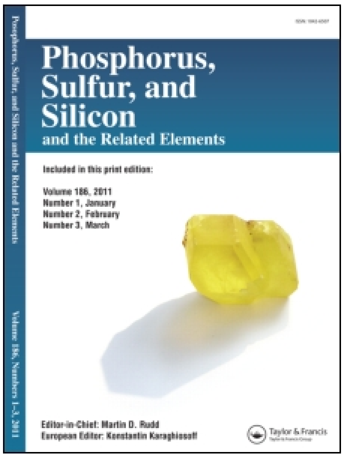


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

STRUCTURE AND SYNTHESIS OF 1,3,5,7-TETRAMETHOXYDITHIENO-[3,4-*b*;3',4'-*e*][1,4] DITHIIN

Stephan Friederichs[a]; Thorsten Link[a]; Günter Klar[a]
[a] Institut für Anorganische und Angewandte Chemie der Universität Hamburg, Hamburg, Bundesrepublik, Deutschland

To cite this Article Friederichs, Stephan , Link, Thorsten and Klar, Günter(1995) 'STRUCTURE AND SYNTHESIS OF 1,3,5,7-TETRAMETHOXYDITHIENO-[3,4-*b*;3',4'-*e*][1,4] DITHIIN', Phosphorus, Sulfur, and Silicon and the Related Elements, 107: 1, 279 — 283

To link to this Article: DOI: 10.1080/10426509508027944

URL: http://dx.doi.org/10.1080/10426509508027944

Phosphorus, Sulfur, and Silicon, 1995, Vol. 107, pp. 279–283
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V. Published in The Netherlands
under license by Gordon and Breach Science
Publishers SA
Printed in Malaysia

Communication

STRUCTURE AND SYNTHESIS OF 1,3,5,7-TETRAMETHOXYDITHIENO-[3,4-*b*;3′,4′-*e*][1,4] DITHIIN

STEPHAN FRIEDERICHS, THORSTEN LINK and GÜNTER KLAR*
Institut für Anorganische und Angewandte Chemie der Universität Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg, Bundesrepublik Deutschland

(Received May 2, 1995)

Starting from thiophene (**6**), the sequence 2,5-diiodothiophene (**7**), 2,5-bismethoxythiophene (**8**), 3,4-dibromo-2,5-bismethoxythiophene (**9**) finally leads to the title compound **5**. The ^{1}H- and ^{13}C-NMR, the MS and IR data and the structure of **5** are reported.

Key words: Dithieno-1,4-dithiin, X-ray structure.

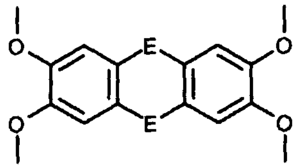
INTRODUCTION

Electronrich dibenzodichalcogenins or dibenzochalcogenophenes, especially their tetramethoxy-derivatives **1** and **2** as donors, form charge-transfer complexes with acceptors like 7,7,8,8-tetracyanoquinodimethane (TCNQ) or 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).[1–4] These complexes possess column type structures in their solid states and reveal the properties of semiconductors.

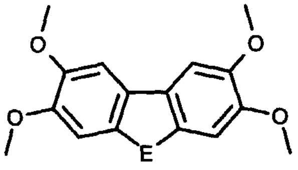
Dithienodithiins in which the characteristic moieties of **1** and **2** are combined therefore seem to be further attractive candidates to be studied. Until now only the nonsubstituted compounds dithieno[2,3-*b*;3′,2′-*e*][1,4]dithiin (**3**)[5] and dithieno[3,4-*b*;3′,4′-*e*][1,4]dithiin (**4**)[6] have been described and structurally characterized.[7] Here, the synthesis and structure of the tetramethoxy compound **5** are reported.

SYNTHESIS

1,3,5,7-Tetramethoxydithieno[3,4-*b*;3′,4′-*e*][1,4]dithiin (**5**) was obtained in a four-step synthesis starting from thiophene (Scheme I). 2,5-Diiodothiophene (**7**) and 2,5-bismethoxythiophene (**8**) were synthesized according to Barker *et al.*[8,9] 2,5-Dimethoxythiophene was brominated with N-bromosuccinimide to yield the hitherto unknown 3,4-dibromo-2,5-bismethoxythiophene (**9**). From **9**, 3,4-dilithio-2,5-bismethoxythiophene was prepared in situ using two equivalents of butyllithium at −78°C. Due to the low stability of lithiothiophenes[10] subsequent coupling with bis(phenylsulfonyl)sulfide,[11] however, gave the title compound only in low yields of ca. 5%.

