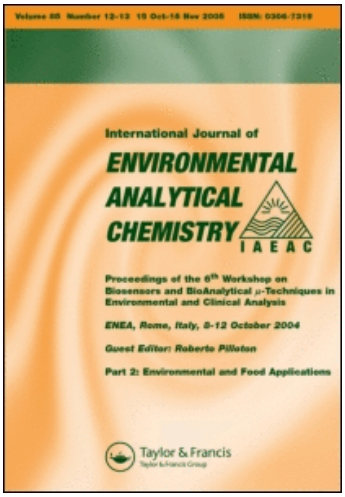

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SUBSTITUTED DIBENZOTHIOPHENES II: SYNTHESIS, CHROMATOGRAPHY, MASS SPECTROMETRY AND STRUCTURE ELUCIDATION BY ^{1}H NMR SPECTROSCOPY OF 3–MONOCHLORO-, 1,3–DICHLORO-, 1,3,4–TRICHLORO- AND SOME OTHER SUBSTITUTED DIBENZOTHIOPHENES

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As a continuation of earlier research some more polychlorinated and polymethylated dibenzothiophenes (PCDBTs and PMetDBTs, respectively) have been synthesized and separated. The synthesis mixtures have been fractionated by reversed-phase HPLC to obtain pure isomers. The influence of reaction time and reaction temperature on the production of the isomers has been studied. The reaction temperature was found to have a major influence on the isomer pattern obtained in the product mixture. The structures of the pure fractions were studied by GC-MS and ^{1}H NMR. Formation of 3–monochloro-, 1,3–dichloro- and 1,3,4–trichlorodibenzothiophene can be ascertained by computer based ^{1}H NMR spectral analysis. In addition, structures for several tri-and tetra-Met/CDBTs can be given based on the ^{1}H NMR results.

KEY WORDS: Methylated dibenzothiophenes, chlorinated dibenzothiophenes, reversed-phase HPLC, mass spectrometry, ^{1}H NMR spectroscopy

INTRODUCTION

Polychlorinated dibenzothiophenes (PCDBTs) are potentially highly toxic compounds like polychlorinated dibenzo-p-dioxins and dibenzofurans. In Finland PCDBTs have been found to be formed in waste combustion in seemingly high concentrations[1]. Rappe et al. have detected very low concentrations of PCDBTs in aquatic organisms in Newark Bay and in some fly ash samples[2,3]. This has made further screening of these compounds in different environmental samples and toxicological studies very important. For environmental analy-

sis, identification of the different structural isomers and for toxicological studies a higher number of pure PCDBT congeners are needed. The preparation of some substituted DBTs has been reported previously[4,5]. However, the yields in the synthesis were low and only a few pure compounds have been obtained by HPLC in amounts large enough to allow determination of their structures. In the present work more PCDBT and PMetDBT isomers have been synthesized by varying the reaction conditions, and isolated as pure compounds. The structures of the pure isomers have been studied by GC-MS and ^{1}H NMR.

EXPERIMENTAL

Synthesis

The following substituted biphenyls (synthesized by us) were used as starting material for substituted DBTs: 2–chlorobiphenyl, 4–chlorobiphenyl, 2,4,5–trichlorobiphenyl, a mixture of 3,3′,4,4′–tetrachlorobiphenyl and 2,3,3′,4′,–tetrachlorobiphenyl, a mixture of 3,3′,4,4′-tetramethylbiphenyl and 2,3,3′,4′,–tetramethylbiphenyl and a mixture of 2,3,4,5–tetrachloro-2′,3′,4′–trimethylbiphenyl and 2,3,4,5–tetrachloro-3′,4′,5′–trimethylbiphenyl. The temperatures used were 120°C, 160°C, 200°C and 240°C. The reaction times were from 5 to 50 h.

The substituted biphenyls (50–200 mg) were heated with sulphur (20–100 mg) and $AlCl_3$ (a few mg) in closed tubes in an oven constructed for this purpose. After cooling the reaction mixtures were extracted with toluene.

Purification and fractionation of the synthesis mixtures

Carbon and alumina column chromatography Carbon (Alltech, SK 4, 80/100) column chromatography was used for preliminary purification of the synthesis mixtures after their extraction with toluene. Toluene (Rathburn, Glass Distilled Grade) used in extraction was evaporated completely and the synthesis mixtures were dissolved in 0.5 ml of hexane (Rathburn, HPLC grade). The carbon column contained about 50 mg of activated charcoal in a tube which was turned upside down after elution with 10 ml of hexane-dichloromethane (50:50) to be eluted then with 12 ml of toluene[6].

Large aluminium oxide (100–200 g Al_2O_3) columns were used for purification and separation of some simple mixtures. The elution from the Al_2O_3 (Merck Aluminiumoxid 90, 70–230 mesh ASTM) columns was done with hexane.

