Macromolecules **1996,** *29,* 5981−5989

Poly(tetrafluorobenzo[*c*]thiophene). Structure Analysis of Oligomers and Model Compound Based on 1D and 2D NMR Spectroscopy

R. Kiebooms,* P. Adriaensens, D. Vanderzande, and J. Gelan

Institute for Materials Research (IMO), Division Chemistry, Limburg University, Universitaire Campus, B-3590 Diepenbeek, Belgium

M. J. Swann and D. Bloor

Physics Department, Science Laboratories, South Road, Durham DH1 3LE, England

C. J. Drury and G. M. Brooke

Chemistry Department, Science Laboratories, South Road, Durham DH1 3LE, England

Received February 26, 1996; Revised Manuscript Received June 4, 1996⊗

ABSTRACT: In order to help provide a more detailed structural analysis of poly(4,5,6,7-tetrafluorobenzo-[*c*]thiophene), a series of aromatic fluorinated oligomers ($n = 1-4$) and 1,3-dithienyl-4,5,6,7-benzo[*c*]-thiophene have been synthesized. Structure analysis of these compounds by means of 1D and 2D NMR techniques provides a set of spectroscopic NMR data which can be considered as characteristic for the aromatic structure of the corresponding polymer. In addition to ^{19}F-decoupled ^{13}C NMR spectroscopy and attached fluorine tests, the method of full chemical shift assignment based on two-dimensional ^{1}H−^{13}C heteronuclear correlation (HETCOR) experiments optimized for $J_{CH} = 140$ Hz and $J_{CH} = 8$ Hz was extended with two-dimensional ^{19}F−^{13}C heteronuclear correlation (HETCOR) experiments optimized for $J_{CF} = 255$ Hz and $J_{CF} = 45$ Hz and ^{19}F−^{19}F homonuclear correlation spectroscopy (COSY).

1. Introduction

Low-band-gap conjugated polymers form an important class of advanced materials offering a combination of intriguing properties. In addition to an enhanced intrinsic conductivity the anticipated enhanced nonlinear optical properties suggested that these compounds may play an important role in the future development of polymer-based electronics and photonics.

In order to design new low-band-gap conjugated polymers an in-depth understanding of the relationship between the structure and the corresponding electronic properties of these materials is essential. Since poly(benzo[*c*]thiophene) (PBcT, poly(isothianaphthene), PITN) possesses a 1 eV band gap[1] as determined by optical absorption, this polymer has been under investigation for some time in order to establish a deeper understanding of the relationship between its structure and its observed low band gap. The first quantum chemical calculations by Brédas[2] were performed on the “aromatic” form **1** using the geometry of the monomer as a basis. These results correctly confirmed the 1 eV reduction of the band gap going from polythiophene to PBcT. However, Lee et al.[3] using a MNDO geometry optimization, suggested that PBcT should possess a “quinoid” structure **[2]** in its ground state. Subsequently, with the partial retention of diatomic differential overlap, Nayak et al.[4] found that the quinoid form of PBcT is very slightly favored over the aromatic one. Since there was a lack of experimental evidence the question whether the structure of PBcT is aromatic or quinoid, remained open. It is only recently that experimental results based on comparison of model compounds with NMR[5,6] and FT-Raman[7−12] spectroscopic data of the polymer indicate that PBcT should possess a geometric structure with a strong quinoid character. Therefore, in order to succeed in the targeted development of new low-band-gap polymers, theoretical techniques to estimate electronic properties should be combined with experimental structural data.

The surprisingly low band gap of PBcT and its transparancy upon doping[1,13,14] lead to the investigation of PBcT derivatives with enhanced processability and stability.[15−18] Since it was suggested[19] that the replacement of hydrogen by fluorine should provide, due to the absence of hydrogen, more stable materials less susceptible to atmospheric oxidation and an improved solubility, Brooke et al.[20] attempted the synthesis of poly(4,5,6,7-tetrafluorobenzo[*c*]thiophene) (PTFBcT) **[3]**. PTFBcT is a PBcT derivative which is surprisingly soluble in chlorinated as well as in other organic solvents. However the UV−visible spectrum shows a band gap of 2.1 eV. This result is in sharp contrast with the value of 1 eV obtained for PBcT. Increased nonbonding and dipole−dipole interactions induced by the substitution of fluorines in the 4 and 7 positions, causing nonplanar conformations, were proposed as an explanation for the enlargement of the band gap. Quantum-chemical calculations performed on TFBcT oligomers in the aromatic form[21] clearly indicate that these molecules are strongly nonplanar. Moreover, the rotation barrier to the planar conformation appears to be quite large. Therefore, packing effects would most probably not be sufficient to lead to a planar structure in the solid state. In any case, to understand more clearly the structural cause of this enlargment of the band gap, a detailed analysis of the structure of the polymer is required.

Since the presence of the fluorine atoms has a drastic effect on the geometric structure of PTFBcT, we wondered if we could find spectroscopic evidence for a shift toward an aromatic from a quinoid structure for PTFBcT. For this purpose we need a set of oligomeric model compounds which should allow us to determine by extrapolation the spectroscopic characteristics of the corresponding polymer.

⊗ Abstract published in *Advance ACS Abstracts,* July 15, 1996.

S0024-9297(96)00311-7 CCC: $12.00

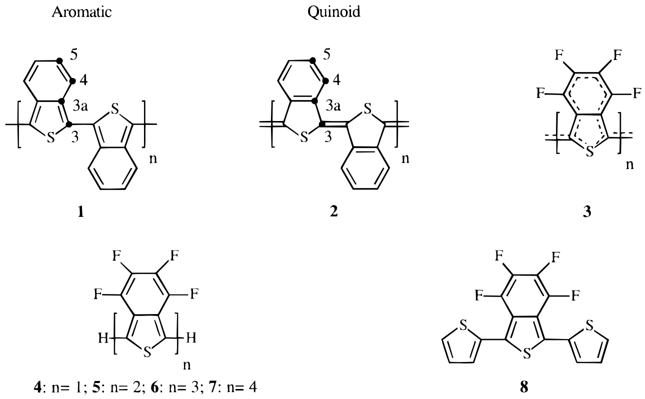
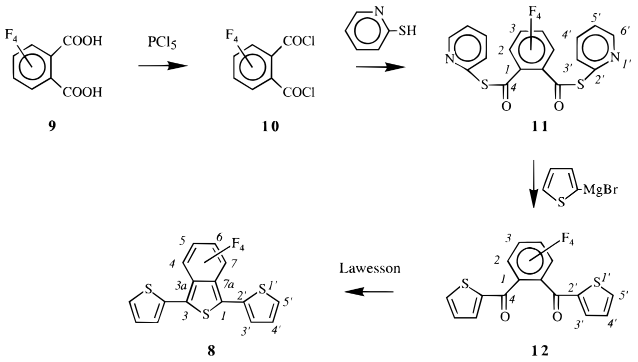


Figure 1. Aromatic **[1]** and quinoid **[2]** structures of PITN, TFPITN **[3]**, the fluorinated aromatic oligomers **[4−7]** and an aromatic model compound, 1,3-dithienyl-4,5,6,7-tetrafluorobenzo[*c*]thiophene **[8]**.

Scheme 1. Synthesis of 1,3-Dithienyl-4,5,6,7-tetrafluorobenzo[*c*]thiophene [8][a]



[a] The indicated numbering is used for assignment of the different NMR chemical shifts.