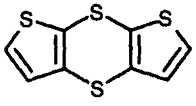


1

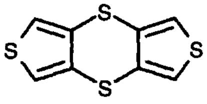


2

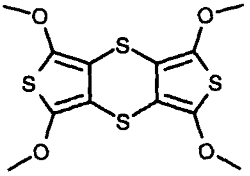
(E=S,Se)



3



4



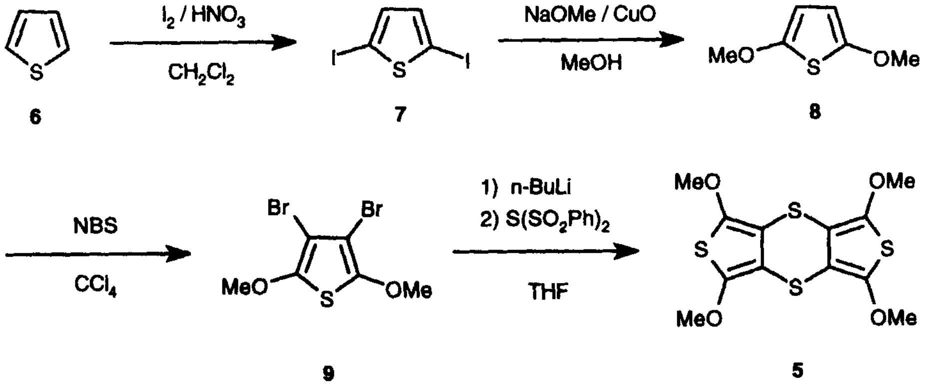
5

MS DATA

The mass spectrum of **5** is characterized by successive elimination of the fragments CH_3, CO and S, typical for methoxy substituted sulfur heterocycles.[12–14] Although the peak of highest intensity is that of $M^+ - CH_3$, the molecular peak is also found in the spectrum (relative intensities 100:70) thus indicating that the compound can easily be oxidized.

CRYSTAL STRUCTURE DATA

The X-ray structure determination showed compound **5** to be folded at the S—S axes of the central 1,4-dithiin ring by which it gets the boat conformation like the nonsubstituted dithienodithiin **4**[7] (Figure 1). The angle of fold (127.1°) lies in the normal range found for diannellated dithiins (122–135°).[18] Each thiophene ring forms a plane in which the sulfur atoms of the dithiin unit are included.



SCHEME I

TABLE I

MS-data of compound **5** (Finnegan MAT, CH 7, 70 eV)

mass	intensity	fragment
348	69.8%	M^+
333	100%	$M^+ - CH_3$
318	11.8%	$M^+ - 2CH_3$
303	48.2%	$M^+ - 3CH_3$
275	15.5%	$M^+ - 3CH_3, - CO$
271	45.5%	$M^+ - 3CH_3, - S$
243	10.3%	$M^+ - 3CH_3, - CO, - S$
228	4.1%	$M^+ - 4CH_3, - CO, - S$
215	8.5%	$M^+ - 3CH_3, - 2CO, - S$

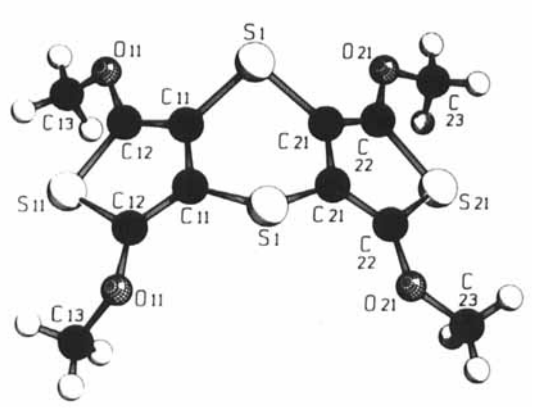


FIGURE 1 Molecular structure of **5** and numbering scheme of atoms.

