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EPR investigations of β-deuteriated 5,5″-dimethyl-2,2′:5′,2″-terthiophenes

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The unambiguous assignment of the β-hyperfine coupling constants of the radical cations of 5,5″-dimethyl-2,2′:5′,2″-terthiophene (11) has been achieved by EPR spectroscopic investigations of the deuteriated compounds 12, 13 and 14. The syntheses of these substances were achieved by cross-coupling following the Negishi and Kumada reaction starting from deuteriated derivatives of chloromethylated thiophene derivatives. The generation of the radical cations was carried out by electrochemical oxidation at a constant potential in the EPR spectrometer. In the presence of acidic compounds a D–H exchange at the β-positions of oligothiophenes was observed. The experimentally determined spin density distribution was rationalized by means of semiempirical quantum mechanical calculations (RHF-INDO-SP). Theoretical and experimental assignments are in good agreement.

Introduction

Oligothiophenes are interesting compounds because of their application as constituents of mesogenic compounds,[1,2] liquid-crystalline polymers and particularly as well defined model oligomers for conducting polymers.[3,4] The first step during the formation of electrical conducting polymers is the oxidation of suitable monomers, *e.g.* oligothiophene derivatives. For a better understanding of the polymerization reaction the electron spin density distribution of the reactive intermediates in these reactions is very important. In a previous paper[5] we reported in detail the EPR and ENDOR studies of radical cations of various β-methylated and methyl end-capped α-linked bi-, ter- and quater-thiophenes. Blocking the reactive α-positions of the radical cations by methyl groups causes increasing stability. The structural assignment of the hyperfine coupling constants (hfc) was possible by RHF-INDO-SP calculations.[6] It has been demonstrated that the differences between the experimental and theoretical values are small.[7] Bäuerle *et al.*[8] also used the RHF-INDO-SP method for the characterization of the electronic structure of an oxidized sexithiophene. Other often used methods for calculating the hyperfine coupling constants are the McConnel,[9] the McLachlan,[10] the INDO[11] and the MINDO/3[12] procedures. Often the evaluation of the same hfcs by different calculation methods, *e.g.* INDO, MINDO/3 and McLachlan, gives different qualitative results.[13] For a reliable identification the synthesis and EPR investigation of deuteriated compounds is indispensable.

Our aim in this paper is to show the exact identification of the electron spin density distribution in the β-positions of the 2,2′:5′,2″-terthiophene system by using the deuteriated compounds **12–14**.

Results and discussion

The synthesis of the new deuteriated end-capped terthiophene derivatives **12–14** was carried out by cross-coupling by the Kumada reaction,[14] starting with the corresponding deuteriated chlorothiophene **8** and the deuteriated chloromethylthiophenes **6** and **7** (Scheme 1).

The preparation of the compounds **6–8** is shown in Scheme 2. The deuteriation grade of the compounds **12–14** is more than 93%.

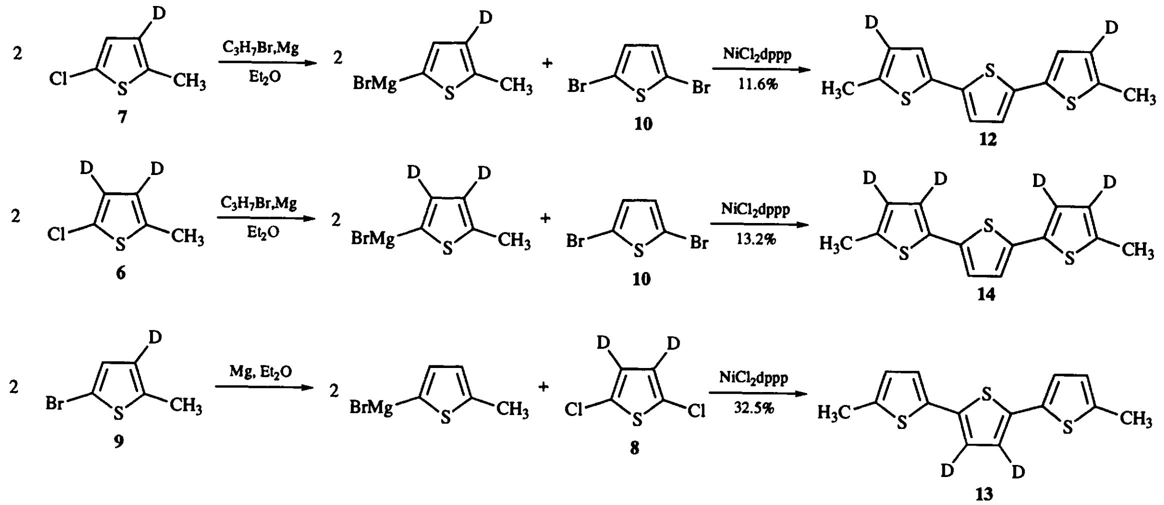
The synthesis of **1**, **2**, **9**, **10**, 5,5″-dimethyl-2,2′:5′,2″-terthiophene (**11**), 5,5′-dimethyl-2,2′-bithiophene (**15**) and 5,5‴-dimethyl-2,2′:5′,2″:5″,2‴-quaterthiophene (**16**) is described in the literature. Compound **11** serves as a reference substance. The structure of the deuteriated terthiophenes was proven by MS, IR, ^{1}H and ^{13}C NMR spectroscopy. Fig. 1 demonstrates the influence of the different sets of deuterium atoms in the ^{1}H NMR spectra of **11–14**.