Recently,[22] the synthesis of aromatic fluorinated benzo[*c*]thiophene oligomers has been accomplished. In this paper we focus on a detailed NMR analysis of this set of aromatic fluorinated benzo[*c*]thiophene oligomers **[4−7]** containing up to four monomer units. As shown previously,[6] the ^{13}C chemical shifts of the central carbon atoms in these kind of oligomers tends to reach a convergence limit from the trimer. We synthesized also 1,3-dithienyl-4,5,6,7-tetrafluorobenzo[*c*]thiophene **[8]**. This molecule can be considered as a model compound for the aromatic structure of the corresponding fluorinated benzo[*c*]thiophene polymer. Comparison of its spectroscopic data with the data obtained from analysis of the series of oligomers should test the possibility of use of **8** as a model for the aromatic structure.

2. Experimental Section

2.1. Measurements. ^{1}H, ^{13}C, and ^{19}F NMR spectra of the model compounds were obtained with a Varian Unity 400 spectrometer. All the spectra were recorded in $CDCl_3$ at 30 °C. The chemical shifts of the carbon and the hydrogen being 77.0 and 7.24 ppm, respectively, from tetramethylsilane were used to reference the ppm scale. The fluorine spectra were referenced externally against monofluorobenzene (35% in $CFCl_3$ with 12.5% $CDCl_3$ for lock) at −113.43 ppm which was referenced against $CFCl_3$ at 0 ppm.[23,24] Assignments were based on the coupling patterns, the integration, attached proton tests (APT), attached fluorine tests (AFT), selective irradiation experiments, two-dimensional ^{19}F−^{19}F COSY experiments, two dimensional ^{1}H−^{13}C heteronuclear correlation (HETCOR) experiments optimized for J_{CH} = 140 Hz and J_{CH} = 8 Hz, and two-dimensional ^{19}F−^{13}C heteronuclear correlation (HETCOR) experiments optimized for J_{CF} = 255 Hz and J_{CF} = 45 Hz. The IR spectra were recorded with a Philips Pye Unicam SP-300. The FT-IR and the FT-Raman data were obtained via an 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. 4,5,6,7-Tetrafluorobenzo[*c*]thiophene oligomers [4−7]. Oligomers were synthesized as previously reported[22] by lithiation of TFBcT monomer and coupling with copper(II) chloride followed by workup and separation by column chromatography.

•**4,5,6,7-Tetrafluorobenzo[*c*]thiophene (monomer) [4].** IR (KBr, ν, cm^{-1}): 3131, 1683, 1653, 1579, 1541, 1495, 1440, 1408, 1355, 1262, 1191, 1159, 1120, 1036, 992, 868, 763, 681, 625, 483. FT-Raman (ν, cm^{-1}): 3135, 1686, 1581, 1541, 1498, 1382, 1359, 1322, 1297, 1265, 1158, 1126, 990, 892, 874, 767, 748, 682, 631, 612, 486, 453, 404, 349, 296, 279, 228, 194, 153, 122, 86. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, in ppm relative to TMS): 7.82 (t, 2, J = 1.5 Hz, H3). ^{13}C NMR (400 MHz, $CDCl_3$, 30 °C, in ppm relative to TMS): 115.55 (C3), 125.68(C3a), 136.66 (C5), 138.34 (C4). ^{19}F NMR (400 MHz, $CDCl_3$, 30 °C, in ppm relative to TMS): −149.22 (J = 1.5, 15.6; F4), −162.99 (J = 15.6; F5).

•**Dimer [5].** IR (KBr, ν, cm^{-1}): 1671, 1641, 1570, 1508, 1489, 1429, 1409, 1372, 1349, 1248, 1219, 1160, 1135, 1077, 1055, 1037, 978, 958, 912, 853, 835, 802, 754, 728. FT-Raman (ν, cm^{-1}): 3134, 3111, 1685, 1584, 1547, 1491, 1445, 1356, 1249, 1230, 1193, 1138, 1120, 1048, 1024, 975, 943, 898, 761, 749, 720, 705, 648, 632, 534, 492, 461, 403, 375, 324, 295, 282, 239, 207, 188, 126, 81. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, in ppm relative to TMS): 8.00 (H3). ^{13}C NMR (400 MHz, $CDCl_3$, 30 °C, in ppm relative to TMS): 117.51 (C3), 123.74 (C1), 123.92 (C7a), 126.60 (C3a), 136.68 (C5), 137.96 (C6), 138.01 (C4), 139.46 (C7). ^{19}F NMR (400 MHz, $CDCl_3$, 30 °C, in ppm relative to TMS): −149.31 (F4), −150.10 (F7), −160.36 (F6), −162.06 (F5).

•**Trimer [6].** IR (KBr, ν, cm^{-1}): 3128, 2957, 2925, 2855, 1677, 1656, 1639, 1628, 1581, 1526, 1490, 1467, 1450, 1438, 1380, 1350, 1255, 1232, 1186, 1141, 1123, 1085, 1060, 1027, 995, 958, 930, 881, 760, 748, 717, 674, 646, 627, 525, 431. FT-Raman (ν, cm^{-1}): 1583, 1546, 1495, 1454, 1355, 186, 125. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, in ppm relative to TMS): 8.05 (H3(A)). ^{13}C NMR (400 MHz, $CDCl_3$, 30 °C, in ppm relative to TMS): 118.10 (C3(A)), 122.81 (C1(A)), 124.06 (C7a(A)), 124.70 (C3a(B)), 125.37 (C3(B)), 126.72 (C3a(A)), 136.79 (C5(A)), 137.97 (C5(B)), 138.076 (C4(A)), 138.178 (C6(A)), 139.30 (C4(B)), 139.45 (C7(A)). ^{19}F NMR (400 MHz, $CDCl_3$, 30 °C, in ppm relative to TMS): −148.97 (F4(A)), −149.41 (F4(B)), −149.70 (F7(A)), −159.666 (F6(A)), −159.672 (F5(B)), −161.66 (F5(A)).

•**Tetramer [7].** IR (KBr, ν, cm^{-1}): 3112, 2920, 2851, 1681, 1579, 1526, 1489, 1352, 1260, 1234, 1182, 1135, 1058, 1031, 1000, 952, 911, 884, 802, 761, 711, 658, 627, 474. FT-Raman (ν, cm^{-1}): 3113, 1682, 1584, 1540, 1493, 1458, 1354, 1265, 1234, 1198, 1155, 1125, 1066, 988, 954, 892, 804, 764, 740, 691, 643, 628, 544, 491, 467, 440, 405, 384, 366, 327, 286, 271, 243, 189, 156, 117, 94. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, in ppm relative to TMS): 8.07 (H3(A)). ^{13}C NMR (400 MHz, $CDCl_3$, 30 °C, in ppm relative to TMS): 118.310 (C3(A)), 122.560 (C1(A)), 124.082 (C7a(A)), 124.302 (C1(B)), 124.721 (C3a(B)), 124.778 (C7a(B)), 126.000 (C3(B)), 126.724 (C3a(A)), 136.800 (C5(A)), 138.011 (C5(B)), 138.078 (C4(A)), 138.140 (C6(B)), 138.217 (C6(A)), 139.261 (C4(B)), 139.338 (C7(B)), 139.428 (C7(A)). ^{19}F NMR (400 MHz, $CDCl_3$, 30 °C, in ppm relative to TMS): −148.96 (F4(A)), −149.20 (F4(B)), −149.20 (F7(B)), −149.78 (F7(A)), −159.14 (F6(B)), −159.45 (F5(B)), −159.56 (F6(A)), −161.65 (F5(A)).

•**3,4,5,6-Tetrafluorophthaloyl Chloride [10].** 3,4,5,6-Tetrafluorophthalic acid **[9]** (0.0084 mol) and 0.0252 mol (5.25 g) phosphorus pentachloride were slowly heated till 180 °C was reached (caution: HCl evaporates at a temperature of about 60 °C). The mixture was kept for 2 h at 180 °C under vigorous stirring and then allowed to cool to room temperature. The remaining phosphorus pentachloride was removed by filtration of the liquid into a vacuum distillation apparatus.