HPLC fractionation and GC/MS The HPLC fractionation was done as described previously[5]. The HPLC system contained a Merck-Hitachi L6200 Intelligent Pump, a Shimadzu SPD GAV UV-VIS spectrophotometer and a Perkin Elmer 565 Recorder. A 25 cm × 0.4 mm I.D. Spherisorb S5 ODS-2 reversed-phase column with precolumn and acetonitrile-water eluents were used for the separation. The flow rate was 1 ml/min and detection was done at 254 nm.

GC-MS was done with a Hewlett-Packard HP 5970 mass-selective detector connected to a HP 5890 gas chromatograph equipped with a HP–5 (25 m, 0.2 mm; film thickness 0.11 μm) column. Helium (30 cm/s) was used as the carrier gas. The temperature programme was 100°C (1 min) – 20°C/min – 180°C – 5°C/min – 290°C (20 min). The temperature of the injector was 250°C and that of the transfer line 300°C. The electron ionization potential was 70 eV.

Selected ion monitoring (SIM) with the M and M+2 ions of tri-, tetra-, penta-, hexa- and heptachloroDBTs (ten ions together) was run in the same way for the synthesis mixtures and for the fractions obtained from HPLC.

RESULTS AND DISCUSSION

HPLC and GC-MS

Activated carbon chromatography removed most starting compounds and some sulphur from the synthesis mixtures. However, the separation was not complete. Part of the chlorinated and methylated biphenyls was found in the second fraction while part of the substituted dibenzothiophenes was found in the first fraction.

HPLC fractionation was done after carbon column fractionation. Acetonitrile-water (90:10 to 80:20) was used as eluent. For PCDBTs acetonitrile-water (88:12) gave the best results. For PMetDBTs acetonitrile-water (85:15) was used.

The relatively large concentrations of elemental sulphur used in the synthesis caused some difficulties in the HPLC separation. Some TriCDBTs and TeCDBTs eluted very close to or coeluted with sulphur, which made fractionation difficult. Activated copper was tried to remove sulphur; however, it destroyed the substituted DBTs.

The chlorination and methylation degree of the compounds was obtained by GC-MS.

Products from the synthesis

Figure1 summarizes the syntheses when 2–chlorobiphenyl, 4–chlorobiphenyl and 2,4,5–trichlorobiphenyl were used as reagents. 2–Chlorobiphenyl produced unsubstituted DBT in good yield, 4–chlorobiphenyl produced 3–CDBT and 2,4,5–trichlorobiphenyl produced 1,3,4–TriCDBT and 1,3–DiCDBT.

In Part I[5] a mixture of 3,4,3′,4′–tetrachlorobiphenyl and 2,3,3′,4′–tetrachlorobiphenyl was used to prepare TeCDBTs. Theoretically it is possible to obtain five different TeCDBTs, if it is supposed that no dechlorination or other side reactions/rearrangements occur. There were large differencies in the products obtained at different reaction temperatures. A temperature of 120°C was too low for any PCDBTs to be produced. At 240°C there was a prominent cleavage of chlorine and TriCDBTs were produced in high yields. The HPLC fractionation and the GC-MS analysis of the fractions showed the main products in the synthesis to be two TriCDBTs and three TeCDBTs (Figure 2). Ortho chlorines from the