A very good method for generating radical cations from oligothiophenes is chemical oxidation in trifluoroacetic acid with small amounts of oxygen.[15] Oligothiophene radical cations without substituents in the β-positions are planar and exist as *cis* and *trans* conformers.[5] Conformational analysis of various β-methylated oligothiophene radical cations is also given in this paper. Using compound **11**, Kirste *et al.*[5] demonstrated that deuteriated trifluoroacetic acid changes the EPR spectrum. A better example of this is given by 5,5′-dimethyl-2,2′-bithiophene (**15**). When deuteriated trifluoroacetic acid was used as solvent, rapid exchange of all ring protons was observed, resulting in only a septet pattern due to the six methyl protons (a = 0.895 mT). Furthermore, a second splitting is obvious with a hfc of 0.0625 mT, caused by one set of the deuterium atoms (Fig. 2). For this reason it makes no sense to measure the deuteriated terthiophenes **12–14** under these conditions.

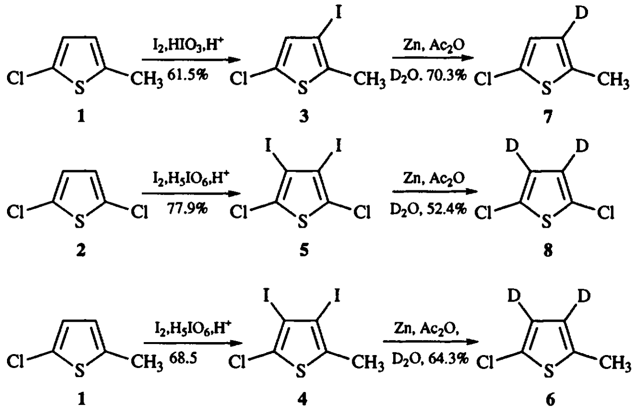
Hill *et al.*[16] reported EPR investigations of electrochemically generated radical cations of end-capped terthiophenes. This publication inspired us to construct an electrolysis cell which, in combination with an EPR flat cell, gave a useful arrangement for dynamical *in situ* measurements (Fig. 3). For experimental details see the Experimental section.

For the unambiguous identification of the three types of β-positions in the radical cation of compound **11** two sets of β-hfcs must be completely resolved. With our system of measurement it was possible to detect two ring-hfcs, one of them appears only as a shoulder. For a better separation of the peaks, the second derivative of the EPR signal was recorded (Fig. 4).

Under the following conditions it was possible to reproduce



Scheme 1



Scheme 2

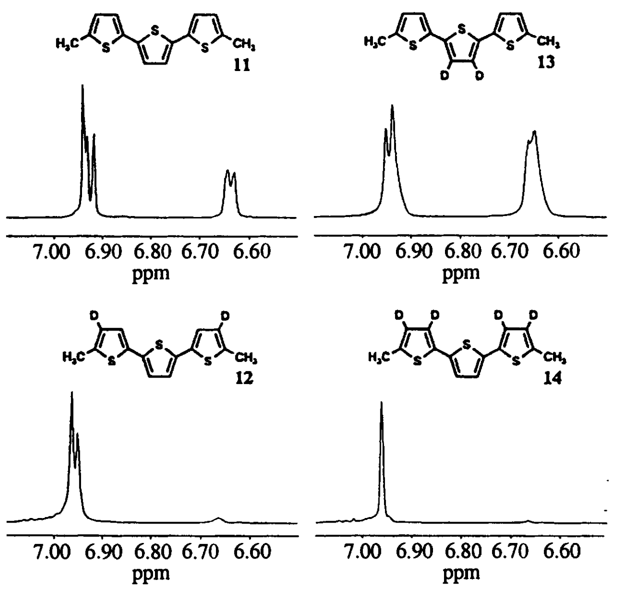


Fig. 1 ^{1}H NMR spectra (250 MHz, TMS) of the different β-deuteriated terthiophenes **11**–**14**