The reaction flask was washed with 10 mL of toluene and transferred to a vacuum distillation apparatus. The purification by vacuum distillation yields a liquid which was further used in the thioester synthesis. Yield: 2.2 g (94%). Bp: 180 °C (5mmHg). IR (KBr, ν, cm^{-1}): 1770, 1490, 1390, 1205, 1100, 930, 910, 720; MS (CI, *m*/*e*): 275 (MH$^+$), 239, 221, 165. ^{13}C NMR (CDCl$_3$, 400 MHz, in ppm relative to TMS): 120.06 (C), 143.6 (CF), 145.5 (CF), 161.5 (CO). ^{19}F NMR (fluorobenzene, 400 MHz, in ppm relative to CFCl$_3$): −134.56, −144.82.

•1,2-Bis((*S*)-(2-pyridinyl))-3,4,5,6-tetrafluorobenzenedithioate [11]. The reaction should be carried out in a glovebox under nitrogen atmosphere at an ambient temperature of 10 °C because of the sensitivity of the thioester toward moisture. A sodium methanolate solution was prepared by adding at 0 °C 0.015 mol (0.35 g) Na to 50 mL of methanol and 0.0168 mol (1.86 g) of 2-mercaptopyridine, and this mixture was then cooled to −78 °C. A solution of 0.0084 mol (2.3 g) of 3,4,5,6-tetrafluorophthaloyl chloride **[10]** in 25 mL of toluene was added dropwise under vigorous stirring. The precipitate is filtered off and rapidily washed with methanol (−78 °C). Yield: 1.53 g (43%). Mp: 71.5 °C (decomposition). IR (KBr, ν, cm^{-1}): 1690, 1655, 1560, 1490, 1450, 1435, 1410, 1350, 1300, 1280, 1130, 1085, 980, 810, 790, 760, 740. FT-Raman (ν, cm^{-1}): 3147, 3130, 3072, 3057, 2995, 2894, 1697, 1667, 1620, 1575, 1563, 1512, 1452, 1424, 1362, 1303, 1284, 1160, 1140, 1121, 1090, 1046, 990, 899, 820, 798, 752, 724, 686, 621, 587, 559, 488, 448, 411, 395, 365, 325, 310, 219, 206, 134, 109, 93. MS (EI, *m*/*e*): 424 (M$^+$), 333, 314, 305, 286, 258, 242, 223, 214, 195, 167, 148, 117. ^{1}H NMR (CDCl$_3$, 400 MHz, in ppm relative to TMS): 7.30 ($J = 6.05, 4.84, 2.55$; H5′), 7.73 (H4′, H3′), 8.60 ($J = 4.71, 1.22$; H6′). ^{13}C NMR (CDCl$_3$, 400 MHz, in ppm relative to TMS): 121.67 (C1), 124.29 (C5′), 130.24 (C3′), 137.52 (C4′), 142.25 (C3), 144.94 (C2), 149.74 (C2′), 150.64 (C6′), 184.06 (CO). ^{19}F NMR (fluorobenzene, 400 MHz, in ppm relative to CFCl$_3$): −135.81 (F2), −147.31 (F3).

•1,2-Dithienoyl-3,4,5,6-tetrafluorobenzene [12]. The Grignard reagent was prepared by adding 0.02 mol of 2-bromothiophene (2 mL) in 50 mL of THF to 0.02 mol of activated Mg (0.5 g) together with an iodine crystal in 50 mL of THF. This mixture was heated under vigorous stirring for 3.5 h. Then a solution of 0.01 mol of crude tetrafluoro thioester **[11]** (4.2 g) in 150 mL of THF was prepared and cooled to 0 °C. The Grignard reagent was added slowly to this solution. After the addition was completed, the mixture was stirred for another 1.5 h. The reaction was completed by adding 200 mL of HCl (10%). After extraction with diethyl ether the combined fractions were successively washed with 500 mL NaOH (10%), 500 mL NaHCO$_3$ (10%), and 500 mL of water. Further purification of the product can be done by direct crystallization from CHCl$_3$/*n*-hexane or by performing a column chromatogaphic purification (silica, CHCl$_3$/*n*-hexane). Yield: 3.5 g (95%). Mp: 118 °C; IR (KBr, ν, cm^{-1}): 1620, 1510, 1470, 1410, 1375, 1350, 1310, 1240, 1320, 1090, 1080, 1060, 815, 795, 765, 730, 680. FT-Raman (ν, cm^{-1}): 3116, 3096, 2539, 1648, 1511, 1410, 1383, 1355, 1317, 1237, 1082, 1063, 941, 867, 804, 753, 672, 627, 567, 498, 472, 417, 366, 311, 232, 182, 139, 103. MS (EI, *m*/*e*): 370 (M$^+$), 325, 287, 271, 166, 111, 83. ^{1}H NMR (CDCl$_3$, 400 MHz, in ppm relative to TMS): 7.09 (t; $J = 4.8, 1.1$; H4′), 7.51 (dd; $J = 3.8, 0.9$; H3′), 7.74 (dd; $J = 3.9, 5.1$; H5′). ^{13}C NMR (CDCl$_3$, 400 MHz, in ppm relative to TMS): 123.45 (C1), 128.60 (C4′), 136.17 (C3′), 136.85 (C5′), 141.57 (C3), 143.13 (C2′), 144.85 (C2), 180.54 (C4). ^{19}F NMR (fluorobenzene, 400 MHz, in ppm relative to CFCl$_3$): −136.68 (F2), −150.35 (F3).

•1,3-Dithienyl-4,5,6,7-tetrafluorobenzo[*c*]thiophene [8]. A mixture of 0.0014 mol of 1,2-dithienoyl-3,4,5,6-tetrafluorobenzene **[12]** (0.5 g), 0.0014 mol Lawesson reagent (0.4 g) and 50 mL of dichloromethane were stirred for a maximum of 1 h at 45 °C. After evaporation of the dichloromethane 50 mL of ethanol was added and the mixture was refluxed for another 30 min. Finally, 100 mL of water was added and the product was extracted with diethyl ether. The combined diethylether fractions were washed with 500 mL of NaOH (10%) and 500 mL of water and dried on magnesium sulfate. Finally, a column chromatographic purification (silica, *n*-hexane) yielded 0.48 g (95%). Mp: 184.6 °C. IR (KBr, ν, cm^{-1}): 2920, 1660, 1560, 1470, 1415, 1365, 1340, 1260, 1215, 1125, 1080, 1040, 1020, 1010, 970, 955, 855, 800, 750, 695. FT-Raman (ν, cm^{-1}): 3118, 3070, 2959, 2655, 2568, 1674, 1539, 1526, 1493, 1441, 1398, 1347, 1240, 1225, 1167, 1145, 1080, 1061, 1042, 857, 836, 751, 737, 704, 647, 629, 580, 508, 487, 407, 364, 315, 266, 250, 201, 185, 110, 73. MS (EI, *m*/*e*): 370 (M$^+$), 203 (M$^+$ − 2Ar). ^{1}H NMR (CDCl$_3$, 400 MHz, in ppm relative to TMS): 7.11 (t; $J = 5.1, 1.0$; H4′), 7.27 (dd; $J = 3.4, 1.4$; H3′), 7.43 (dd; $J = 5.1, 3.6$; H5′). ^{13}C NMR (CDCl$_3$, 400 MHz, in ppm relative to TMS): 121.78 (C3a), 127.85 (C4′), 127.85 (C5′), 127.86 (C3), 129.16 (C3′), 132.70 (C2′), 137.15 (C5), 139.13 (C4). ^{19}F NMR (fluorobenzene, 400 MHz, in ppm relative to CFCl$_3$): −145.68 (F4), −161.70 (F5). UV−vis (λ_{max}, ϵ) in *n*-hexane: 400 (12 656), 269(16 372), 227(23 159).

