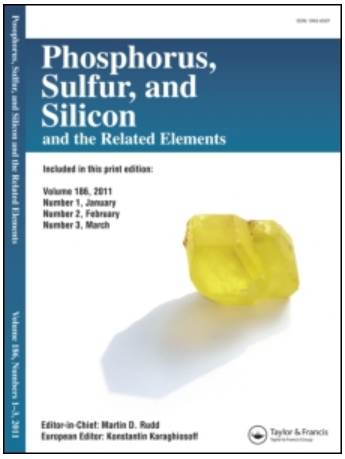


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS OF 2,3,7,8-TETRAKIS- (ALKYLTHIO)DIBENZOTHIOPHENES AND STRUCTURE OF 2,3,7,8-TETRAKIS-(METHYLTHIO)DIBENZOTHIOPHENE

Marc Döotze[a]; Günter Klar[a]
[a] Institut für Anorganische and Angewandete Chemie der Universität Hamburg, Hamburg, Bundesrepublik Deutschland

To cite this Article Döotze, Marc and Klar, Günter(1996) 'SYNTHESIS OF 2,3,7,8-TETRAKIS-(ALKYLTHIO)DIBENZOTHIOPHENES AND STRUCTURE OF 2,3,7,8-TETRAKIS-(METHYLTHIO)DIBENZOTHIOPHENE', Phosphorus, Sulfur, and Silicon and the Related Elements, 117: 1, 197 — 203
To link to this Article: DOI: 10.1080/10426509608038786
URL: http://dx.doi.org/10.1080/10426509608038786

Phosphorus, Sulfur, and Silicon, 1996, Vol. 117, pp. 197–203
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS OF 2,3,7,8-TETRAKIS-(ALKYLTHIO)DIBENZOTHIOPHENES AND STRUCTURE OF 2,3,7,8-TETRAKIS-(METHYLTHIO)DIBENZOTHIOPHENE

MARC DÖTZE and GÜNTER KLAR*

Institut für Anorganische und Angewandete Chemie der Universität Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg, Bundesrepublik Deutschland

(Received 11 March 1996; Revised 10 June 1996)

Bis[2-lithio-4,5-(dialkylthio)phenyl]sulfides, obtained from the corresponding dibromo compounds **5** and butyllithium, are oxidized by cupric chloride to the tetrakis(alkylthio)dibenzothiophenes **4**, the ^{1}H-NMR and MS data of which are reported. Furthermore, an X-ray analysis of **4a** has been carried out, showing a columnar structure for the solid state with stacks in which the planar molecules are arranged parallel to each other.

Keywords: 2,3,7,8-tetrakis(methylthio)- and bis(1,4-dithiano)-[2,3-*b*;2′,3′-*i*]dibenzothiophene; synthesis; 2,3,7,8-tetrakis-(methylthio)dibenzothiophene; structure determination

INTRODUCTION

In the course of our investigations into the oxidation products[1] and charge-transfer complexes[2–4] of electron-rich chalcogenanthrenes **1** we also became interested in the corresponding compounds of the structurally related dibenzochalcogenophenes **2**.[5] Having already prepared the tetrakis(alkylthio)thianthrenes **3**, the synthesis of the tetrakis(alkylthio)dibenzothiophenes **4** suggested itself, the more so as both types of compounds should be accessible from the same educts. Bis[2-lithio-4,5-di(alkylthio)phenyl]sulfide, which is easily obtained from the corresponding dibromo compound **5** and butyllithium, has been transformed to **3** by reaction with bis(phenylsulfinyl)sulfide[6] whereas its oxida-

*Corresponding author.

tion should lead to the dibenzothiophene **4**. Halides of transition metals in higher oxidation states, often used for coupling of carbanions,[7–9] should be possible oxidants.

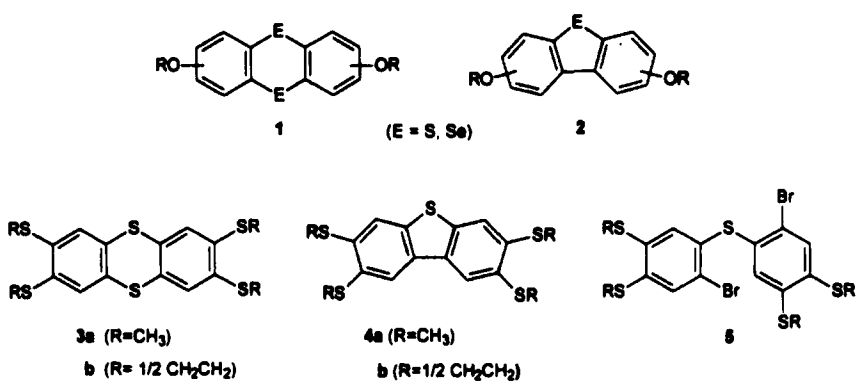
SYNTHESIS

Cupric chloride proved to be a suitable oxidant[10–12] and was also used for the preparation of the dibenzothiophenes **4**, according to the following general procedure:

To a stirred solution of bis[2-bromo-4,5-di(alkylthio)phenyl]sulfide **5**[6] (6.5 mmol) in tetrahydrofuran (200 ml) *n*-butyllithium (8.1 ml, 1.6 M solution in hexane, 13 mmol) was added dropwise at −78°C. After 15 min powdered anhydrous cupric chloride (1.8 g, 15 mmol) was added, cooling was removed after 1h and the mixture was stirred for further 15 h at room temperature. Then the solvent was evaporated, the residue extracted with dichloromethane (600 ml), the extract washed with dilute hydrochloric acid, dried ($MgSO_4$) and filtered over neutral aluminia. The elution of the product was completed with additional dichloromethane (300 ml), the residue of the eluate was purified by crystallization.

2,3,7,8-Tetrakis(methylthio)dibenzothiophene (***4a***). Crystallization from toluene; yield 1.08 g (2.0 mmol, 45%); mp. 232°C; ^{1}H-NMR (BRUKER WP250, 250 MHz, $CDCl_3$): δ [ppm] = 7.98, 7.59 (s, H_{arom}), 2.59, 2.56 (s, H_{alk}), integrated intensities 1:1:3:3.

$C_{16}H_{16}S_5$ (368.2)
calc.: C 52.1 H 4.4 S 43.5
found: C 52.3 H 4.3 S 43.3.



SCHEME 1

Bis(1,4-dithiano)[2,3-b;2',3'-i]dibenzothiophene (***4b***). Crystallization from trichloromethane/ethanol 2:1 (after having dissolved impurities in small amounts of dichloromethane); yield 528 mg (1.4 mmol, 22%); mp. 270°C (dec.); ^{1}H-NMR (BRUKER WP250, 250 MHz, $CDCl_3$): δ [ppm] = 7.87, 7.63 (s, H_{arom}), 3.32 (s, H_{alk}), integrated intensities 1:1:4.

$C_{16}H_{12}S_5$ (364.6)
calc.: C 52.7 H 3.3 S 44.0
found: C 52.7 H 3.3 S 44.2.

MS DATA

The results of mass spectroscopic investigations on **4a** and **4b** are given in (TABLE I). For both compounds the peaks of highest intensity are the parent peaks M^+, indicating that the compounds can easily be oxidized. This is also documented by the observation of the M^{2+} peaks in the spectra.

In the case of the methylthio compound **4a** different fragmentation paths are observed: (1) from each methylthio group elimination of (a) CH_3 with formation of a thioquinone or (b) CH_2S to give the hydrogen substituted derivative, (2) from two methylthio groups in *ortho*-position extrusion of (a) CH_4 to give a methylenedithio group which can be dehydrogenated to the aromatic dithiolium compound, or (b) $2CH_3+S$ with formation of a thiacyclopropene derivative, and (3) from the central thiophene ring loss of S to the biphenylene derivative is found.

TABLE I MS data of the dibenzothiophenes (Finnegan MAT CH7, 70 eV)

4a			*4b*		
mass	*intensity*	*fragment*	*mass*	*intensity*	*fragment*
368	100%	M^+	364	100%	M^+
352	1%	M^+-CH_4	349	7%	M^+-CH_3
320	9%	M^+-CH_4,-S	336	9%	M^+-C_2H_4
307	6%	M^+-CH_3,-CH_2S	308	12%	M^+-$2C_2H_4$
306	12%	M^+-$2CH_3$,-S	264	6%	M^+-$2C_2H_4$,-CS
291	7%	M^+-$3CH_3$,-S	182	4%	M^{2+}
290	6%	M^+-CH_4,-$2CH_3$,-S			
289	21%	M^+-CH_4,-H,-$2CH_3$,-S			
259	8%	M^+-CH_4,-CH_3,-CH_2S,-S			
241	5%	M^+-CH_4,-CH_3,-3S			
184	8%	M^{2+}			

By contrast, the ethylenedithio groups of **4b** are more labile; therefore, preferably ethene is eliminated to form the corresponding dithiete. Also CH_3 giving the dithiolium compound or C_2H_4+CS leading to a thiocyclopentadienone derivative can be extruded. But no loss of sulfur from the central thiophene ring is observed.