the spectral pattern of the EPR spectra: $c_{\mathrm{D_{ep}}} = 10^{-3}$ mol l^{-1}, 0.1 M TEABF$_4$–AN, potentiostatic coulometry at 1 V *vs.* SCE, flow rate = 0.018 ml s^{-1} and an amplitude of modulation of 0.05 mT. All substances were measured according to these specifications. Fig. 5 shows the experimental and simulated second derivatives of the EPR spectra for compounds **11**–**14**. The spectra of compound **11** and **12** are identical.

The simulations were carried out in the following way: integrating the experimental spectra (second derivatives), simulating the resulting first derivatives and comparing the spectra. If the experimental and simulated spectra were identical, then the procedure was stopped. To compare the simulated and experimental spectra directly the calculated first derivatives were differentiated. For the EPR spectrum of compound **14** a program with automatic fit was used.[17] The obtained hfcs (mT) and linewidths (lw) (mT) are summarized in Table 1. With the calculated hfcs and the linewidths it was possible to reproduce the experimental spectra completely in contrast to a 'stick' diagram. The least squares method serves as a criterion of exactness.

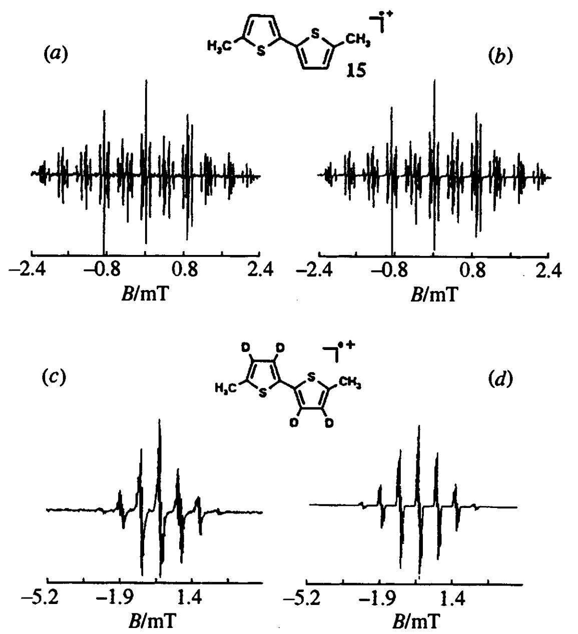


Fig. 2 Influence of deuteriated trifluoroacetic acid on the EPR spectrum of 5,5′-dimethyl-2,2′-bithiophene (**15**); (*a*, *c*) measured and (*b*, *d*) simulated

For a better understanding of the classification of hfcs in Fig. 6, the hfcs and the corresponding β-ring positions of the radical cations of compound **11** are shown. To demonstrate this, the second derivative of the EPR signal was used.

Comparison of the EPR spectra of the compounds **11** and **12** in Fig. 5 shows that the deuteriation of the 4,4″-positions of compound **11** has no influence on the spectrum of **11** in contrast to that for the terthiophene **14**. Here both the 4,4″ and 3,3″ ring positions are deuteriated. The EPR spectrum of **14** shows the greatest change of all spectra with respect to the undeuteriated compounds. The complete simulation of the experimental spectra was possible by taking into consideration 3.4% of non-

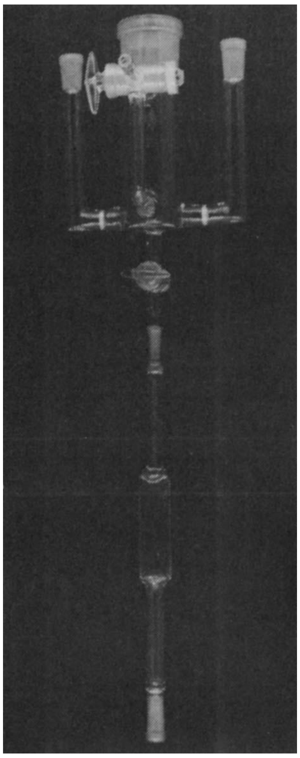


Fig. 3 A combination of an electrolysis cell and an EPR flat cell was used for the *in situ* investigation of the deuteriated terthiophenes **11**–**14**. The lower end of the flat cell was closed by a capillary.