3. Full ^{1}H, ^{13}C, and ^{19}F Chemical Shift Assignment

3.1. General Approach. The fluorinated aromatic oligomeric compounds **4−7** and **8** contain exclusively sp^2 carbon nuclei causing signals in the ^{13}C NMR spectra which are located in a narrow chemical shift region. For the structural analysis of the oligomers and the model compound we need to perform an unambiguous chemical shift assignment of the carbon, proton, and fluorine signals.

An analysis strategy[6] which permits discrimination between carbon or proton atoms even if their NMR signals are very close together in the spectra has already been developed. In this paper we show how this approach can be extended to a full unambiguous assignment of the chemical shifts in compounds containing fluorine nuclei, bearing in mind that the main principles also apply to other NMR nuclei.

In this procedure, we start with the unambiguous assignment of at least one carbon, hydrogen, or fluorine atom based on the molecular structure in order to be able to establish a further assignment pathway. For this purpose one makes use of *chemical shift*, *first-order splitting or coupling pattern*,[25] *coupling values*,[26] and *peak areas*. If necessary *specific 1D NMR techniques* (nuclear Overhauser effect (NOE), attached proton test (APT), attached fluorine test (AFT), proton and fluorine (de)coupling, selective irradiation, e.g.) and the *heteronuclear coupling behavior* of a particular atom in 2D NMR experiments will be applied to obtain an additional objective starting point. The chemical shifts of these assigned atoms are then used as starting points to elaborate a pathway for further assignment of the signals originating from the other nuclei.

In general 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). However, in these fluorinated compounds the direct and long range ^{1}H−^{13}C heteronuclear correlations will be further used as the starting point for the two-dimensional fluorine homonuclear (^{19}F−^{19}F COSY) and heteronuclear (^{19}F−^{13}C HETCOR) correlation pathway.

3.2. Parametrization of 1D and 2D ^{19}F NMR Experiments. Before the ^{19}F NMR experiments were started, the fluorine spectra were referenced externally against fluorobenzene (35% in CFCl$_3$ with 12.5% CDCl$_3$ for lock) at −113.43 ppm which was referenced against CFCl$_3$ at 0 ppm.[23,24]

For optimization of the parameters used in ^{19}F decoupling and ^{19}F−^{13}C HETCOR experiments 2,2-difluorotetrachloroethane, CClF$_2$CCl$_3$, was used. The fluorines have a chemical shift of −61.448 ppm, and the carbon shifts are 126.193 and 96.375 ppm. Since two fluorines are present on the same carbon nucleus, the

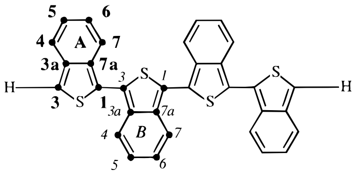


Figure 2. Numbering of the benzo[*c*]thiophene ring systems in the tetrafluorinated oligomers **[4−7]**.

^{19}F-coupled ^{13}C NMR spectrum shows a triplet for the fluorinated carbon atom, which was used to calibrate the Waltz decoupling modulation. For the $^{19}F-^{13}C$ HETCOR experiments the ^{19}F pulse width needed to be calibrated very accurately by means of a DEPT sequence.

Direct $^{19}F-^{13}C$ HETCOR experiments were performed with optimization at different values for J. The best results for direct $^{19}F-^{13}C$ heteronuclear correlation were obtained at an optimization value for $J = 255$ Hz. Geminal coupling between ^{19}F and ^{13}C occurs at values of J between 20 and 45 Hz. To exclude vicinal couplings ($^3J = 10-20$ Hz) the heteronuclear correlation experiment was optimized for $J = 45$ Hz. At this optimization some direct couplings are still present. In order to be able to distinguish between different types of fluorinated carbon atoms an analoguous pulse sequence as for the APT was used to discriminate between CF and CF_3 fluorinated carbon atoms and C and CF_2 carbon nuclei. In this type of 1D NMR experiment, the signals of CF and CF_3 carbons become negative while those of C and CF_2 carbons remain positive when the correct parameters are used. The evolution time in this case was set at $1/J_{CF} = 3.92 \times 10^{-3}$ s. Due to its analogy with APT this test will further be referred to as attached the fluorine test (AFT). Notice that the fluorine coupling remains in the APT spectra while the proton coupling remains in the AFT spectra. The numbering of the hydrogen, carbon, and fluorine nuclei used in the NMR analysis is shown in Figure 2. In the monomer for reasons of symmetry the nuclei at positions 4[A] and 7[A] have identical chemical shifts, as have the nuclei at positions 5[A] and 6[A]. The same remark can be made for ring B in the trimer.

3.3. Aromatic Model Compounds. (1) 4,5,6,7-Tetrafluorobenzo[*c*]thiophene (monomer) [4]. Since only two hydrogen atoms with the same chemical surrounding are present for these compounds, the signal in the ^1H NMR spectrum at 7.82 ppm can be assigned to H3. With the aid of the direct $^1H-^{13}C$ HETCOR spectrum optimized for $J_{CH} = 140$ Hz, C3 can be assigned to the signal at 115.55 ppm, which is confirmed by APT. The long range $^1H-^{13}C$ HETCOR spectrum optimized for $J_{CH} = 8$ Hz (vicinal couplings) can then be used to assign C4 to 138.34 ppm because C4 is the only fluorinated carbon which can couple with H3 since C5 is too far removed from H3. From this assignment and the AFT it follows that the signal at 136.66 ppm belongs to C5, the remaining fluorinated carbon. The remaining quaternary carbon atom C3a can be assigned to the signal at 125.68 ppm. This is confirmed by the combination of APT and AFT. On the basis of the direct $^{19}F-^{13}C$ HETCOR spectrum optimized for $J_{CF} = 255$ Hz we can assign F4 and F5 to −149.22 and −162.99 ppm, respectively. This assignment is in agreement with literature data[27] of comparable compounds.

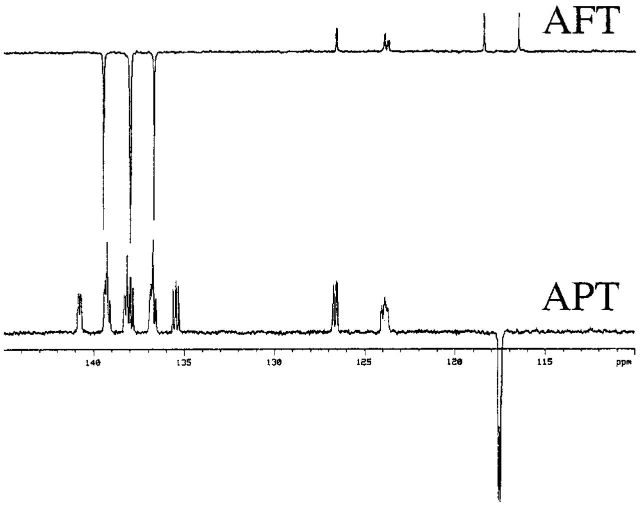


Figure 3. Attached fluor test (AFT) and attached proton test (APT) of **5** ($CDCl_3$, 30 °C).

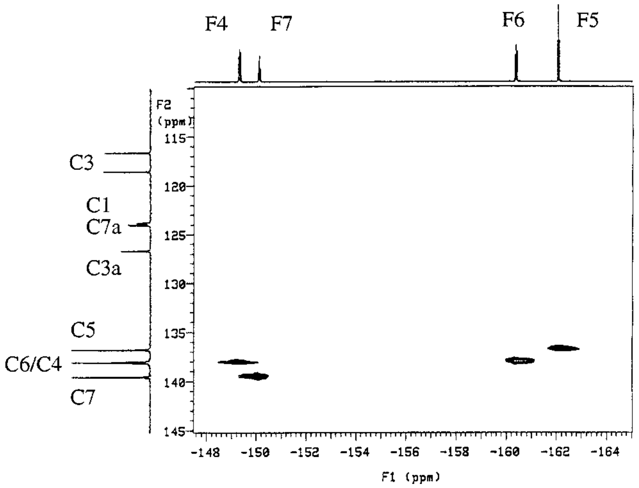


Figure 4. 2D heteronuclear $^{19}F-^{13}C$ correlation spectrum of **5** optimized for $J_{CH} = 255$ Hz ($CDCl_3$, 30 °C).