CRYSTAL STRUCTURE DATA OF 4a

A Syntex $P2_1$ four-circle diffractometer (Mo-Kα radiation with λ = 70.926 pm, $\omega/2\theta$ scan mode with $4.5 \leq 2\theta \leq 55°$, Lorentz and polarization corrections) and the programs SHELX-76[13] and SHELXS-86[14] were used for the X-ray analysis. The structure was determined by direct methods. Subsequent Fourier syntheses and full-matrix least-squares calculations allowed all non-hydrogen atoms to be located with anisotropic temperature factors. The positions of the hydrogen atoms were calculated with fixed distances of 96 pm and isotropic temperature factors. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited with the Fachinformationszentrum (FIZ) Karlsruhe, and can be ordered by quoting the authors, the journal and depositing number CSD 59320.

Molecular Structure

The molecule of **4a** is totally planar (FIG. 1). Within experimental error, the bond lengths and angles of the dibenzothiophene moiety (TABLE II) are iden-

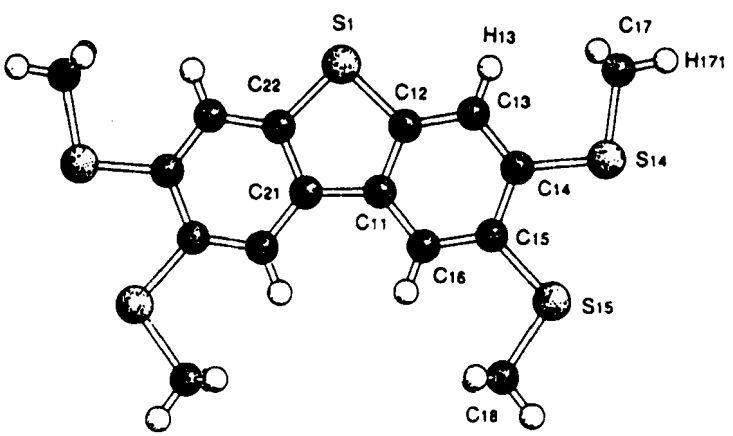


FIGURE 1 Molecular structure of **4a** and numbering scheme of atoms.

TABLE II Mean values of relevant bond lengths [pm] and bond angles [°] for **4a** (e.s.d.'s in parentheses)

thiophene moiety		*methylthio groups*	
C-S	174.7(3)	C_{ar}-S	176.4(3)
C(S)-C(S)	139.5(3)	C_{alk}-S	178.5(3)
C(C)-C(C)	145.7(3)		
		CSC	103.9(1)
CSC	91.1(1)	CCS(endo)	116.5(1)
CCS(endo)	112.6(1)	CCS(exo)	123.7(2)
CCS(exo)	126.3(2)		
CCC	111.9(1)		

tical to those of dibenzothiophene itself[15] and its 2,3,7,8-tetramethoxy derivative[16]. The methylthio substituents are coplanar to the phenyl rings they belong to, all in *exo*-positions. An analogous situation is also found for the comparable 2,3,7,8-tetramethoxy-[17] and 2,3,7,8-tetrakis(methylthio)thianthrenes.[6] Due to steric interactions between the methyl group and the hydrogen atom in *ortho*-position of the phenyl ring the angles CCS(exo) are larger and the corresponding angles CCS(endo) smaller than the ideal values of 120°. As expected, the distances $C_{arom}S$ are somewhat shorter than those of $C_{alk}S$.

Crystal Structure

In the crystal of **4a** all molecules are arranged in parallel planes (FIG. 2). Stacks of eclipsed molecules are formed in the *a*-direction, the molecular planes are inclined to the stacking axis at 44.9°, the interplanar distances of 390 pm being longer than the van der Waals distances (half thickness of an aromatic nucleus 185 pm[18]). Although all sulfur atoms in successive molecules of a stack are

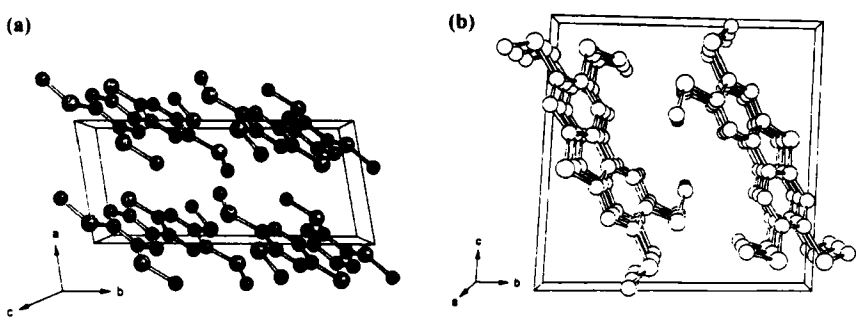


FIGURE 2 (a) Unit cell of **4a**, (b) stacks of eclipsed molecules in the crystal of **4a** (Projection on the *b,c*-plane).