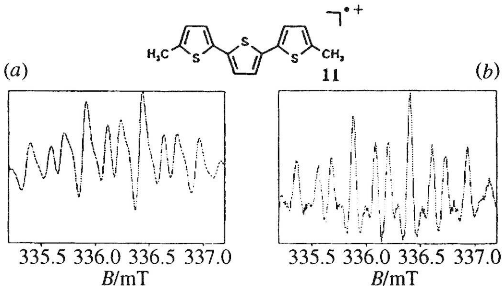


Fig. 4 Part of the experimental EPR spectra of the radical cations of compound **11**; (*a*) first derivative and (*b*) second derivative of the EPR signals

deuteriated compound **11** and the hfcs from Table 1. Therefore it must be concluded that the 3,3″-positions have the largest hfc of the β regions and the 4,4″ positions the smallest. The EPR spectrum of compound **13** with deuteriated 3′,4′-positions is reduced by one set of peaks in comparison to the spectrum of compound **11**. The missing hfc (0.2112 mT) corresponds to the middle value of the three β hfcs. Experimentally, the following sequence was obtained: hfc 3,3″ (0.3266 mT) > hfc 3′,4′ (0.2112 mT) > hfc 4,4″ (smaller than the linewidth). It is remarkable that by RHF-INDO-SP-calculations not only the sequence of the hfcs is correct, but also its amounts are of an excellent quality (Fig. 7). This result underlines not only the superiority of this quantum mechanical method for the investigation of oligothiophenes, but also of the high quality of the experiments performed in this study.

Experimental

5-Chloro-3-iodo-2-methylthiophene (3)

According to Gronowitz and Hagen,[18] to a solution of 24.0 g (0.18 mol) 2-chloro-5-methylthiophene (**1**) in 43 ml tetrachloromethane, 115 ml acetic acid, 53 ml water and 2 ml concentrated sulfuric acid, 18.1 g (71 mmol) iodine and 6.4 g (36 mmol) HIO_3 were added. After refluxing and stirring for 11 h, the mixture was cooled to room temperature. The organic phase was separated, washed with 2 M aqueous sodium hydrogensulfite, water and dried with sodium sulfate. The solvent was evaporated and the crude product was distilled *in vacuo*; yield 28.73 g **3**, 62%; red liquid, bp 62–64 °C/0.05 mbar; n_D^{20} = 1.6341; ν(KBr)/cm^{-1} 3099 (m), 2949 (schw), 2915 (m), 2851 (schw), 1522 (st), 1378 (m), 1296 (m), 1141 (st), 1028 (st), 817 (st), 768 (st), 640 (m) and 577 (m); δ_H($CDCl_3$, TMS, 250 MHz) 6.76 (s, 1 H, H4) and 2.34 (s, 3 H, CH_3); δ_C($CDCl_3$, TMS, 62.9 MHz) 137.477, 132.93, 131.868, 128.03 and 18.085 (CH_3); *m*/*z* 260/258 (36.4/100.0) [M^+], 223 (3.7) [$(M - Cl)^+$], 133/131 (13.0/36.3) [$(M - I)^+$], 96 (7.0) [$(M - Cl - I)^+$] and 95 (7.0) [$(M - Cl - I - H)^+$] (Found: C, 23.16; H, 1.38; Cl, 14.15; I, 48.56; S, 12.75. C_5H_4ClIS requires C, 23.23; H, 1.56; Cl, 13.71; I, 49.09; S, 12.41%).