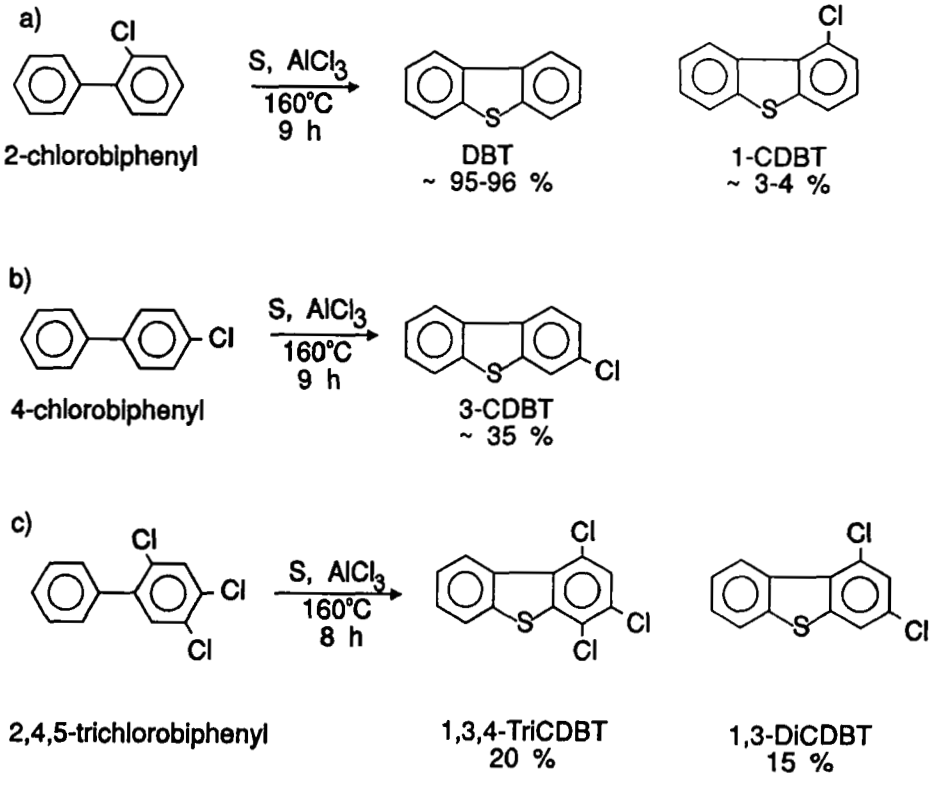

Figure 1 Synthesis of chlorinated dibenzothiophenes a) from 2-chlorobiphenyl, b) from 4-chlorobiphenyl and c) from 2,4,5-trichlorobiphenyl.

polychlorobiphenyls used to prepare the PCDBTs are quite easily removed. Rappe et al. have found that the ortho chlorines are removed in the formation of PCDBTs from PCBs and sulphur at high temperature (540°C)[7]. If we suppose that the ortho chlorines are cleaved then the main reaction products in this synthesis are 2,3,8–TriCDBT, 2,6,7–TriCDBT, 2,3,7,8–TeCDBT, 3,4,6,7–TeCDBT and 2,3,6,7–TeCDBT (Figure 3). At 160°C five TeCDBTs were produced. No appreciable cleavage of chlorine was found to occur (Figure 3).

The TeMetDBT synthesis from a mixture of 3,3',4,4'–tetramethylbiphenyl and 2,3,3',4'–tetramethylbiphenyl produced 2,3,7,8–TeMetDBT, 2,3,6,7–TeMetDBT, 2,3,7–TriMetDBT and 1,7,8–TriMetDBT (Figure 4; also see next section).

^1H *NMR analysis of the HPLC fractions*

Interpretation of ^1H *NMR spectra of PMetDBTs.* ^{1}H NMR spectra of HPLC fractions 1–3 (TriMetDBTs) and fractions 4 and 5 (TeMetDBTs) as indicated in Figure 4. are shown in Figure 5. The degree of methylation of these fractions was derived from their mass spectra.

As in our previous study[5], there exist in all fractions groups of singlet resonance lines in