This unambiguous chemical shift assignment allows us to further analyze some aspects of the 2D $^{19}F-^{13}C$ HETCOR spectra. From the direct $^{19}F-^{13}C$ HETCOR spectrum optimized for $J_{CF} = 255$ Hz we can localize the direct $^{19}F-^{13}C$ coupling signals. With this knowledge and with the full chemical shift assignment we can now investigate the $^{19}F-^{13}C$ HETCOR spectrum optimized for $J_{CF} = 45$ Hz. Besides the expected geminal and some direct couplings for C3a, C4 and C5, an unanticipated long-range ^4J coupling between C3 and F5 is also clearly observed.

(2) Dimer [5]. H3 can be assigned to the signal at 8.00 ppm in the proton spectrum. The assignment strategy is similar to that employed for the monomer. Again H3 is used as the starting point for further assignments. The direct $^1H-^{13}C$ HETCOR spectrum optimized for $J_{CH} = 140$ Hz permits the assignment of C3 to the signal at 117.51 ppm which is confirmed by APT and AFT (Figure 3). For the assignment of C4 the long range $^1H-^{13}C$ HETCOR spectrum optimized for $J_{CH} = 8$ Hz is used. Thus C4 corresponds to the signal at 138.01 ppm. This assignment is further confirmed by the fact that a proton coupling of 3.8 Hz is present on the ^{19}F-decoupled carbon signal. On the basis of the direct $^{19}F-^{13}C$ HETCOR spectrum optimized for $J_{CF} = 255$ Hz (Figure 4) we can assign F4 to the signal at −149.31 ppm. For further assignment we need to identify F5 or F6. Due to the value of a F−F ortho (20 Hz) and F−F para (12−14 Hz) coupling,[23] the $^{19}F-^{19}F$ COSY (Figure 5) will show correlation signals for F4

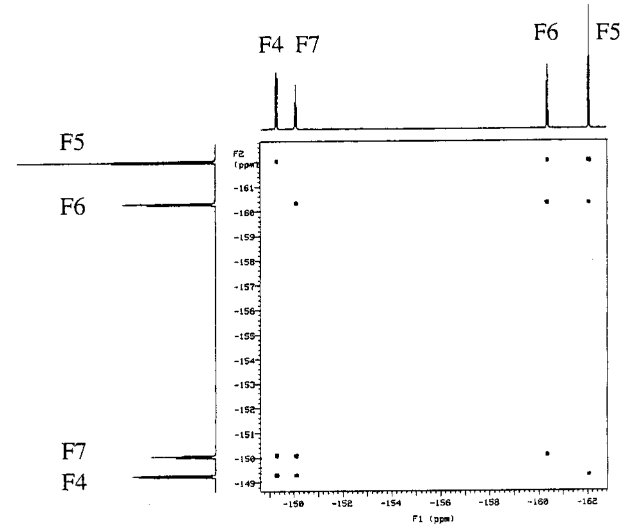


Figure 5. 2D heteronuclear $^{19}F-^{19}F$ correlation spectrum (COSY) of **5** ($CDCl_3$, 30 °C).

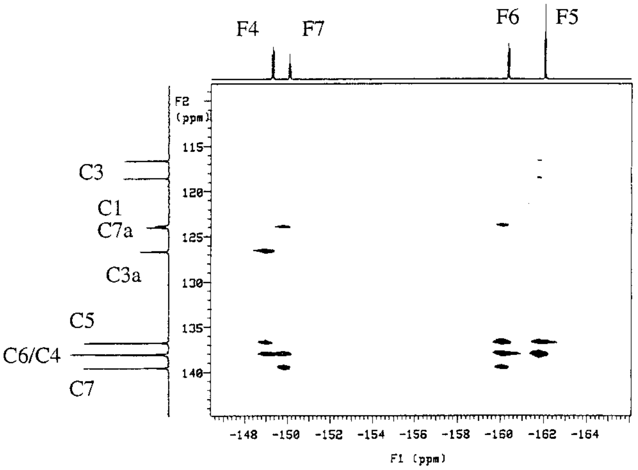


Figure 6. 2D heteronuclear $^{19}F-^{13}C$ correlation spectrum of **5** optimized for $J_{CH} = 45$ Hz ($CDCl_3$, 30 °C).

with both F7 and F5, while F6 (F−F meta coupling: 2−3 Hz) will not correlate with F4 and therefore can be assigned to −160.36 ppm. Through the direct $^{19}F-^{13}C$ HETCOR spectrum optimized for $J_{CF} = 255$ Hz we can now assign C6 to 137.96 ppm. With F4/C4 and F6/C6 known, we can now analyze the $^{19}F-^{13}C$ HETCOR spectrum optimized for $J_{CF} = 45$ Hz (Figure 6) for assignment of C5 and C7. From analysis of the monomer spectrum we find that only direct and geminal $^{19}F-^{13}C$ couplings will be present as far as the fluorinated carbon nuclei are concerned. Since the direct $^{19}F-^{13}C$ couplings of F4/C4 and F6/C6 can be identified through the $^{19}F-^{13}C$ HETCOR spectrum optimized for $J_{CF} = 255$ Hz the other correlation signals originate from a geminal coupling. F4 can only show a geminal coupling with the C5. This allows us to assign C5 to 136.68 ppm. On the other hand F6 has a geminal coupling with C5 and C7. Since C5 has been assigned previously, the remaining signal at 139.46 belongs to C7. On the basis of the $^{19}F-^{13}C$ HETCOR-spectrum optimized for $J_{CF} = 255$ Hz we can now assign F5 and F7 to −162.06 and −150.10 ppm, respectively. This assignment was expected from the monomer ^{19}F spectrum (F4 and F7 around −150 ppm and F5 and F6 around −160 ppm).

Finally, we only have to assign the quaternary carbon atoms. For this purpose we have to analyze again the $^{19}F-^{13}C$ HETCOR spectrum optimized for $J_{CF} = 45$ Hz (Figure 6). For consistency with the $^{19}F-^{13}C$ HETCOR spectrum optimized for $J_{CF} = 45$ Hz of the monomer, we identify all the correlation signals present as originating only from direct and geminal couplings. Although no other long range correlation signals than geminal correlations are present, we again notice a correlation between the protonated carbon C3 and F5. This ^4J coupling was also present in the monomer and probably finds its origin in the particular geometry of the benzo[*c*]thiophene ring system. If such a coupling exists between C3 and F5 then an analogous coupling should exist between C1 and F6. Indeed, in the $^{19}F-^{13}C$ HETCOR spectrum optimized for $J_{CF} = 45$ Hz there is a correlation signal between F6 and the quaternary carbon atom at 123.74 ppm, which therefore can be assigned to C1. The two remaining correlation signals from F4 and F7 with the other quaternary carbon atoms result from a geminal coupling. This allows us to assign C3a and C7a to the signals at 126.60 and 123.93 ppm, respectively. In the fluorine-decoupled spectrum the presence of a proton coupling of 2.5 Hz (^2J) on the carbon signal at 126.60 ppm (C3a) and of 7.9 Hz (^3J) on the carbon signal at 123.93 ppm (C7a) and 123.74 ppm (C1) confirms these assignments. Since for C1 the value of the coupling corresponds with a vicinal long range coupling, this means that in this specific case coupling takes place across a heteroatom.