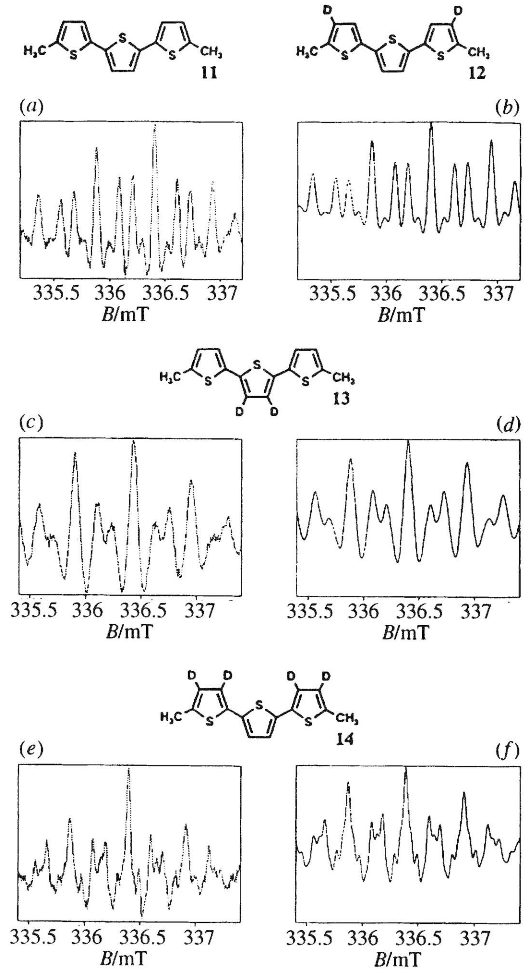
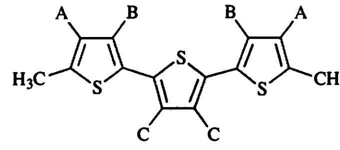


Fig. 5 Parts of the experimental (*a*, *c*, *e*) and simulated (*b*, *d*, *f*) second derivatives of the EPP signal of **11** and the different β-deuteriated terthiophenes **12**–**14**

2-Chloro-3,4-diiodo-5-methylthiophene (4)

According to Ayres *et al.*,[19] a mixture of 24.4 g (0.18 mol) 2-chloro-5-methylthiophene (**1**), 39.4 g (0.15 mol) iodine, 17.8 g (78 mmol) periodic acid, 115 ml acetic acid, 24 ml water and 3.2 ml concentrated sulfuric acid was stirred at 90 °C. During the reaction the product was precipitated, filtered off after cooling and stirred for 2 h in a saturated aqueous sodium dithionite solution at 60 °C. The product was separated, washed with water and ethanol and recrystallized from ethanol; yield 45.4 g **4**, 64%; pale yellow crystals; mp 64 °C (ethanol); ν(KBr)/cm^{-1} 2908 (schw), 1946/1930 (m), 1657 (m), 1499 (m), 1435 (st), 1000 (m), 819 (st), 724 (m) and 692 (m); δ_H($CDCl_3$, TMS, 250 MHz) 2.5 (s, 3 H), CH_3); δ_C($CDCl_3$, TMS, 62.9 MHz) 138.426, 127.769, 95.396, 92.617 and 20.424 (CH_3); *m*/*z* 386/384 (36.1/100.0) [M^+], 259/257 (14.5/39.7) [$(M - I)^+$], 132/130

Table 1 Measured and calculated hfcs (a) and linewidth (lw) for compounds **11**–**14**



A	B	C	No.	$a(CH_3)$/mT	a(B)/mT	a(C)/mT	rel. Int.%	lw/mT
H	H	H	**11**	0.5361	0.3266	0.2112	100	0.09
H	H	D	**13**	0.5253	0.3205	0.028	100	0.065
D	H	H	**12**	0.5361	0.3266	0.2112	100	0.09
D	D	H	**14**	0.5188	0.0502	0.2072	96.6	0.076
				0.5218	0.3217	0.1995	3.4 (**11**)	0.07

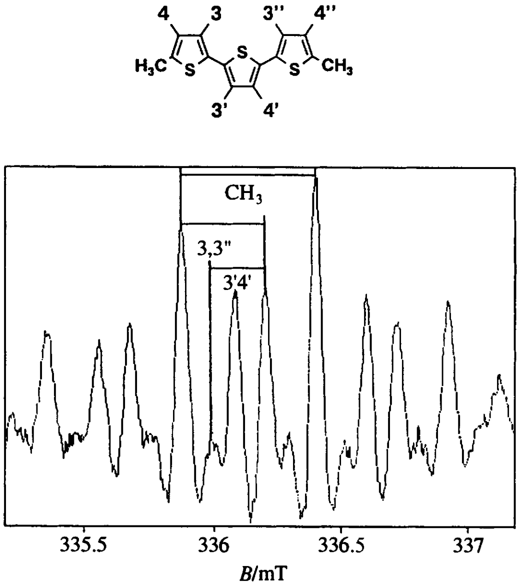


Fig. 6 Coherence between the hfcs of the radical cations of **11** and the nomenclature of the β-ring positions

(24.4/65.3) [(M − 2I)$^+$] and 95 (36.3) [(M − 2I − Cl)$^+$] (Found: C, 15.85; H, 0.84; Cl, 8.85; I, 66.57; S, 8.03. $C_5H_3ClI_2S$ requires C, 15.62; H, 0.79; Cl, 9.22; I, 66.03; S, 8.34%).