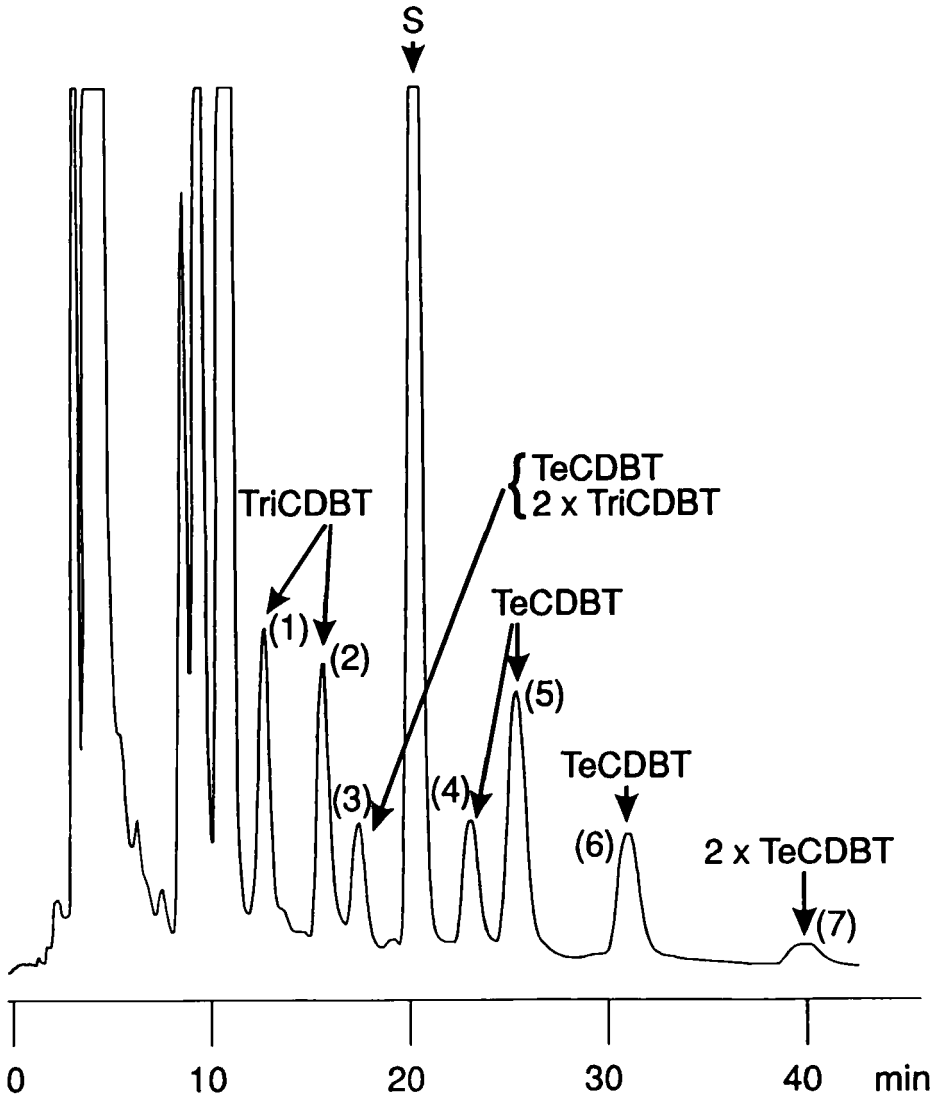

Figure 2 HPLC of the TeCDBT synthesis mixture (240°C); acetonitrile-water (90:10) at 1 ml/min, Spherisorb ODS and UV 254 nm.

the area 2.2 – 2.6 ppm characteristic for the methyls bound in an aromatic ring. Additionally, all fractions give signals in the typically aromatic region 7.2 – 8.0 ppm. As shown in our previous paper[5], CD_2Cl_2 is an excellent solvent in analysing MetDBTs. By using thick-walled tubes solvent volume can be diminished to 25% from that of standard 5 mm thin walled NMR tubes.

In our present experiments, the impurity multiplet in the area of 7.51 – 7.72 ppm did not interfere, because the concentrations of DBT derivatives were much higher than before.

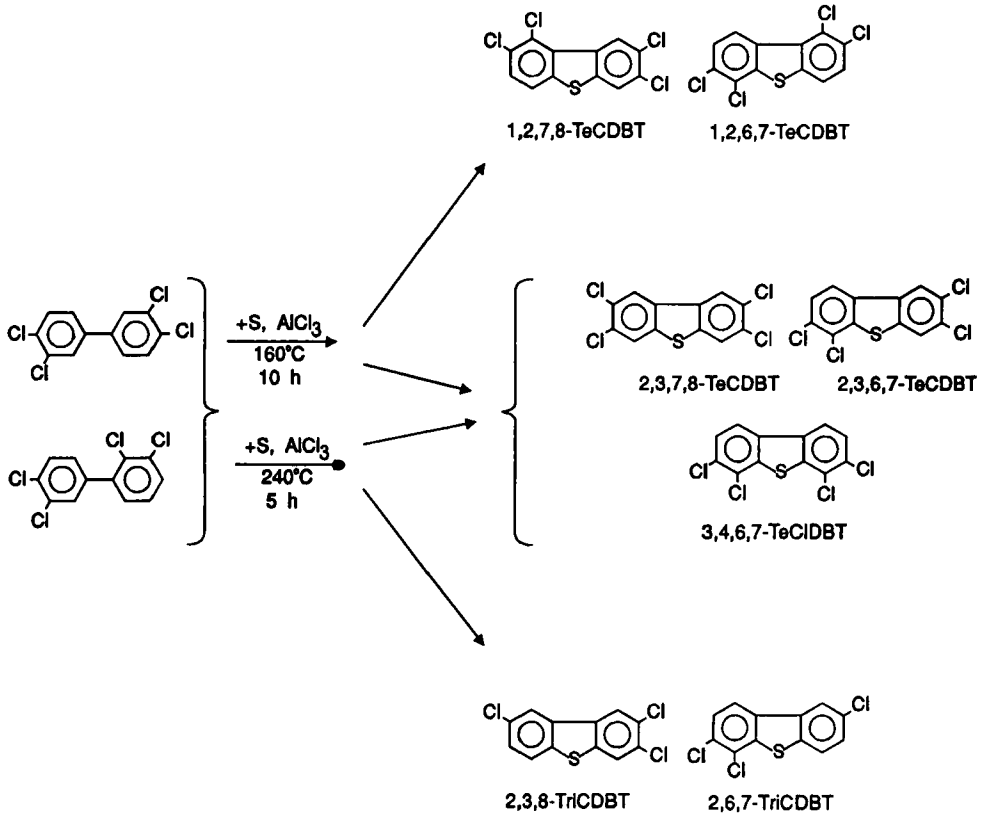

Figure 3 Synthesis of TeCDBTs at 240°C and 160°C from a mixture of 3,4,3′,4′-tetrachlorobiphenyl and 2,3,3′,4′-tetrachlorobiphenyl.

Thus reliable spectral interpretations were now possible. The assignment of the resonances of DBT and its derivatives is based on a paper by Jayalakshmi *et al.* [9] and the characteristic couplings between aromatic protons.