(3) Trimer [6]. For the trimer and tetramer, only a selected number of figures is shown. Since the chemical shift assignment is, however, rather crucial, a short description of the main arguments used in the assignment (see also Experimental Section) strategy is given below as for the monomer and dimer.

H3(A) can easily be assigned to the signal at 8.05 ppm. As previously, the direct $^1H-^{13}C$ HETCOR spectrum optimized for $J_{CH} = 140$ Hz permits us to assign C3(A) to the signal at 118.10 ppm, which is confirmed by APT. Through the long range $^1H-^{13}C$ HETCOR spectrum optimized for $J_{CH} = 8$ Hz we can associate C4(A) with the signal at 138.08 ppm, which is confirmed by the presence of some proton coupling in the fluorine-decoupled spectrum. This allows us using the direct $^{19}F-^{13}C$ HETCOR spectrum optimized for $J_{CF} = 255$ Hz to assign F4(A) to the signal at −148.97 ppm.

In the $^{19}F-^{19}F$ COSY F4(A) shows a coupling signal with the fluorine signals at −161.66 and −149.70 ppm. Since we know from the analysis of monomer and dimer that the signals of F4/F7 and F5/F6 are situated around −150 and −160 ppm, respectively, we are able to assign the signals at −161.66 and −149.70 ppm to F5(A) and F7(A), respectively. Therefore F6(A) should be assigned to the multiplet between −159.6 and −159.8 ppm. For the identification of F4(B) and F5(B) it is quite reasonable to make the assumption, which is based on the assignment of the fluorine atoms in the monomer and dimer. Therefore we assign F4(B) to the remaining signal at −149.41 ppm. F5(B) on the other hand can also be associated with the multiplet between −159.6 and −159.8 ppm. Through selective irradiation of F7(A) and F4(B) it is, however, possible to discriminate between F6(A) and F5(B). The triplet of F6(A) should transform in a doublet when F7(A) is irradiated whereas the doublet of F5(B) should become a singlet upon irradiation of F4(B). This allows us to assign F6(A) and F5(B) to the signals at −159.66 and −159.67 ppm, respectively. Since all the fluorine chemical shifts are known the fluorinated carbon atoms can easily be assigned through the direct $^{19}F-^{13}C$ HETCOR spectrum

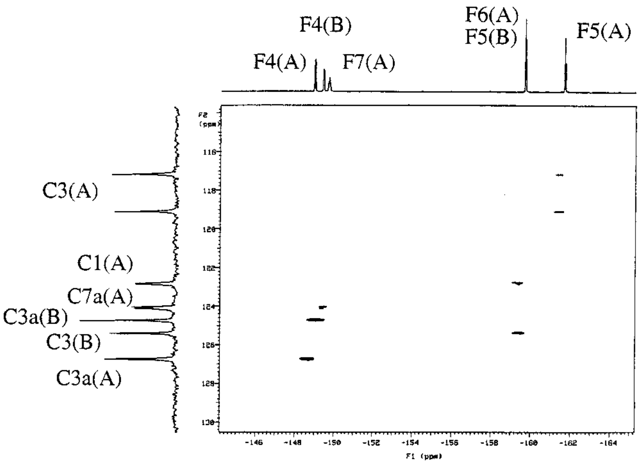


Figure 7. 2D heteronuclear $^{19}F-^{13}C$ correlation spectrum of **6** optimized for J_{CH} = 45 Hz ($CDCl_3$, 30 °C) showing the quaternary carbon nuclei.

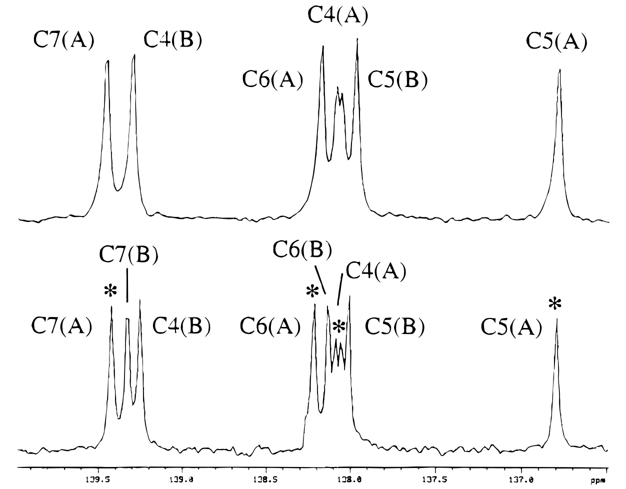


Figure 8. Comparison of the ^{19}F-decoupled ^{13}C NMR spectra of the fluorinated carbon nuclei of **6** (top) and **7** (bottom). (*: assigned on the basis of HETCOR, COSY, ...)

optimized for J_{CF} = 255 Hz. Therefore F5(A), F6(A), F7(A), F4(B), and F5(B) are associated with the signals at 136.79, 138.18, 139.45, 139.30, and 137.97 ppm, respectively. The assignment of the quaternary carbon atoms can only be based on the analysis of the $^{19}F-^{13}C$ HETCOR spectrum optimized for J_{CF} = 45 Hz. The part of the 2D spectrum showing the correlation signals between the fluorinated carbon atoms and the fluorines conforms with the particular pattern that one may expect from a combination of direct and geminal couplings. Furthermore we notice the ^4J correlation between C3(A) and F5(A) as in the monomer and dimer. In analogy with the assignment in the dimer we can assign C1(A) to 122.81 ppm based on the presence of a ^4J correlation signal with F6(A) and the presence of a proton coupling originating from H3. As we may expect C3a(A) and C7a(A) to show only geminal correlations with F4(A) and F7(A), respectively, we can assign them to the signals at 126.72 and 124.06 ppm, respectively. This assignment is confirmed by the presence of a geminal and vicinal proton−carbon coupling of 2.7 and 7.8 Hz, respectively. Since the presence of the ^4J correlation signal is consistent in the monomer, dimer, and ring A of the trimer (Figure 7) we can now use this phenomenon to assign C3(B) to the signal at 125.37 ppm. As a consequence the remaining quaternary signal at 124.70 ppm should therefore be assigned to C3a(B), which is confirmed by its geminal coupling with F4(B).

(4) Tetramer [7]. The assignment of the only proton H3(A) to 8.068 ppm is rather straightforward. From the fluorine-decoupled spectrum we can easily assign C3(A) to the signal at 118.31 ppm. As in the other oligomers one of the fluorinated carbon signals (138.08 ppm) shows a small proton coupling and can therefore be assigned to C4(A). This allows identification of F4(A) at −148.96 ppm using the direct $^{19}F-^{13}C$ HETCOR spectrum optimized for J_{CF} = 255 Hz. Through $^{19}F-^{19}F$ COSY we found F5(A) to correspond with the signal at −161.65 ppm and as a consequence C5(A) is located at 136.80 ppm with the aid of the direct $^{19}F-^{13}C$ HETCOR spectrum optimized for J_{CF} = 255 Hz. On the basis of the same reasoning as for the trimer we found from $^{19}F-^{19}F$ COSY that F6(A) and F7(A) are to be assigned to the signals at −159.56 and −149.78 ppm, respectively. Direct fluorine−carbon coupling allows us to assign C6(A) and C7(A) to the signals at 138.22 and 139.43 ppm, respectively. To assign the other fluorinated carbons and fluorines of ring B we have to take recourse to comparison of the ^{19}F-decoupled ^{13}C NMR spectrum of the trimer and the tetramer (Figure 8). The chemical shifts marked with an asterisk in the spectrum of the tetramer have been assigned using HETCOR and COSY. The assigned shifts from ring A differ very little from the corresponding shifts in the trimer spectrum. We can thus presume the carbon signals of C4(B) and C5(B) do not undergo an important change in chemical shift. Therefore we assign C4(B) and C5(B) to 139.26 and 138.01 ppm, respectively. From this comparison between trimer and tetramer it appears that the carbons C4/C7 and C5/C6 are grouped around 139 and 138 ppm, respectively, with the exception of C4(A) and C5(A). This observation can be used to assign the two remaining carbon signals at 139.34 and 138.14 ppm to C7(B) and C6(B), respectively. This assignment is in agreement with the direct $^{19}F-^{13}C$ HETCOR spectrum optimized for J_{CF} = 255 Hz. Indeed, C4(B) and C7(B) show a coupling with the multiplet at −149.20, the “F4/F7” side of the fluorine spectrum. On the other hand C5(B) and C6(B) show a correlation signal with −159.45 and −159.14 ppm, two multiplets at the “F5/F6” side of the fluorine spectrum. This allows us in addition to assign F4(B), F7(B), F5(B), and F6(B) to −149.20, −149.20, −159.45, and −159.14 ppm, respectively. This assignment is further confirmed with the aid of selective irradiation at the different fluorine resonances.