2,5-Dichloro-3,4-diiodothiophene (5)

Compound **5** was prepared analogously to **4** with 43.6 g (0.28 mol) 2,5-dichlorothiophene (**2**), 60.9 g (0.24 mol) iodine, 27.5 g (0.12 mol) periodic acid, 178 ml acetic acid, 36 ml water and 5 ml sulfuric acid; yield 89.9 g **5**, 78%; pale yellow crystals; mp 80 °C (ethanol); ν(KBr)/cm^{-1} 1471 (st), 1410 (st), 1238 (st), 1030 (st), 826 (st) and 733 (m); m/z 408/406/404 (13.3/68.0/100.0) [M$^+$], 281/279/277 (3.0/16.2/23.4) [(M − I)$^+$], 154/152/150 (4.4/21.9/33.4) [(M − 2I)$^+$], 127 (11.3) [I$^+$] and 117/115 (5.0/15.5) [(C_4SCl)$^+$] (Found: C, 11.81; Cl, 17.44; I, 62.44; S, 8.31. $C_4Cl_2I_2S$ requires C, 11.87; Cl, 17.51; I, 62.7; S, 7.92%).

5-Chloro-3-deuterio-2-methylthiophene (7)

31.3 g (0.12 mol) 5-chloro-3-iodo-2-methylthiophene (**3**) was mixed with 101.0 g (1.54 mol) Zn dust in an Ar atmosphere. A mixture of 78.0 g (0.76 mol) freshly distilled acetic anhydride and 46.0 g (2.3 mol) heavy water was added at the same time. After gently heating the reaction began spontaneously and vehemently. Subsequently the reaction mixture was refluxed for 2 h and then cooled. The liquid phase was decanted and the remaining Zn dust was washed three times with methanol and five times with diethyl ether. The combined organic phases were washed with 3 M aqueous sodium hydroxide. This procedure was complete when the aqueous solution gave a basic reaction. Subsequently the organic phase was washed three times with water and dried with sodium sulfate. The solvent was gently distilled off and the crude product was purified by distillation at normal pressure; yield 11.34 g **7**, 70%; colourless liquid; bp 152 °C; n_D^{20} = 1.5362; ν(KBr)/cm^{-1} 3091 (schw), 2951 (schw), 2920 (m), 2859 (schw), 1529 (m), 1457 (st), 1444 (st), 1165 (st), 1025 (st), 836 (st), 672 (st) and 464 (st); δ_H($CDCl_3$, TMS, 250 MHz) 6.66 (s, 1 H, H4) and 2.38 (s, 3 H, CH_3); δ_C($CDCl_3$, TMS, 62.9 MHz) 138.346, 126.475, 125.671 and 124.126 (t); m/z 135/134/133/132/131 (28.9/29.5/80.9/66.7/7.2) [M$^+$] and 98 (100.0) [(M − Cl)$^+$] (Found: C, 44.78; H, 4.41; Cl, 26.46; S, 24.35. C_5DH_4ClS required C, 44.95; H, 4.52; Cl, 26.53; S, 23.99%).

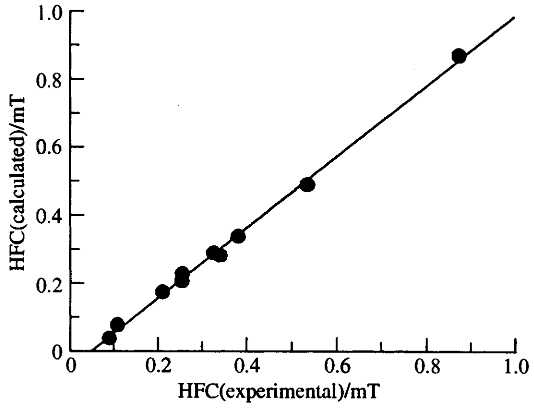


Fig. 7 Graph for the experimental and RHF-INDO-SP calculated hfcs (mT) for **11**, **15** and **16**[7]

2-Chloro-3,4-dideuterio-5-methylthiophene (6)