Fraction 4 (TeMetDBT) (identical with fraction 6 in Part I) shows only two signals in the methyl region, viz. 2.37 and 2.40 ppm, with the same intensity, and two strong singlet peaks, 7.55 and 7.84 ppm, from the protons located at the 1,4 or para positions in both aromatic rings of DBT, viz. the 2,3 and 7,8 positions. This fraction therefore is 2,3,7,8–TeMetDBT (see Table 1).

Fraction 5 (TeMetDBT) (identical with fraction 7 in Part I) exhibits four signals at 2.38, 2.40, 2.41 and 2.45 ppm with the same intensity. Two of these show almost the same chemical shifts as observed with fraction 4, viz. 2.37 and 2.40 ppm. Therefore, one can conclude that one of the rings is 2,3– (or 7,8–) dimethyl substituted. This conclusion is supported by two singlets at 7.59 and 7.85 ppm in the aromatic region very similarly with fraction 4. In addition, a typical AB quartet (7.21, 7.24, 7.80 and 7.83 ppm) exists in the

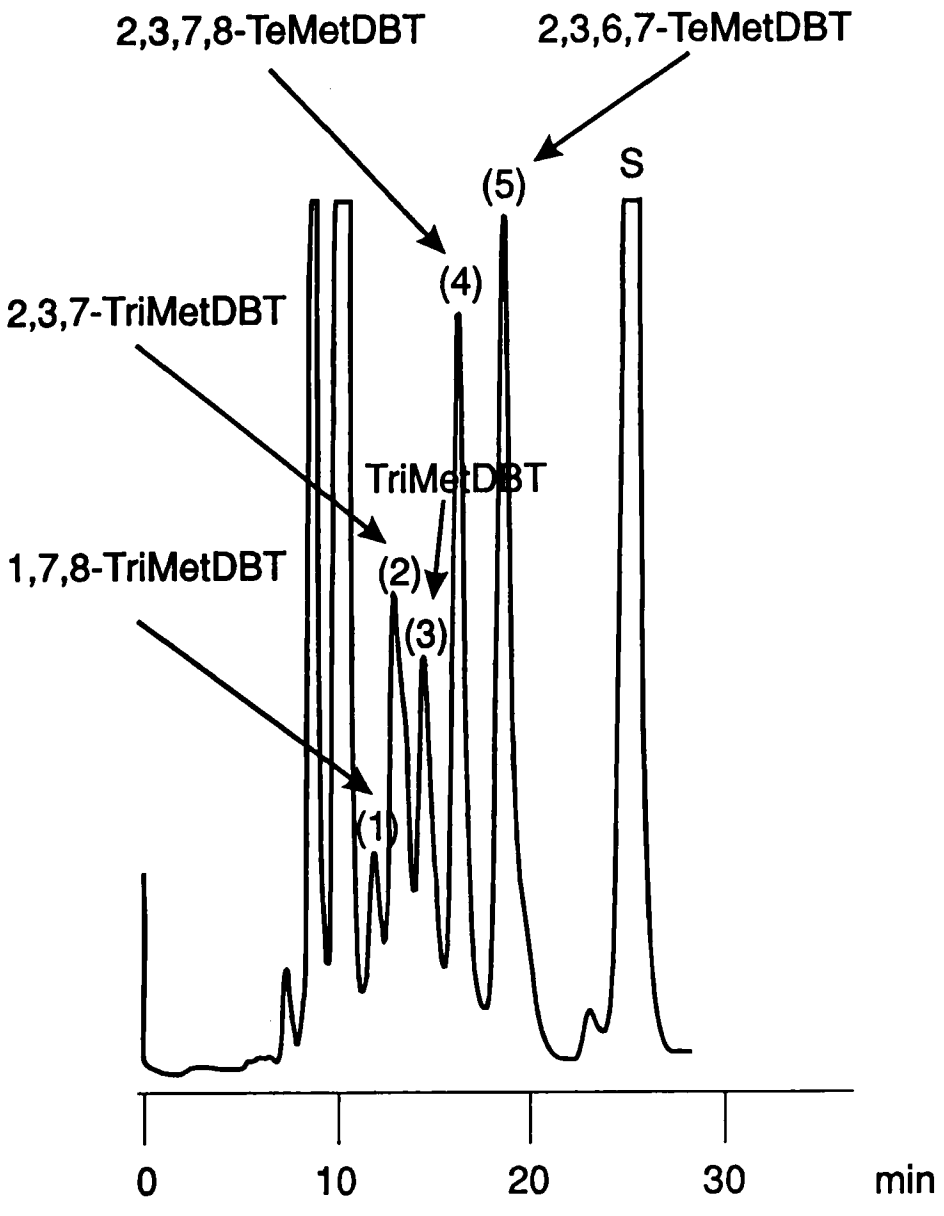

Figure 4 HPLC of the TeMetDBT synthesis mixture (160°C); acetonitrile-water (85:15) at 1 ml/min, Spherisorb ODS and UV 254 nm.

