 in comparison to the second-order model compound **Q2**. But in contrast to the aromatic case, the shift of C4 has also significantly changed. As a consequence, the interaction between H4 and the neighboring S atom, mainly weakened in aromatic isothianaphthene systems by inter-ring rotation, is more intense in planar quinoid systems.

For the comparison to PITN, only the carbons C3a, C4, and C5 of **A7** and **Q4** are valuable since C3 shows almost the same shift in the aromatic and the quinoid model compound. The shift of the three former carbons in PITN and in the quinoid model compound **Q4** correspond well while there is still no correspondence whatsoever between PITN and the aromatic tetramer (**A7**). These results are in favor of our previous conclusions,[2] indicating that the structure of PITN possesses a strong quinoid character. It should be noticed however that, because of the small energy difference ($\approx$2 kcal/mol per repeat unit) between the quinoid and the aromatic form derived from theoretical calculations, the structure of PITN may be determined much more by the chemistry of polymerization rather than the energy difference between the alternative structures. In fact the synthesis of the aromatic oligomers **A4**–**A7** can be viewed as an illustration of this principle. Further research will aim on the development of such a control of the geometry of low-band-gap polymers.

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Erratum

In our previous article (Hoogmartens et al. *Macromolecules* **1992**, *25*, 7347) on p 7355, left column, lines 26 and 27, δC3 should be replaced by δC3a.

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