The methoxy groups are coplanary arranged to the rings they are attached to, which is the normal situation for compounds with methoxy substituted aryl rings.[15-18] The bond distances O—C(arom) = 135.8(5), O—C(Me) = 142.3(6) pm and the bond angle C—O—C 116.04(4) agree within experimental error with the corresponding values of other methoxy compounds.[15-18]

In comparison with **4** the additional methoxy substituents of **5** especially effect the CS bonds in the thiophene units and the CSC bond angles in both, the thiophene and dithiin units (Table II), indicating a less pronounced aromatic character of the thiophene rings.

EXPERIMENTAL

3,4-Dibromo-2,5-bismethoxythiophene (**9**). To a solution of 2,5-bismethoxythiophene (**8**) (2 g, 13.87 mmol) in tetrachloromethane (75 ml) was added N-bromosuccinimide (5.43 g, 30.51 mmol). The suspension was stirred at room temperature for 24 h. After filtration the solvent was evaporated and the residue was purified by chromatography (silica column, eluent: dichloromethane/cyclohexane 1:1, R_f:

TABLE II

Mean values of bond lengths (pm) and angles (°) within the rings of **5** and **4** for comparison (with e.s.d.'s in parentheses)

		5	4
Dithiin unit	S-C	176.4(5)	176.2(3)
	C-C	143.7(8)	142.9(3)
	C-S-C	97.5(2)	99.5(1)
	S-C-C	122.9(2)	123.4(2)
Thiophene units	S-C	174.2(4)	171.3(3)
	C-C	135.4(7)	137.7(3)
	C-S-C	90.4(3)	92.2(1)
	C-C-C	112.7(3)	112.5(2)

0.46) to yield (**9**) as a dark-red solid (2.82 g, 9.3 mmol, 67.3%), mp 57.1°C; ^{1}H-NMR (200 MHz, $CDCl_3$): δ [ppm] = 3.89 (s, $-OC\underline{H}_3$); IR [cm^{-1}]: 2930, 2832, 1739, 1704, 1652, 1559, 1450, 1436, 1244, 1163, 1137; MS (70 eV): m/z (%) = 304, 302, 300 (17.0, 28.6, 14.8, M^+), 289, 287, 285 (53.7, 100, 50.0, M^+-CH_3) 261, 259, 257 (9.0, 18.6, 9.2, M^+-CH_3, $-C_2H_4$).

$C_6H_6Br_2O_2S$ (302.0) C 24.04 (23.86), H 1.93 (2.00)

1,3,5,7-Tetramethoxydithieno[3,4-b;3',4'-e]-[1,4]dithiin (**5**). A solution of **9** (1.67 g, 5.53 mmol) in tetrahydrofuran (150 ml) was cooled to −78°C, then butyllithium (7.12 ml, 1.6 M solution in *n*-hexane, 11.4 mmol) was added dropwise. Afterwards bis(phenylsulfonyl)sulfide (2.14 g, 6.8 mmol) was added in small portions during a period of 1 h. The solution was stirred additional 4 h at −78°C and then was allowed to warm overnight to room temperature. The solvent was evaporated and the residue was purified by chromatography (silica column, eluent: dichloromethane/cyclohexane 1:1, R_f: 0.29). The product was washed several times with cyclohexane and recrystallized from dichloromethane to yield **5** in colourless crystals (117 mg, 0.33 mmol, 6.1%), mp 159.8°C; ^{1}H-NMR (200 MHz, $CDCl_3$): δ [ppm] = 3.87 (s, $-OC\underline{H}_3$); ^{13}C-NMR (62.8 MHz, $CDCl_3$): δ [ppm] = 146.75 (s, $CH_3O—\underline{C}_{arom}$), 108.23 (s, $\underline{C}_{arom}$), 62.74 (s, $-O\underline{C}H_3$); IR [cm^{-1}]: 2962, 2930, 2834, 1569, 1551, 1529, 1464.