aromatic region and this stems from two adjacent (ortho) protons in the other aromatic ring. A better resolution of the present spectra compared with those previously recorded and a significant chemical shift difference between these protons suggests that one of these protons

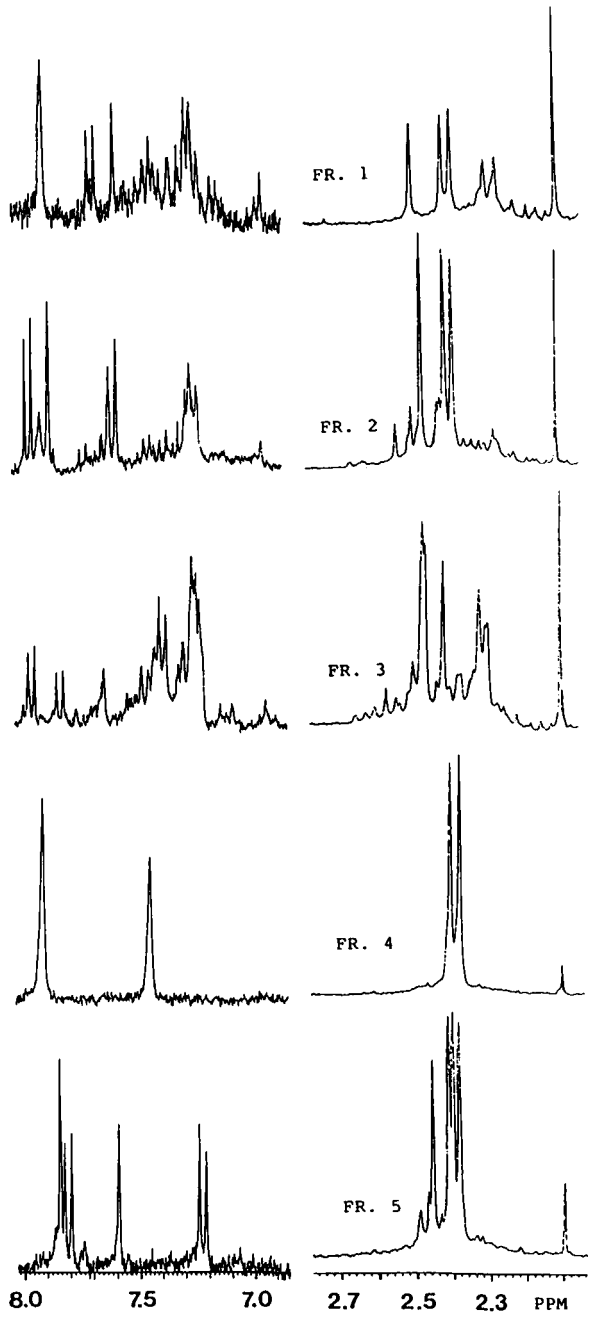

Figure 5 ^{1}H NMR spectra of the fractions 1-5 from the HPLC fractionation of the TeMetDBT synthesis mixture.

Table 1 ^{1}H NMR chemical shifts (ppm) of dibenzothiophene and its tetramethylated derivatives measured in CD_2Cl_2 solutions at 30°C. The digital resolution was 0.01 Hz.

Proton	*DBT*	*Chemical shift (ppm)* *2,3,7,8-TeMetDBT*	*2,3,6,7-TeMetDBT*
1	8.174	7.8442.401(Me)[a]	7.845
2	7.464	2.375(Me)[a]	2.384(Me)[a]
3	7.464	7.553	2.414(Me)[a]
4	7.864	7.553	7.592
6	7.864	2.375(Me)[a]	2.468(Me)[a]
7	7.464	2.401(Me)[a]	2.402(Me)[a]
8	7.464	7.884	7.229
9	8.174	7.835	

[a]Assignment ambiguous.

is located at position 1 or 9, as in DBT itself. Thus, different from our earlier proposal (1,2,7,8-TeMetDBT), fraction 5 is now interpreted to be 2,3,6,7-TeMetDBT.

Fraction 2 shows three main signals at 2.47, 2.40 and 2.38 ppm in the methyl region in its ^{1}H NMR spectrum. Two of these, at 2.40 and 2.38 ppm, are almost identical with the signals of fraction 4 revealing the presence of a 2,3-dimethylated ring. Aromatic signals support this conclusion. The third methyl signal overlaps with one of the main signals in fraction 3. Similarly, in the aromatic part one doublet, viz. 7.97 and 7.94 ppm, is exactly the same as in the trimethylated fraction 3, but differs from that of fraction 5. Consequently, a 3,4-dimethylated ring can not be present in this fraction. Comparison of the chemical shifts of the aromatic signals of fraction 2 with the signals of fraction 5 suggests that the third methyl is located in position 7. The singlet at 7.57 ppm is very close to the signal of proton 4 in fraction 4 and is thus probably from the similar proton 6. The remaining AB quartet (7.97, 7.94, 7.25 and 7.23 ppm) should be due to protons 8 and 9. The suggested structure of this fraction is therefore 2,3,7-TriMetDBT.