Compound **6** was prepared analogously to **7** from 42.3 g (0.11 mol) 2-chloro-3,4-diiodo-5-methylthiophene (**4**), 150.0 g (2.29 mol) Zn dust, 86.0 g (0.84 mol) acetic anhydride and 50.0 g (2.5 mol) heavy water; yield 9.62 g **6**, 64.3%; colourless liquid, bp 52 °C/15 Torr; n_D^{20} = 1.5361; ν(KBr)/cm^{-1} 2951 (schw), 2920 (m), 2858 (schw), 1442 (st), 1158 (st), 1032 (st), 624 (st) and 452 (st); δ_H($CDCl_3$, TMS, 250 MHz) 2.44 (s, 3 H, CH_3); δ_C($CDCl_3$, TMS, 62.9 MHz) 138.346, 126.377, 124.45, 124.05 (t) and 15.343; m/z 136/134 (29.5/78.9) [M]$^+$, 135/133 (28.6/61.8) [M − H]$^+$ and 99 (100.0) [M − Cl]$^+$ (Found: C, 44.47; H, 5.31; Cl, 26.59; S, 23.63. $C_5H_3D_2Cl$ required C, 44.61; H, 5.24; Cl, 26.33; S, 23.82%).

2,5-Dichloro-3,4-dideuteriothiophene (8)

Compound **8** was prepared analogously to **7** from 89.0 g (0.22 mol) 2,5-dichloro-3,4-diiodothiophene (**5**), 296.0 g (4.53 mol) Zn dust, 170.0 g (1.66 mol) acetic anhydride and 100.0 g (5 mol) heavy water; yield 17.86 g **8**, 52.4%; colourless liquid, bp 48 °C/13 Torr; n_D^{20} = 1.5608; ν(KBr)/cm^{-1} 1494 (st), 1414 (st), 1039 (st), 940 (st), 761 (m) and 622 (st); δ_C($CDCl_3$, TMS, 62.9 MHz) 127.132 (C3,4) and 125.558 (t, C2,5); m/z 158/156/154 (13.4/68.9/100.0) [M]$^+$ and 121/119 (14.7/23.1) [M − Cl]$^+$ (Found: C, 31.27; Cl, 45.31; D, 2.87; S, 20.55. $C_4Cl_2D_2S$ requires C, 30.99; Cl, 45.73; D, 2.60; S, 20.68%).

4,4″-Dideuterio-5,5″-dimethyl-2,2′:5′,2″-terthiophene (12)

Following the method of Kumada *et al.*,[14] to a solution of 2.7 g (20.4 mmol) 5-chloro-3-deuterio-2-methylthiophene (**7**) and 0.74 g (30.6 mmol) Mg turnings in 20 ml dry diethyl ether a solution of 2.5 g (20.4 mmol) propyl bromide in 10 ml diethyl ether was added dropwise. After complete addition the reaction mixture was refluxed for 4 h under stirring and then cooled. The resulting mixture was transferred into a dropping funnel by pressing with inert gas, separating from the unreacted Mg. The Grignard solution was dropped into a solution of 2.47 g (10.2 mmol) 2,5-dibromothiophene (**10**) in 40 ml dry diethyl ether and 460 mg (0.85 mmol) $NiCl_2$dppp [1,3-bis(diphenylphosphino)propane nickel(II) chloride]. After refluxing for 6 h under stirring the mixture was poured into ice-water, followed by three-fold extraction with each 100 ml diethyl ether, drying with $CaCl_2$, distilling off the solvent *in vacuo* and purifying the crude product by chromatography on silica gel (40–63 μm) with hexane; yield 0.33 g **12**, 11.6%; yellow crystals; mp 94 °C; ν(KBr)/cm^{-1} 3060 (schw), 2938 (schw), 2908 (m), 1848 (schw), 1504 (st), 1442 (st), 1243 (m), 1164 (st), 840 (st), 793 (st) and 680 (st); δ_H($CDCl_3$, TMS, 250 MHz) 6.95 (s, 2 H, H3′,4′), 6.93 (s, 2 H, H3,3″) and 2.46 (s, 6 H, CH_3-5,5″); δ_C($CDCl_3$, TMS, 62.9 MHz) 138.987, 135.989, 134.881, 125.693 (t), 123.427, 123.259 and 15.253; *m*/*z* 278 (100.0) $[M]^+$, 263 (5.4) $[M - CH_3]^+$, 245 (9.6) $[M - SH]^+$ and 139 (7.9) $[M]^{2+}$ (Found: C, 60.16; H, 4.77; S, 34.73. $C_{14}D_2H_{10}S_3$ requires C, 60.39; H, 5.06; S, 34.55%).