$C_{12}H_{12}O_4S_4$ (348.5) C 41.15 (41.36), H 3.51 (3.47)

Crystal data for **5**: Empirical formula $C_{12}H_{12}O_4S_4$; M = 348.46; crystal system orthorhombic, space group Pnma; a = 769.9(2), b = 1703.7(3), c = 1088.6(2) pm; V = $1427 \cdot 10^6$ pm^3; Z = 4, D = 1.621 g·cm^{-3}; μ = 62.1 cm^{-1}, scan range $4.8 < 2\Theta < 76.4$; temperature of measurement 153(1) K; number of independent reflections 1536, number of reflections with $|F_0| \geq 4\sigma(|F_0|)$ 1284; number of refined parameters 98; R = 0.0777; wR_2 = 0.21116; S = 1.060.

The data were recorded on a Enraf-Nonius CAD4 four-circle diffractometer (Cu-Kα radiation with λ = 154.18 pm, $\omega/2\Theta$ scan mode, Lorentz and polarization corrections); the structure was determined by direct methods (programm SHELXTL-PLUS[19]) and refined (programm SHELXL-93[20]); an empirical absorption correction with Ψ-scans was carried out, too (programm XEMP[19]); subsequent Fourier syntheses and full-matrix least squares calculations allowed the positions of all non-hydrogen atoms to be determined, these atom positions were refined with anisotropic temperature factors; the positions of the hydrogen atoms were calculated with fixed distances of 96 pm. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Fachinformationszentrum (FIZ) Karlsruhe, and can be ordered on quoting the authors, the journal and the depository number, CSD 401661.

ACKNOWLEDGEMENTS

We thank the Fonds der Chemischen Industrie for financial support.

REFERENCES

1. W. Hinrichs and G. Klar, *J. Chem. Res.*, (*S*) 336, (*M*) 3540 (1982).
2. W. Hinrichs, P. Berges, G. Klar, E. Sánchez Martínez and W. Gunßer, *Synthetic Metals*, **20,** 357 (1987).
3. E. Sánchez Martínez, R. Díaz Calleja, W. Gunßer, P. Berges and G. Klar, *Synthetic Metals*, **30,** 67 (1989).
4. R. Díaz Calleja, P. Klar, E. Sánchez Martínez, J. Behrens, J. Kudnig and G. Klar, *J. Mater. Chem.*, **3,** 489 (1993).
5. M. G. Woronkow and A. N. Pereferkowitsch, *Angew. Chem.*, **81,** 257; *Int. Edn. (Engl.)*, **8,** 272 (1969).
6. M. J. Janssen and J. Bos, *Angew. Chem.*, **81,** 570; *Int. Edn. (Engl.)*, **8,** 598 (1969).
7. H. Hiemstra and C. T. Kiers, *Acta Crystallogr., Sect. B*, **35,** 1140 (1979).
8. J. M. Barker, P. R. Huddleston and M. L. Wood, *Synthetic Communications*, **5,** 59 (1975).
9. J. M. Barker, P. R. Huddleston and S. W. Shutler, *J. Chem. Soc., Perkin Trans. I*, 2483 (1975).
10. A. Hallberg, T. Frejd and S. Gronowitz, *J. Chem. Soc., Perkin Trans. 1*, 1390 (1980).
11. F. de Jong and M. J. Janssen, *J. Org. Chem.*, **36,** 1645 (1971).
12. P. Schulz and G. Klar, *Phosphorus and Sulfur*, **29,** 377 (1987).
13. P. Berges and G. Klar, *Z. Naturforsch.*, **43b,** 599 (1988).
14. P. Schulz, V. Mansel and G. Klar, *Phosphorus and Sulfur*, **42,** 227 (1989).
15. K. von Deuten and G. Klar, *Cryst. Struct. Commun.*, **8,** 1017 (1979).
16. W. Hinrichs, H.-J. Riedel and G. Klar, *J. Chem. Res.*, (*S*) 334, (*M*) 3501 (1982).
17. W. Hinrichs, P. Berges and G. Klar, *Z. Naturforsch.*, **42b,** 169 (1987).
18. V. Mansel and G. Klar, *J. Chem. Res.*, (*S*) 158, (*M*) 1201 and literature cited therein (1992).
19. G. M. Sheldrick, SHELXTL-PLUS, Release 4.21/0, Copyright 1990 Siemens Analytical X-Ray Instruments.
20. G. M. Sheldrick, SHELXL-93, Universität Göttingen, 1993.