Fraction 3 (TriMetDBT) shows three main peaks, viz. 2.44 ppm and two with almost identical chemical shifts of 2.47 ppm in the methyl region. Two of those are very close to two signals of fraction 5, viz. 2.43 and 2.46 ppm. In addition, there exist in the aromatic region two resolved doublets, 7.97 and 7.94, and 7.84 and 7.82 ppm characteristic for left sides of two separate AB quartets. The doublet at 7.84 and 7.82 corresponds with the aromatic doublet of fraction 5. This supports the idea that one of the rings is 3,4-dimethylated. The other part of the second AB quartet (7.97 and 7.94 ppm) differs appreciably from the AB-quartet of fraction 5, but is the same as in fraction 2 and thus probably originates from proton 9, which is coupled to proton 8.

Fraction 1 (TriMetDBT) show three main peaks, 2.49, 2.41 and 2.39 ppm, in the methyl region. Two of these, 2.41 and 2.39 ppm, are characteristic for 2,3-dimethyl substitution, as is again supported by two singlets, 7.90 and 7.58 ppm, in the aromatic region. Because there

Table 2 ^{1}H NMR chemical shifts (ppm) and spin-spin coupling constants (Hz) of dibenzothiophene and its chlorinated derivatives measured in CD_2Cl_2 solutions at 30°C. The digital resolution was 0.01 Hz.

Proton	*DBT*	*Chemical shift (ppm) of 3-CDBT*	*1,3-DiCDB*	*1,3,4-TriCDBT*
1	8.174a	8.084	-	-
2	7.464	7.431	7.481	7.573
3	7.464	-	-	-
4	7.864	7.838	7.778	-
6	7.864	7.850	7.868	7.916
7	7.464	7.472	7.523	7.556
8	7.464	7.472	7.508	7.556
9	8.174	8.132	8.916	8.909
		Coupling constant (Hz)		
J(1,2)	7.71±0.54	8.47±0.07	-	-[b]
J(1,3)	1.46±0.54	-	-	
J(1,4)	0.62±0.11	<0.1	-	-
J(2,3)	7.28±0.10	-	-	-
J(2,4)	0.78±0.59	2.03±0.07	1.82±0.05	-
J(3,4)	8.43±0.59	-	-	-
J(6,7)	8.43±0.59	8.19±0.38	8.12±0.05	-
J(6,8)	0.78±0.59	1.05±0.38	1.10±0.05	-
J(6,9)	0.62±0.11	0.57±0.04	0.59±0.03	-
J(7,8)	7.28±0.10	7.17±0.04	7.13±0.05	-
J(7,9)	1.46±0.54	1.19±0.37	1.17±0.04	-
J(8,9)	7.71±0.54	8.00±0.36	8.34±0.05	-

The obtained parameters and their standard deviations are based on the computerized analysis of the spectra[8].
[a] standard deviation of chemical shifts is < 0.001 ppm.
[b] coupling constants are approximately the same as in DBT

exist complex coupling patterns originating from three adjacent protons and because the AB quartets, which are present in fractions 2,3 and 5 are missing, one can conclude that the remaining methyl is probably located in position 9 (or in position 1 if the ring is numbered in the opposite direction). The tentative structure assignment therefore is 1,7,8-TriMetDBT.

Interpretation of the ^{1}H NMR spectra of PCDBTs Such interpretation is more difficult than that of their methyl analogues, because all interpretation must be based on the aryl signals alone. Based on the comparison of chemical shifts and computerized analysis of their spectra, the products from the syntheses b) and c) described in Figure 1 are 3-CDBT, and 1,3-DiCDBT and 1,3,4-TriCDBT respectively (see Table 2).

With TeCDBTs, in addition to the general ^{1}H NMR analysis problem, for safety reasons the syntheses were performed on a smaller scale than for PMetDBTs. Based on a mass spectral analysis four TeCDBTs were found in the HPLC fractions 4-6 in Figure 2.

Fraction 6 of Figure 2 showed a pattern of two doublets with a coupling constant of 8.6 Hz characteristic for ortho protons in an aromatic ring. Based on their chemical shifts these protons probably are in positions 1 [9] (8.87 ppm) and 2 [8] (7.78 ppm). The structure therefore most probably is 3,4,6,7-TeCDBT.