The assignment of the quaternary carbon atoms is complicated in the higher order oligomers by the fact that we have to rely only on long range correlations to complete our assignment. Moreover, since we have to differentiate between several quaternary carbon nuclei, a relatively high resolution long range $^{19}F-^{13}C$ HETCOR spectrum is needed. However, the low solubility of the tetramer makes this long range HETCOR experiment rather time-consuming. This led us at first to rely on additional information provided by the comparison of ^{19}F- and ^1H-decoupled ^{13}C NMR spectra. The signals at 122.56, 124.08, and 126.72 ppm are the only quaternary carbon atom signals to possess a proton coupling (Figure 9) and should therefore belong to nuclei of ring A. When we compare subsequently this part of the ^1H-decoupled ^{13}C NMR spectrum of trimer and tetramer, we are able to assign these signals to C1(A), C7a(A), and C3a(A), respectively. This assignment is further confirmed by a long range $^{19}F-^{13}C$ HETCOR spectrum

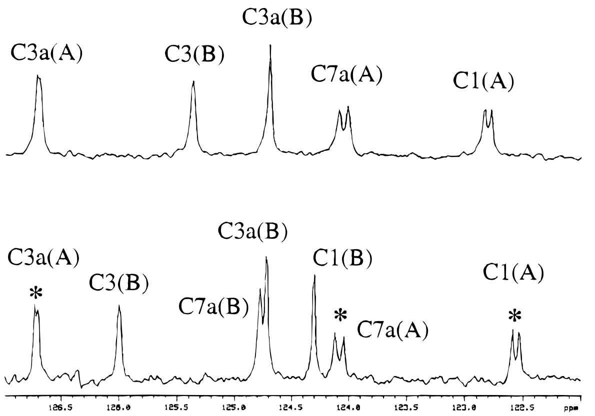


Figure 9. Comparison of the ^{19}F-decoupled ^{13}C NMR spectra of the quaternary carbon nuclei of **6** (top) and **7** (bottom). (*: assigned on the basis of the coupling pattern.)

optimized for $J_{CF} = 45$ Hz (spectrum not shown). This spectrum allows us to associate C3a(B) and C7a(B) with the signals at 124.72 and 124.78 ppm, respectively. Comparison of the ^{1}H-decoupled ^{13}C NMR spectrum of trimer and tetramer permits us to assign C3a(B) to 124.72 ppm, which implies that C7a(B) should be assigned to the signal at 124.778 ppm. For the assignment of the remaining quaternary carbon atoms C3(B) and C1(B) we have to take recourse to the specific ^4J coupling between C1−F5 and C3−F6 consistently present in the long range ^{19}F−^{13}C HETCOR spectrum optimized for $J_{CF} = 45$ Hz of the other oligomers. This allows us to assign C1(B) and C3(B) to 124.30 and 126.00 ppm, respectively.

(5) 1,3-Dithienyl-4,5,6,7-tetrafluorobenzo[c]thiophene [8]. After investigation of the molecular structure of compound **8** one might come across two starting points. The first one is the ^{1}H NMR shift of H4′ which is characterized by its specific coupling pattern. This coupling pattern is made up by two coupling constants originating from two different ortho couplings. Therefore H4′ can be assigned to the multiplet at 7.11 ppm. Following this, C4′ can be assigned to the signal at 129.85 ppm using the direct ^{1}H−^{13}C HETCOR spectrum optimized for $J_{CH} = 140$ Hz. From the long range ^{1}H−^{13}C HETCOR spectrum optimized for $J_{CH} = 8$ Hz C2′ can be assigned to the chemical shift at 132.70 ppm, since it is the only quaternary carbon nucleus to be able to show a long range coupling with H4′. The presence of proton coupling on this signal in the fluorine-decoupled spectrum confirms this assignment.

On the basis of quantitative ^{13}C, APT, and AFT experiments the signal at 127.85 ppm in the proton-decoupled ^{13}C NMR spectrum appears to be the result of the collapse of a quaternary and two protonated carbon signals. Since this makes it impossible to use the long range ^{1}H−^{13}C HETCOR spectrum optimized for $J_{CH} = 8$ Hz for identification of the other thiophene proton and carbon signals, we have to resort to comparison with analogous 1,3-dithienylbenzo[c]thiophene compounds.[6,28] This allows us to assign H3′ and H5′ to 7.43 and 7.27 ppm, respectively. With the aid of the direct ^{1}H−^{13}C HETCOR spectrum optimized for $J_{CH} = 140$ Hz we can as a consequence assign C3′ and C5′ to the signals at 129.16 and 127.845 ppm.

Since one of the remaining quaternary carbon signals is collapsing with C5′, it is impossible to use as a second starting point the fact that C3 is the only remaining quaternary carbon atom within the benzo[c]thiophene ring to be able to show a long range coupling with H3′ of the thiophene ring. Indeed, the correlation signal corresponding with H3′ in the long range ^{1}H−^{13}C HETCOR spectrum optimized for $J_{CH} = 8$ Hz can also originate from the coupling of C5′ with H3′ and, as a consequence, it is not clear whether the correlation signal of the signal at 127.845 ppm with H3′ is the result of two couplings, namely C3 with H3′ and C5′ with H3′, or results from the coupling of C5′ with H3′ alone. Since, in this circumstance, it is impossible to determine whether the quaternary carbon atom at 127.6 ppm shows a long range coupling with H3′ or not, we need another starting point for further analysis.

Table 1. ^{13}C Chemical Shifts (CDCl$_3$) of the Fluorinated Monomer [4], Dimer [5], Trimer [6], and Tetramer [7] of 4,5,6,7-Tetrafluorobenzo[c]thiophene and the Shifts of the Benzo[c]thiophene ring of 1,3-Dithienyl-4,5,6,7-tetrafluorobenzo[c]thiophene [8]

			6		**7**		
	4	**5**	ring A	ring B	ring A	ring B	**8**
C$_3$	115.55	117.51	118.10	125.37	118.31	126.00	127.68
C$_{3a}$	125.68	126.60	126.72	124.70	126.72	124.72	121.78
C$_4$	138.34	138.01	138.08	139.30	138.08	139.26	139.13
C$_5$	136.66	136.68	136.79	137.97	136.80	138.01	137.15
C$_6$		137.96	138.18		138.22	138.14	
C$_7$		139.46	139.45		139.43	139.34	
C$_{7a}$		123.92	124.06		124.08	124.78	
C$_1$		123.74	122.81		122.56	124.30	

From the NMR analysis of the benzo[c]thiophene ring systems of the fluorinated oligomers, it was noticed that the F4/F7 side of the spectrum always was localized at about −149 ppm while the F5/F6 side was situated around −160 ppm. So the two fluorine signals at −145.68 and −161.70 ppm were associated with F4 and F5, respectively. As the fluorine signals have been assigned, we can now use the direct ^{19}F−^{13}C HETCOR spectrum optimized for $J_{CF} = 255$ Hz to assign the fluorinated carbon atoms. Thus C4 and C5 correspond with the shifts at 139.13 and 137.15 ppm, respectively. Using the long range ^{19}F−^{13}C HETCOR spectrum optimized for $J_{CF} = 45$ Hz we can next assign C3a to the signal at 121.78 ppm due to the presence of a geminal correlation signal. This assignment is further confirmed by the presence of a pronounced fluorine coupling in the proton-decoupled ^{13}C NMR spectrum. Also here we noticed a ^4J long range coupling between F5 and a quaternary carbon atom in the long range ^{19}F−^{13}C HETCOR spectrum optimized for $J_{CF} = 45$ Hz. For the fluorinated oligomers this observation appeared to be very characteristic for fluorinated benzo[c]thiophene ring systems. Since we were able to identify this correlation signal as the result of a coupling between F5 and C3, we can assign C3 to the quaternary carbon signal at 127.86 ppm.