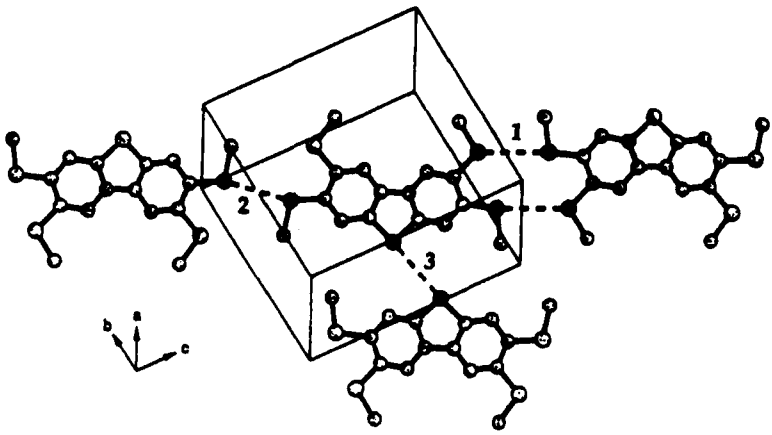


FIGURE 3 Intermolecular S · · · S contacts in the crystal of **4a**: (1) 341 pm, (2) 361 pm, (3) 373 pm.

brought to a line, their distances (552 pm) are far from the van der Waals distance (370 pm[18]); however, between sulfur atoms of molecules in adjacent stacks S · · · S-contacts slightly shorter than 370 pm are found (FIG. 3).

Acknowledgements

We thank the Fonds der Chemischen Industrie for financial support.

References

[1] W. Hinrichs, P. Berges and G. Klar, *Z. Naturforsch.*, **42b**, 169 (1987).
[2] W. Hinrichs and G. Klar, *J. Chem. Res.*, (*S*) 336; (*M*) 3540 (1982).
[3] P. Berges, J. Kudnig, G. Klar, E. Sánchez Martínez and R. Díaz Calleja, *Z. Naturforsch.*, **44b**, 211 (1989).
[4] U. Behrens, R. Díaz Calleja, M. Dötze, U. Franke, W. Gunßer, G. Klar, J. Kudnig, F. Olbrich, E. Sánchez Martínez, M. J. Sanchis and B. Zimmer, *J. Mater. Chem.*, **6**, 547 (1996).
[5] R. Díaz Calleja, P. Klar, E. Sánchez Martínez, J. Behrens, J. Kudnig and G. Klar, *J. Mater. Chem.*, **3**, 489 (1993).
[6] M. Dötze and G. Klar, *Phosphorus, Sulfur, and Silicon*, **84**, 95 (1993).
[7] G. Wittig and G. Lehmann, *Chem. Ber.*, **90**, 875 (1957).
[8] G. Wittig and G. Klar, *Liebigs Ann. Chem.*, **704**, 91 (1967).
[9] G. Wittig and F. Bickelhaupt, *Chem. Ber.*, **91**, 883 (1958).
[10] J. Krizewsky and E. E. Turner, *J. Chem. Soc.*, **115**, 559 (1919).
[11] E. Sakellarios and T. Kyrimis, *Ber. Dtsch. Chem. Ges.*, **57**, 322 (1927).
[12] R. Nast and W. Pfab, *Chem. Ber.*, **89**, 415 (1956).
[13] G. M. Sheldrick, SHELX-76, (1976). *Programs for Crystal Structure Determination*, University of Cambridge, England.
[14] G. M. Sheldrick, SHELXS-86, (1986). *Programs for Crystal Structure Solution*, University of Göttingen.
[15] R. M. Schaffrin and J. Trotter, *J. Chem. Soc. (A)*, 1561 (1970).

[16] P. Berges, Dissertation, University of Hamburg (1987).
[17] W. Hinrichs, H. -J. Riedel and G. Klar, *J. Chem. Res.*, (*S*) 334, (*M*) 3501 (1982).
[18] "Handbook of Chemistry and Physics", CRC Press, Cleveland, Oh, 58th edn., 1977–1978, p. D-178.