3′,4′-Dideuterio-5,5″-dimethyl-2,2′:5′,2″-terthiophene (13)

6.0 g (34 mmol) 2-bromo-5-methylthiophene (**9**) was reacted with 1.24 g (51 mmol) Mg turnings and a small amount of iodine in 10 ml dry diethyl ether to form the corresponding Grignard reagent. According to the synthesis of **12** the cross coupling was carried out with 2.23 g (14.4 mmol) 2,5-dichloro-3,4-dideuteriothiophene (**8**) and 690 mg (1.28 mmol) $NiCl_2$dppp in 40 ml dry diethyl ether; yield 1.3 g **13**, 32.5%; yellow crystals; mp 94 °C; ν(KBr)/cm^{-1} 3070 (schw), 2939 (schw), 2906 (schw), 2850 (schw), 1441 (m), 1288 (m), 1241 (m), 1189 (m), 1147 (m), 1045 (m), 1010 (m), 796 (st), 655 (st) and 461 (st); δ_H($CDCl_3$, TMS, 250 MHz) 7 (d, 2 H, $J_{3,4}$ 3.75 Hz, H3,3″), 6.72 (d, 2 H, $J_{4,3}$ 3.75 Hz, H4,4″) and 2.52 (s, 6 H, CH_3-5,5″); δ_C($CDCl_3$, TMS, 62.9 MHz) 139.031, 135.862, 134.846, 125.906, 123.293, 123.295 (t) and 15.279; *m*/*z* 278 (100.0) $[M]^+$, 277 (26.2) $[M - H]^+$, 263 (5.4) $[M - CH_3]^+$, 245 (9.6) $[M - SH]^+$ and 139 (7.9) $[M]^{2+}$ (Found: C, 60.58; H, 4.87; S, 34.95. $C_{14}H_{10}D_2S_3$ requires C, 60.83; H, 5.07; S, 34.54%).

5,5″-Dimethyl-3,3″,4,4″-tetradeuterio-2,2′:5′,2″-terthiophene (14)

This compound was prepared as described above for **12** with 3.3 g (24.9 mmol) 2-chloro-3,4-dideuterio-5-methylthiophene (**6**), 3.1 g (24.9 mmol) propylbromide, 0.9 g (37.4 mmol) Mg turnings, a small quantity iodine, 460 mg (0.85 mmol) $NiCl_2$dppp and 3 g (12.4 mmol) 2,5-dibromothiophene (**10**); yield 0.46 g **14**, 13.2%; yellow crystals; mp 94 °C; ν(KBr)/cm^{-1} 3059 (schw), 2938 (schw), 2907 (m), 2848 (schw), 1500 (m), 1435 (m), 1266 (schw), 1234 (schw), 1163 (schw), 1059 (schw), 854 (m), 7.93 (st), 771 (m), 640 (st) and 454 (st); δ_H($CDCl_3$, TMS, 250 MHz) 6.86 (s, 2 H, H3′,4′) and 2.4 (s, 6 H, CH_3-5,5″); δ_C($CDCl_3$, TMS, 62.9 MHz) 139.436, 136.389, 135.208, 126.26 (t), 123.854, 123.474 (t) and 15.698; *m*/*z* 280 (100.0) $[M]^+$, 279 (33.8) $[M - H]^+$, 264 (3.5) $[M - H - CH_3]^+$, 247 (9.0) $[M - SH]^+$ and 140 (4.8) $[M]^{2+}$ (Found: C, 60.30; H, 5.97; S, 33.93. $C_{14}H_8D_4S_3$ requires C, 59.95; H, 5.75; S, 34.30%).

Electrochemical method

The electrolysis was carried out under the following conditions: $c_{Dep} = 10^{-3}$ mol l^{-1}, 0.1 M $TEABF_4$–AN, potentiostatic coulometry at $E = 1$ V (*vs.* SCE), Pt electrode (area ≈ 10 cm^2). A potentiostat PG 284/IEC (Heka Elektronik) was used with a coulometry cell which was a divided cup-cell (vol. ≈ 30 ml).

EPR investigations

EPR spectra were recorded on an EPR-X-Band-Spectrometer (ERS 300, Zentrum für wissenschaftlichen Gerätebau, Berlin), using an amplitude of modulation = 0.05 mT, a varian-cell (17 × 50 × 0.5 mm) with a capillary at the upper part of the cell for a constant flow. A flow rate ≈ 0.02 ml s^{-1} was used with the flow through the cell by gravity (no oxygen diffusion into the cell). There was direct connection between the EPR and coulometry cell

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