4. Discussion

It has been shown previously[5,6] that the ^{13}C chemical shifts of the central part of suitable oligomers can be used to discriminate between different molecular structures, e.g. between aromatic and quinoid geometries. Therefore the chemical shifts of the carbons C3, C3a, C4, and C5 of the central part of the fluorinated aromatic model compounds will now be compared with each other in order to ascertain if within these series of model compounds convergence in the chemical shifts has been reached.

The ^{13}C chemical shift data of the oligomers **4**−**7** are summarized in Table 1. For these oligomers to be useful as model compounds for resonance assignment of the

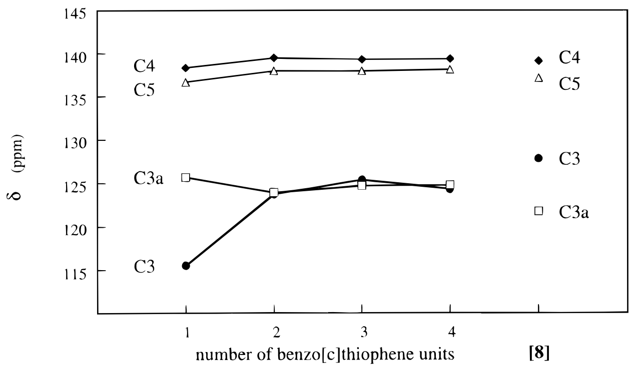


Figure 10. Evolution of the ^{13}C chemical shifts of the "central" carbon atoms C3, C3a, C4, and C5 of the fluorinated benzo[*c*]thiophene oligomers **[4−7]** as a function of the chain length. Comparison of the ^{13}C chemical shifts of the "central" carbon atoms C3, C3a, C4, and C5 of the fluorinated tetramer **[7]** with the "central" carbon atoms of 1,3-dithienyl-4,5,6,7-tetrafluorobenzo[*c*]thiophene **[8]**.

corresponding polymer, they should contain one or more benzo[*c*]thiophene rings which are no longer influenced by the end groups, which in this case contains a hydrogen nucleus, H3(A). That this is indeed the situation 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 10). 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 10 it can be seen that the shifts for C4 and C5 are almost independent of the end groups; therefore, the chain length is unimportant as far as the shifts of these carbons are concerned. This result is in agreement with analogous results[6] obtained on a set of aromatic disilylated benzo[*c*]thiophene compounds. C3a reaches a plateau from the dimer onward; only the shift in the monomer is not suitable for comparison with the polymer. The most drastic changes take place for the shift of the quaternary carbon atom C3 because it is protonated in the monomer. However, convergence is already reached going from trimer to tetramer. Since C3 can be considered to form the backbone of these oligomers, the chemical shift of this carbon will be subject to more pronounced changes due to a difference in end groups. Going from monomer to dimer, a hydrogen is replaced by a fluorinated benzo[*c*]thiophene group. Hence, for these oligomers, at least three benzo[*c*]thiophene 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).

In the ^{13}C NMR spectrum of the PTFBcT polymer we find three signals. The fluorinated carbons C4 and C5 can be associated with the signals at 139.32 and 138.32 ppm, respectively. The signal at 124.90 ppm corresponds most probably with C3 as well as C3a. From comparison of these chemical shifts with those of the aromatic fluorinated tetramer, there appears to be a strong correspondence.

In order to evaluate to what extent we can extract some structural information from a simpler model compound, we also synthesized 1,3-dithienyl-4,5,6,7-tetrafluorobenzo[*c*]thiophene **[8]**. In this compound the fluorinated benzo[*c*]thiophene core is surrounded by two thiophene ring systems in order to simulate an extended π-system and the spatial interaction between the sulfur and the fluorine of neighboring ring systems. However, it should be noticed that the use of a thiophene ring system to simulate a neighboring fluorinated benzo[*c*]thiophene ring is not ideal. From comparison of the chemical shifts of **8** with the "central" carbon atoms of the fluorinated tetramer we see that there is already a relatively good correspondence between the shifts of C4 and C5 of both compounds. However, a significant difference is present between the quaternary carbon nuclei. Results for the oligomers show that the quaternary carbon nuclei turned out to be more sensitive toward substitution. This difference in chemical shift can be explained when we take into account the fact that we use two electron rich thiophene ring systems to simulate the relatively electron poor neighboring benzo[*c*]thiophene ring systems. Therefore the difference in shift of C3 and C3a of **8** with those of the corresponding atoms of the tetramer can be understood in terms of differences in electron density caused by the thiophene rings. The increase of electron density on C3a will cause an upfield shift, whereas a decrease of the electron density on C3 causes a downfield shift as compared to the tetramer. Despite such inherent imperfection, this model compound allows one to obtain a reliable idea about the chemical shift value of C4 and C5 in an aromatic fluorinated benzo[*c*]thiophene ring system.

6. Conclusion

A detailed analysis based on 1D and 2D NMR techniques was used to evaluate the evolution of the chemical shifts of equivalent carbon nuclei in oligomeric fluorinated benzo[*c*]thiophene model compounds unambiguously possessing an aromatic structure. For this purpose the principle of full chemical shift assignment was extended to include NMR experiments based on fluorine homonuclear (^{19}F−^{19}F COSY) and heteronuclear (^{19}F−^{13}C HETCOR) correlations. Moreover, the classical attached proton test (APT) was adapted for fluorine to discriminate between CF/CF$_3$ and C/CF$_2$ carbon nuclei. From this NMR analysis the shifts of the "central" carbon atoms within these model compounds show a clear convergence from trimer to tetramer. The chemical shift values of the "central" carbon atoms can therefore be considered as being representative of fluorinated poly(benzo[*c*]thiophene) possessing an aromatic structure. Furthermore the analysis of a more simple model compound indicates that from this model compound it is also possible to obtain a reliable indication of the chemical shift values of C4 and C5, despite the important structural and chemical changes induced by the fluorine nuclei.

Finally, from comparison of the chemical shifts of PTFBcT with those of the aromatic fluorinated tetramer, there appears to be a strong correspondence indicating that this fluorinated poly(benzo[*c*]thiophene) derivative possesses an aromatic structure. It is noteworthy that recent quantum-chemical calculations on the aromatic and quinoid forms of PTFBcT also suggest that the aromatic polymer is the most stable structure.[21]

Acknowledgment. The authors are indebted to the Instituut tot Aanmoediging van Wetenschappelijk Onderzoek in Nijverheid en Landbouw (IWONL) and the Vlaams Instituut voor de Bevordering van het Wetenschappelijk-Technologische Onderzoek in de Industrie (IWT), for a predoctoral fellowship to R.K. Research grant aid for M.J.S. and C.J.D. from the Engineering and Physical Science Research Council (EPSRC) is also greatfully acknowledged

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MA960311N