Table 3 Synthetical details and identification methods of the substituted dibenzothiophenes.

biphenyl	*Temp. (°C)*	*Time (h)*	*Products*	*Identification by*
2-C	160	9	DBT (> 90%)	GC/MS
			1-CDBT (3-4%)	GC/MS, ^{1}H NMR
4-C	160	9	3-CDBT (35%)	GC/MS, 1H NMR
2,4,5-TriC	160	9	1,3,4-TriCDBT (20%)	GC/MS, 1H NMR
			1,3-DiCDBT (15%)	GC/MS, 1H NMR
3,3',4,4'-TeC	120	10	-	-
2,3,3',4'-TeC				
3,3',4,4'-TeC			2,3,7,8-TeCDBT, 3,4,6,7-TeCDBT	GC/MS, ^{1}H NMR
2,3,3',4'-TeC	160	10	2,3,6,7-TeCDBT, 1,2,6,7-TeCDBT	GC/MS
			1,2,7,8-TeCDBT	GC/MS, ^{1}H NMR
3,3',4,4'-TeC	200	10	6 TeCDBTs	GC/MS
2,3,3',4'-TeC			2 HeptaTeCDBTs	GC/MS
3,3',4,4'-TeC			2,3,7,8-TeCDBT, 3,4,6,7-TeCDBT	GC/MS, ^{1}H NMR
2,3,3',4'-TeC	240	5	2,3,6,7-TeCDBT	GC/MS
2,3,8-TriCDBT,			2,6,7-TriCDBT	GC/MS
3,3',4,4'-TeMet	160	50	2,3,6,7-TeMetDBT, 2,3,7,8-TeMetDBT	GC/MS, ^{1}H NMR
2,3,3',4'-TeMet			2,3,7-TriMetDBT, 1,7,8-TriMetDBT	GC/MS, ^{1}H NMR
2,3,4,5-TeC-2',3',4'-TriMet			Octachlorofluorene	GC/MS
2,3,4,5-TeC-3',4'5'-TriMet	200	10	TriCTriMetDBT	GC/MS
			Tetrachlorodimethylfluorene	GC/MS

Fraction 4 of Figure 2 gave a complex spectrum characterized by four singlet lines at 9.12, 8.20, 7.99 and 7.97 ppm and two doublets at 7.94 ppm and 7.73 ppm. Two of the singlet lines at 9.12 and 7.97 ppm were found also in fraction 5 of Figure 2. Consequently, fraction 4 is a mixture of at least two isomers. One of them is the symmetric isomer 2,3,7,8-TeCDBT, which is an analogue of 2,3,7,8-TCDD.

CONCLUSIONS

Examples of results from syntheses are collected in Table 3. The formation of substituted DBTs from chlorinated and methylated biphenyls is strongly dependent on the reaction conditions. In the case of MetDBTs the yields of TriMetDBTs and TeMetDBTs were much higher when longer reaction times were used. Within the range of 160-240°C the reaction temperature did not have a big influence on the isomer pattern in the product mixture. In the case of TeCDBTs the reaction temperature was found to have a strong influence on the isomer pattern in the product mixture. More chlorine cleaving occurred at higher temperatures favouring the formation of TriCDBTs. Increasing the reaction time from 5 h to 50 h did not remarkably increase the yields, which remained very low.

The structures of two tetramethylated derivatives, viz. 2,3,7,8- and 2,3,6,7- TeMetDBT were ascertained. Further, the existence of two trimethylated derivatives, viz. 2,3,7- and 1,7,8-TriMetDBTs was proposed.

The structures of three chlorinated derivatives, viz. 3-CDBT, 1,3-DiCDBT and 1,3,4-

TriCDBT were ascertained. In spite of dilute samples (10-20 μg/500μl) and lack of signals in the aliphatic area, also two patterns of tetrachlorinated derivatives, viz. 2,3,7,8- and 3,4,6,7- TeCDBT, were found.

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References

1. S. Sinkkonen, J. Paasivirta, J. Koistinen and J. Tarhanen, *Chemosphere*, **23**, 583-587 (1991).
2. C. Rappe, P-A. Bergqvist, L-O Kjeller, S. Swanson, T. Belton, B. Ruppel, K. Lockwood and P.C. Kahn, *Chemosphere*, **22**, 239-266 (1991).
3. H-R. Buser, I. S. Dolezal, M Wolfensberger and C. Rappe, *Environ. Sci. Technol.*, **25**, 1637-1643 (1991).
4. S. Sinkkonen and J. Koistinen, *Chemosphere*, **21**, 1161-1171 (1990).
5. S. Sinkkonen, E. Kolehmainen and J. Koistinen, *Intern. J. Env. Anal. Chem.*, **47**, 7-20 (1992).
6. J. Koistinen, J. Paasivirta and J. Särkkä, *Chemosphere*, **21**, 1371-1379 (1990).
7. H-R. Buser and C. Rappe, *Anal. Chem.*, **63**, 1210-1217 (1991).
8. R. Laatikainen, *J. Magn. Reson.*, **27**, 169-180 (1977).
9. S. Jayalakshmi, S. Perumal and D. A. Wilson, *Magn. Reson. Chem.*, **27**, 684-686 (1989) and references therein.